{BnF

gallica
BIBLIOTHÈQUE
NUMÉRIQUE

Anonyme. The Journal of physical chemistry. Published at Cornell university [puis Published under the auspices of the American chemical society, the Chemical society and the Faraday society]. 1896 [I]-. 1926.

1/ Les contenus accessibles sur le site Gallica sont pour la plupart des reproductions numériques d'oeuvres tombées dans le domaine public provenant des collections de la BnF.Leur réutilisation  s'inscrit dans le cadre de la loi n°78-753 du 17 juillet 1978 :
*La réutilisation non commerciale de ces contenus est libre et gratuite dans le respect de la législation en vigueur et notamment du maintien de la mention de source.
*La réutilisation commerciale de ces contenus est payante et fait l'objet d'une licence. Est entendue par réutilisation commerciale la revente de contenus sous forme de produits élaborés ou de fourniture de service.

Cliquer ici pour accéder aux tarifs et à la licence

2/ Les contenus de Gallica sont la propriété de la BnF au sens de l'article L.2112-1 du code général de la propriété des personnes publiques.

3/ Quelques contenus sont soumis à un régime de réutilisation particulier. Il s'agit :

*des reproductions de documents protégés par un droit d'auteur appartenant à un tiers. Ces documents ne peuvent être réutilisés sauf dans le cadre de la copie privée sans l'autorisation préalable du titulaire des droits.
*des reproductions de documents conservés dans les bibliothèques ou autres institutions partenaires. Ceux-ci sont signalés par la mention Source Gallica.BnF.fr / Bibliothèque municipale de ... (ou autre partenaire). L'utilisateur est invité à s'informer auprès de ces bibliothèques de leurs conditions de réutilisation.

4/ Gallica constitue une base de données, dont la BnF est producteur, protégée au sens des articles L341-1 et suivants du code la propriété intellectuelle.

5/ Les présentes conditions d'utilisation des contenus de Gallica sont régies par la loi française. En cas de réutilisation prévue par un autre pays, il appartient à chaque utilisateur de vérifier la conformité de son projet avec le droit de ce pays.

6/ L'utilisateur s'engage à respecter les présentes conditions d'utilisation ainsi que la législation en vigueur, notamment en matière de propriété intellectuelle. En cas de non respect de ces dispositions, il est notamment passible d'une amende prévue par la loi du 17 juillet 1978.

7/ Pour obtenir un document de Gallica en haute définition, contacter reutilisation@bnf.fr.

# *Journal of physical chemistry*

**Tome 30**

**Volume 30**

*Washington* **1926**

Source gallica.bnf.fr / Bibliothèque nationale de France

ANNULÉ

CPg 4

# The Journal of Physical Chemistry

Published under the auspices of the American Chemical Society, the Chemical Society, and the Faraday Society

BIBLIOTHÈQUES UNIVERSITÉ DE PARIS · ORSAY

*Editor*

**Wilder D. Bancroft**

*Associate Editors*

| | |
|---|---|
| A. L. Day | T. M. Lowry |
| F. G. Donnan | J. W. McBain |
| G. A. Hulett | W. L. Miller |
| I. Langmuir | J. C. Philip |

## VOLUME XXX

ITHACA, N. Y.
THE EDITOR

1926

BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS
ORSAY

# CONTENTS OF VOLUME XXX

## 1. JANUARY


| | | |
|---|---|---|
| *Jean Oliver and Pearl Smith,* | The Kinetics of Agglutination of Red Blood Cell Suspensions, | 1 |
| *F. W. Bergstrom,* | Reaction of the Type $Cl_2+2KOH=KCl+KClO+H_2O$, | 12 |
| *H. B. Weiser,* | The Antagonistic Action of Ions in the Neutralization of Sols, | 20 |
| *A. L. Marshall,* | Photosensitization by Optically Excited Mercury Atoms. The Hydrogen Oxygen Reaction, | 34 |
| *G. S. Parks and K. K. Kelley,* | The Heat Capacities of Some Metallic Oxides, | 47 |
| *W. R. Brode,* | The Effect of Solvents on the Absorption Spectrum of a Simple Azo Dye, | 56 |
| *A. R. Collett and John Johnston,* | Solubility Relations of Isomeric Organic Compounds. VI, | 70 |
| *Charles Gurchot,* | Reversible Permeability of Membranes and its Relation to Cell Metabolism, | 83 |
| *W. A. Rudisill and C. J. Engelder,* | Catalytic Activation of Titania, | 106 |
| *J. W. McBain and D. G. Hopkins,* | Films of Adhesives, | 114 |
| *Victor Lenher and C. H. Kao,* | Studies on the Chemistry of Gold, | 126 |
| *B. H. Carroll,* | The Photochemical Oxidation of Leuco Bases, | 130 |
| *W. A. Patrick and P. W. Bachman,* | The Adsorption of Ions on a Mercury Surface, | 134 |
| *New Books* | | 136 |


## 2. FEBRUARY


| | | |
|---|---|---|
| *H. S. Taylor,* | Fourth Report of the Committee on Contact Catalysis, | 145 |
| *L. A. Munro and F. M. G. Johnson,* | The Sorption of Vapors by Alumina, | 172 |
| *O. K. Rice,* | Equilibrium in Colloid Systems, | 189 |
| *L. M. Currie,* | Antimony Sulphides, | 205 |
| *J. W. McBain,* | The Apparent Viscosity of Colloidal Solutions and a Theory of Neutral Colloids as Solvated Micelles capable of Aggregation, | 239 |
| *S. B. Hendricks,* | Equilibrium in the System: Arsenic Pentoxide, Barium Oxide, Water, | 248 |
| *F. Hardy,* | Anomalous Flocculation in Colloidal Clays and Soils, | 254 |
| *F. H. Getman,* | The Ultraviolet Absorption Spectra of Aqueous Solutions of Sulphur Dioxide and some of its Derivatives, | 266 |
| *N. R. Dhar,* | Origin of the Formation of Deposits in Gout and Other Diseases, and the Cause of Swelling in Beriberi, | 277 |
| *New Books* | | 282 |

3. MARCH

*W. Mund and W. Koch,* The Chemical Action of Alpha Particles on Acetylene,..... 289

*S. Ghosh and N. R. Dhar,* The Influence of Ions carrying the Same Charge as the Dispersed Particles in the Inversion of Emulsions,..... 294

*W. C. Arsem,* Gel Structure,..... 306

*J. W. McBain, C. E. Harvey and L. E. Smith,* The Apparent Viscosity of Solutions of Nitro Cotton in Various Solvents,..... 312

*W. A. Lazier and Homer Adkins,* Adsorption of Ethylene and Hydrogen by Zinc Oxide, Iron Oxide, Nickel, and Copper,..... 353

*R. W. Harman,* Aqueous Solutions of Sodium Silicates. II,..... 359

*A. F. O. Germann and H. S. Booth,* Thermal Analysis of the System Boron Trifluoride-Hydrogen Sulphide,..... 369

*N. R. Dhar,* Old Age and Death from a Chemical Point of View 378

*C. W. Mason,* Structural Colors in Insects. I,..... 383

*J. T. Burt-Gerrans,* The Electrolysis of Acid Solutions of Copper Sulphate. II,..... 396

*R. B. Mason and J. H. Mathews,* The Effect of Ultra-Violet Light on the Oxidation of Sodium Sulphite by Atmospheric Oxygen,.. 414

*New Books* 421

4. APRIL

*H. S. Harned,* Individual Thermodynamic Behaviors of Ions in Concentrated Solutions including a Discussion of the Thermodynamic Method of computing Liquid-Junction Potentials,..... 433

*R. O. Herzog,* The Nature of the Structure of Cellulose and its Significance in Chemical Transformations,.... 457

*W. L. Nelson and C. J. Engelder,* The Thermal Decomposition of Formic Acid,.... 470

*B. B. Wescott and C. J. Engelder,* The Catalytic Decomposition of Formic Acid,.... 476

*N. R. Dhar,* Influence of Temperature on Metabolism and the Problem of Acclimatization,..... 480

*M. L. Nichols and I. A. Derbigny,* The Reduction of Nitrous Oxide,..... 491

*T. E. Phipps and W. R. Brode,* A Comparative Study of Two Kinds of Colored Rock Salt,..... 507

*Wilder D. Bancroft,* Blue Wood,..... 521

*C. H. Kunsman,* The Thermionic Properties of Some Mixtures used as Catalysts in the Synthesis of Ammonia,.... 525

*V. R. Main,* The Viscosity of Aqueous Solutions of the Silicates of Soda,..... 535

*W. W. Lucasse,* The Transference Numbers of Hydrochloric Acid in Glycerol-Water Mixtures,..... 562

*New Books* 566

5. MAY

*A. F. Scott,* A Relationship between Atomic Numbers and the Properties of Ions in the Crystal Lattice. II,.. 577

*H. V. Tartar and M. F. Perkins,* A Laboratory Study of Nitrogen Fixation in the High Tension Arc,..... 595

| | | |
|---|---|---|
| *J. B. Firth and W. L. Purse,* | Organogels of Silicic Acid—the Replacement of the Water in the Hydrogel by Alcohol,..... | 617 |
| *S. B. Arenson, P. E. Roller and D. J. Brown,* | The Reactive Nature of Aldehydes from the Standpoint of the Apparent Electromotive Force,... | 620 |
| *N. R. Dhar and S. Ghosh,* | Studies in Adsorption. XIII,..... | 628 |
| *Isaac Bencowitz and H. T. Hotchkiss, Jr.,* | Vapor Pressure Lowering as a Function of the Degree of Saturation. II,..... | 643 |
| *R. M. Woodman,* | The Preparation and Conditions of Formation of the Two Possible Types of Emulsion in the System Cresylic Acid—Gelatine—Water,..... | 658 |
| *D. H. Peacock,* | The Benzylation of Amines. III,..... | 673 |
| *B. Bruzs,* | Velocity of Thermal Decomposition of Carbonates, | 680 |
| *F. S. Brown and C. R. Bury,* | Cryoscopic Measurements with Nitrobenzene. IV,..... | 694 |
| *P. B. Ganguly,* | The Scattering of Light by Aqueous Sodium Silicate Solutions,..... | 706 |
| *Hsi-Ching Chen,* | A Laboratory Latex,..... | 713 |
| *New Books* | | 716 |


## 6. JUNE


| | | |
|---|---|---|
| *N. L. Bowen,* | Properties of Ammonium Nitrate. I,..... | 721 |
| *N. L. Bowen,* | Properties of Ammonium Nitrate. II,..... | 726 |
| *N. L. Bowen,* | Properties of Ammonium Nitrate. III,..... | 736 |
| *F. F. Sherwood and E. I. Fulmer,* | The Effect of Temperature upon the Growth of Yeast in Various Media,..... | 738 |
| *A. L. Marshall,* | Mechanism of the Photochemical Reaction between Hydrogen and Chlorine. III,..... | 757 |
| *H. V. Tartar and C. Z. Draves,* | A Study of the Precipitation of Mastic Suspensoids,..... | 763 |
| *J. N. Brönsted,* | The Acid-Basic Function of Molecules and its Dependency on the Electric Charge Type,..... | 777 |
| *J. R. Pound,* | Interfacial Tensions between Organic Liquids and Water or Aqueous Solutions,..... | 791 |
| *C. F. Fryling,* | Heats of Adsorption and the Problem of Promotor Action,..... | 818 |
| *S. Ghosh and N. R. Dhar,* | Studies in Adsorption. XIV,..... | 830 |
| *M. C. Hylan,* | Grain Size and the Quantum Theory of Photographic Exposure,..... | 845 |
| *G. McP. Smith,* | Ionic Activity versus Concentration in the Interpretation of Equilibria between Amalgams and Aqueous Sodium and Potassium Halide Mixtures,..... | 849 |
| *New Books* | | 858 |


## 7. JULY


| | | |
|---|---|---|
| *H. F. Vieweg,* | Frictional Electricity,..... | 865 |
| *W. Mund,* | Ionization by Radon in Spherical Vessels,..... | 890 |
| *W. A. Lazier and Homer Adkins,* | The Formation of Carbon Dioxide from Alcohols,. | 895 |
| *R. C. Cantelo,* | The Thermal Decomposition of Methane. II,..... | 899 |
| *H. B. Oakley,* | The Origin of the Charge on Colloidal Particles,.. | 902 |
| *R. W. Harman,* | Aqueous Solutions of Sodium Silicates. III,..... | 917 |

| | | |
|---|---|---|
| *J. P. McHutchison, W. W. Lucasse and J. McA. Harris, Jr., C. C. Palit and N. R. Dhar, F. L. Usher, H. C. Howard, Jr.,* | The Electrodeposition of Radium D and Radium E, | 925 |
| | The Transition Points of Salt Hydrates in Non-aqueous Solutions, | 930 |
| | Catalytic and Induced Oxidation of Some Carbohydrates, Uric Acid, and Inorganic Substances, | 939 |
| | Electrokinetic Behavior and Electrode Potential, | 954 |
| | Mechanism of the Catalytic Dehydration of Methanol, and Some Properties of the Hydrous Aluminum Oxide Catalyst, | 964 |
| *R. H. Lambert,* | The Ternary System: Silver Bromide—Potassium Bromide—Water, | 973 |
| *W. H. Hampton,* | The Potential of the Iron Electrode, | 980 |
| *A. J. Stamm and E. O. Kraemer,* | A Note on the Mechanism of Emulsification, | 992 |
| *New Books* | | 1001 |

8. AUGUST

| | | |
|---|---|---|
| *A. F. Sco ,* | A Relationship between Atomic Number and the Properties of Ions in the Crystal Lattice, | 1009 |
| *E. J. Miller,* | Adsorption from Solution by Ash-free Charcoals. I, | 1031 |
| *H. A. Neville,* | Adsorption and Reaction. I, | 1037 |
| *A. W. Laubengayer and R. B. Corey,* | Germanium. XIII, | 1043 |
| *A W. Laubengayer and D. L. Tabern,* | Germanium. XIV, | 1047 |
| *L. M. Dennis, W. R. Orndorff and D. L. Tabern,* | Germanium. XV, | 1049 |
| *L M. Dennis and F. E. Hance,* | Germanium. XVI, | 1055 |
| *H. S. Harned and G. M. James,* | The Dissociation of Water in Potassium and Sodium Bromide Solutions, | 1060 |
| *E. Posnjak,* | The Nature of Stannic Acids, | 1073 |
| *A. L. Marshall,* | The Mechanism of Reactions photosensitized by Mercury Vapor, | 1078 |
| *R. W. Harman,* | Aqueous Solutions of Sodium Silicates. IV, | 1100 |
| *J. P. McHutchison,* | Experiments on the Electrolysis of Radium D and Radium E, | 1112 |
| *M. L. Byron,* | The Peptization of Pyroxylin, | 1116 |
| *C. C. Palit and N. R. Dhar,* | Action of Nitric Acid on Metals in presence o Catalysts, | 1125 |
| *R. E. Burk,* | A Possible Mechanism for the Lowering of the Heat of Activation of a Reaction by a Catalytic Surface, | 1134 |
| *New Books* | | 1141 |

9. SEPTEMBER

| | | |
|---|---|---|
| *O. E. Privold,* | The Influence of the Ionic Charge on the Osmotic Behavior of Alcoholic Solutions, | 1153 |
| *E. J. Miller,* | Adsorption from Solution by Ash-free Adsorbent Charcoals. II, | 1162 |
| *J. W. Williams and J. A. Skogstrom,* | Colloidal Systems of Nitromethane, | 1170 |
| *G. S. Parks and K. K. Kelly,* | The Heat Capacity of Calcium Silicate, | 1175 |
| *Simon Klosky and Leo Woo,* | Solubility of Silver Oxide, | 1179 |
| *H. A. Neville,* | Adsorption and Reaction. II, | 1181 |
| *M. R. Mehrotra and N. R. Dhar,* | Studies in Adsorption. XV, | 1185 |

*Wilder D. Bancroft, John McAulay, Jr.*, The Water Equilibrium,..... 1194
Influence on the Solubilities of Salts in Water by the Addition of a Non-electrolyte to the Solution,..... 1202
*H. J. M. Creighton*, Solubility and Electrolytic Conductance of Mesitylene Phosphinous Acid,..... 1209
*H. B. Dunnicliff, I. S. Sikka and R. C. Hoon*, The System: Sodium Sulphate, Sulphuric Acid, Ethyl Alcohol,..... 1211
*O. W. Richards*, A Nomogram for the van't Hoff-Arrhenius Temperature Equation,..... 1219
*E. J. Joss*, The Action of Metals on Nitric Acid,..... 1222
*F. M. Cray*, The Color Change of Congo Red in Acidified Acetone-Water Solutions,..... 1276
*R. M. Woodman*, The System: Water, Acetic Acid, Toluene,..... 1283
*New Books* 1287

## 10. OCTOBER

*Shun-ichi Uchida*, On the Reaction Mechanism of the Catalytic Oxidation of Ammonia,..... 1297
*J. E. Rosenberg and Gebhard Stegeman*, The Adsorption of Ions by Metallic Mercury,.... 1306
*H. Lee Ward*, The Solubility Relations of Naphthalene,..... 1316
*William Rogers, Jr. and H. S. Taylor*, The Rate of Oxidation of Linseed Oil,..... 1334
*O. K. Rice*, The Surface Tension of Charged Surfaces,..... 1348
*G. B. Kistiakowsky*, The Ionisation Potentials of Nitrogen and Hydrogen on Iron and Other Metals,..... 1356
*K. Kawamura*, Adsorption by Humic Acid,..... 1364
*J. H. Yoe and E. B. Freyer*, The Effect of Hydrogen Ion Concentration on the Viscosity of Hydrosols of Aluminum, Chromic and Ferric Oxides,..... 1389
*Maud Garner and W. C. McC. Lewis*, The Effect of Temperature on the Rate of Coagulation of Gold Sol,..... 1401
*Maud Garner*, Note on the Significance of the Variation in the Smoluchowski Coagulation Coefficient ($\beta$),.... 1410
*A. F. Benton, H. A. H. Pray*, A Gel of Metallic Platinum,..... 1415
The Stability of Diazo-Benzene Chloride Solution. I,..... 1417
*P. W. Cunliffe, R. G. Franklin, R. E. W. Maddison, and L. Reeve*, Studies in Photochemical Technique. III,..... 1427
*New Books* 1432

## 11. NOVEMBER

*C. W. Stillwell*, The Color of the Ruby,..... 1441
*E. C. H. Davies and Victorian Sivertz*, Rhythmic Diurnal Bands of Gold and Platinum in Silicic Acid Gel,..... 1467
*H. A. H. Pray*, The Stability of Diazo-Benzene Chloride Solutions. II,..... 1477
*A. F. Benton and T. L. Williams*, The Catalytic Oxidation of Carbon Monoxide in Contact with Quartz Glass,..... 1487
*Mary R. Andrews*, Vapor Pressure of Naphthalene at Low Temperatures,..... 1497

| | | |
|---|---|---|
| *O. K. Rice,* | A Study of the Electrocapillary Curve near its Maximum, | 1501 |
| *L. M. Dennis and A. W. Laubengayer,* | Germanium. XVII, | 1510 |
| *H. B. Weiser,* | The Antagonistic Action of Ions in the Neutralization of Sols, | 1527 |
| *R. A. Beebe,* | Heat of Adsorption of Carbon Monoxide on Copper Catalyst, | 1538 |
| *J. W. McBain and M. C. Field,* | The Equilibrium underlying the Soap-boiling Process. The System Potassium Laurate-Potassium Chloride-Water, | 1545 |
| *S. Ghosh* | Influence of Ageing of a Sol on its Coagulation, | 1564 |
| *New Books* | | 1571 |

12. DECEMBER

| | | |
|---|---|---|
| *Gösta Åkerlof,* | The Solubility of Strong, Simple Electrolytes in Water, | 1585 |
| *A. A. Groening and H. P. Cady,* | Decomposition Potentials and Metal Overvoltages in Liquid Ammonia and Water, | 1597 |
| *M. Bergstein and Martin Kilpatrick, Jr.,* | The Catalytic Minimum Point, | 1616 |
| *L. H. Reyerson, O. E. Harder and L. E. Swearingen,* | The Nature of Metal Films reduced on the Surfaces of Silica Gel, | 1623 |
| *G. S. Forbes and P. A. Leighton,* | Electrolysis of Dichromic Acid under a Mercury Vapor Lamp of High Intensity, | 1628 |
| *A. L. Marshall,* | Synthetic Formaldehyde from Carbon Monoxide and Hydrogen, | 1634 |
| *R. C. Cantelo,* | The Methane Equilibrium. I, | 1641 |
| *D. N. Chakravarti and N. R. Dhar,* | Viscosity Measurements of Certain Sols in presence of Electrolytes, | 1646 |
| *O. K. Rice,* | Equilibrium in Colloid Systems. II, | 1660 |
| *J. C. W. Frazer, B. F. Lovelace and R. K. Taylor,* | The Vapor Pressures of Potassium Nitrate Solutions at 20° C, | 1669 |
| *J. N. Pearce and M. M. Hicks,* | A Sensitive Electrical Precision Apparatus for the Determination of the Boiling Point Elevation, | 1678 |
| *Wilhelm Stenström and Norris Goldsmith,* | Determination of the Dissociation Constants of Phenol and the Hydroxyl Group of Tyrosine by means of Absorption Measurements in the Ultra-violet, | 1633 |
| *J. F. King and R. N. Washburne,* | The Electromotive Determination of Small Amounts of Ferric Iron, | 1688 |
| *Name Index* | | 1698 |
| *Index to New Books* | | 1704 |
| *Subject Index* | | 1706 |


BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS ORSAY

BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS
ORSAY

# THE KINETICS OF AGGLUTINATION OF RED BLOOD CELL SUSPENSIONS*

BY JEAN OLIVER AND PEARL SMITH

In a study of the action of electrolytes on the electric charges and stability of red blood cell suspensions Oliver and Barnard[1] have shown that at a certain concentration of trivalent salts agglutination of the cells proceeds at a maximum speed. It was also observed that at this concentration the electric charge of the cells was completely abolished, whereas in other concentrations

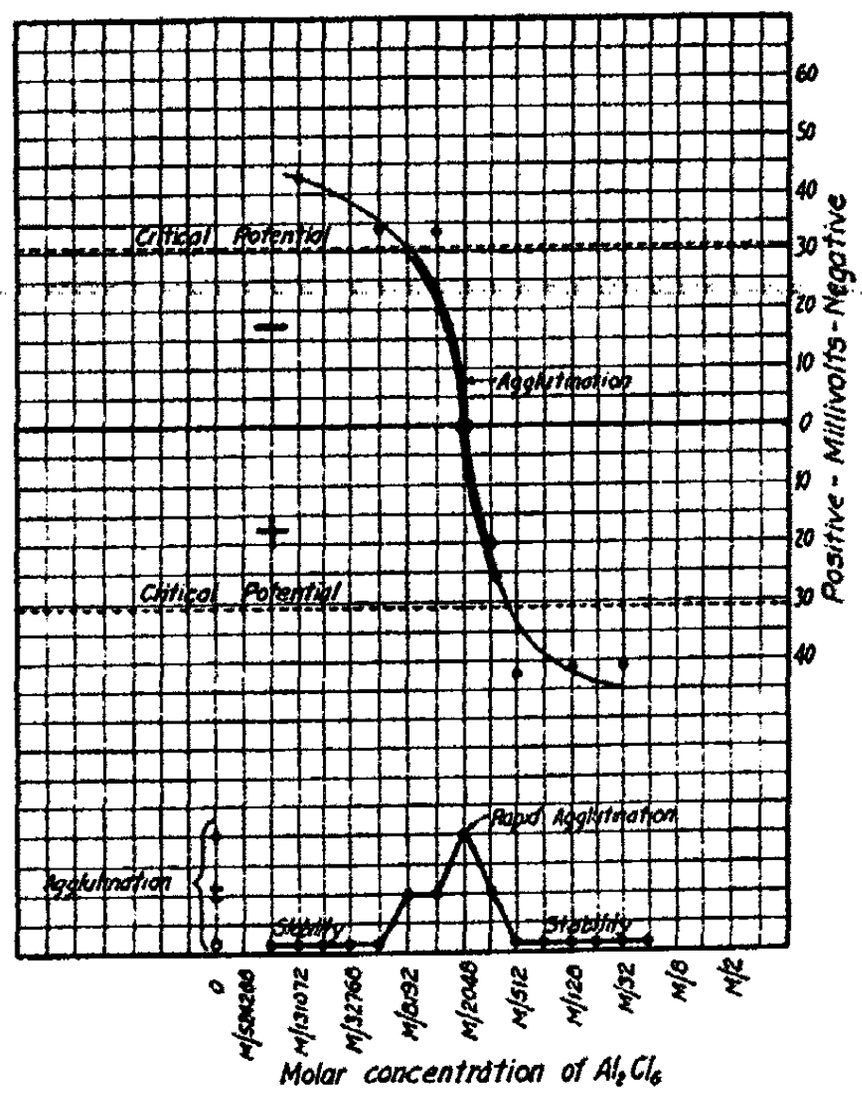



FIG. 1

where the charge had been only depressed below the critical potential, agglutination, although it occurred, was much slower (Fig. 1). It was therefore suggested that the conditions were analogous to those described by Zsigmondy in the coagulation of colloidal solutions by electrolytes.

In his experiments with colloidal gold Zsigmondy[2] found that the time of color change at first decreased rapidly and then became constant as the con-

*From the Department of Pathology of the Medical School of Stanford University, San Francisco, California.

[1] J. Gen. Physiol. 7, 99 (1924).

[2] Z. physik. Chem. 92, 600 (1917).

centration of the coagulating electrolyte was increased and this range of concentration in which the color change was constant he called the zone of "rapid" coagulation. By comparing his measurements with those of Galecki[1] on the cataphoresis of similar particles he assumed that this zone of rapid coagulation lay in the immediate neighborhood of the isoelectric point, and was the result of the complete neutralization of the charge of the particles.

These experiments of Zsigmondy formed the starting point for the development of a theory of coagulation. He assumed that in the rapid coagulation of spherical particles of equal size, any particle which comes within a certain distance of another particle becomes permanently fixed to it since it possesses no electric charge to cause repulsion. This distance he defined as the radius of the attraction sphere of the particle.

The mathematical treatment of the problem was developed by v. Smoluchowski[2] who calculated formulae for the number of single, double, treble and larger aggregates in a suspension from (1) the original number of particles ($V_o$), (2) the radius of the attraction sphere (R), and (3) the velocity constant of Brownian movement (D).

Von Smoluchowski first calculated the probability that any particle will enter the attraction sphere of a given particle by applying the equation for Brownian movement and also the probability that within the time T no particle will enter such an attraction sphere. From these probabilities he calculated the decrease in number of the single particles. By making corrections for the Brownian movements of the particles around which coagulation is supposed to take place, and from the fact that the aggregates already formed act as coagulating nuclei he finally arrived at the following system of equations:

$$V_1 + V_2 + V_3 + \ldots\ldots\ldots \Sigma_v = \frac{V_o}{1 + t/T} \qquad (1)$$

$$V_1 = \frac{V_o}{(1 + t/T)^2} \qquad (2)$$

$$V_2 = \frac{V_o\, t/T}{(1 + t/T)^3} \qquad (3)$$

$$V_K = \frac{V_o\, (t/T)^{K-1}}{(1 + t/T)^{K+1}} \qquad (4)$$

where $\Sigma_v$ = total number of particles; $V_1$ = number of single particles; $V_2$ = number of double particles; $T = 1/4\pi DRV_o$

Von Smoluchowski's theory has been verified by a number of experiments. Zsigmondy[3] first tested the equation $V_1 = V_o / (1 + t/T)^2$ by measuring the decrease in the number of single particles in a gold sol. He was able with the ultramicroscope to distinguish between the single particles and aggregates

[1] Z. anorg. Chem. 74, 199 (1912).
[2] Z. physik. Chem. 92, 129 (1917).
[3] Z. physik. Chem. 92, 600 (1917).

because the former emit green and the latter yellow light. By substituting the actual values in the equation he obtained a value for $1/T$ which was fairly constant for all but the shorter periods of time. With the average value for $1/T$ he calculated the theorectical values of $V_t$ for the various time intervals, and found that they agreed approximately with the experimental figures. With the same data, he obtained values between 2.0 and 3.0 for the ratio between the radius of the attraction sphere and the radius of the particle by applying the formula $T = 1/4\pi DRV_o$ in which the value of D was substituted, giving $R/r = N\ 3\eta/H\theta_2 V_o \cdot 1/T$,* Westgren and Reitstötter[1] studied the change in the total number of particles in gold sols and found that their results were in accord with the equation $\Sigma_v = V_o/(1 + t/T)$, where $H = 8.31 \times 10^7$, gas constant; $N = 6.06 \times 10^{23}$; Avogadro's constant; $\eta = 009$, viscosity of medium; $\theta$ = absolute temperature

Luers[2] has found v. Smoluchowski's formulae applicable to the change of color of Congo red hydrosols when mixed with an electrolyte.

Somewhat divergent results were obtained by Kruyt and van Arkel[3] in their experiments with selenium hydrosols. In several of their experiments, the total number of particles was found to decrease in a way not consistent with v. Smoluchowski's formula. When an agreement with the theory did occur, R/r varied from 0.5 to 1.0.

The formula $\Sigma_v = V_o/(1 + t/T)$ was found by Ehringhaus and Wintgen[4] to apply in experiments with a very different sort of material. In a flux of borax and gold chloride, the particles of gold were found to decrease according to the formula when heated at a temperature of 925 C. for 1 to 500 minutes. In all but one of their series the average value of R/r was 2.39; in one series it was 13.7

In the present investigation an attempt was made to apply v. Smoluchowski's formulae to the "rapid agglutination" of red blood corpuscles.

## Methods

In all of our experiments a 1.5 per cent. suspension of red blood cells in 8.5 per cent. sucrose solution was used. In the preparation of the cells fresh defibrinated rabbit blood was washed three times with 0.9 per cent. NaCl solution and three times with 8.5 per cent. sucrose solution. To highly charge and stabilize the suspension sufficient NaOH was added to made a M/500 solution of the hydroxide, and enough $Al_2Cl_6$ was then added to this mixture to make the concentration of the electrolyte approximately M/4000. This concentration previous experimentation had shown brings the cells of such a suspension to the isoelectric point and produces "rapid agglutination". (Fig. 1).

---

[1] Z. physik. Chem. 92, 750 (1917).
[2] Kolloid-Z., 27, 123 (1920).
[3] Rev. Trav. chim., 39, 656; 40, 916 (1920).
[4] Z. physik. Chem. 104, 301 (1923).

At varying intervals the process of agglutination was interrupted by pipetting 2 ccm. of the mixture into a test tube containing 1.0 cm. of a 1.0 per cent. gelatin solution. The progress of agglutination was followed by making counts of single cells or aggregates of cells from each tube. In each case at least three counts were made on the undiluted suspension, using an ordinary blood counting chamber.

SERIES I

Table I—Exp. II

| Secs. | $V_1 \times 10^{-6}$ Obs | $\beta$ | $V^1 \times 10^{-6}$ Calc | $\frac{R}{r}$ |
|---|---|---|---|---|
| 0 | 60.00 | — | — | |
| 30 | 3.15 | .1131 | 3.42 | |
| 60 | 1.30 | .0973 | 1.10 | |
| 90 | .50 | .1115 | .53 | |
| | Av. | .1071 | | 598.6 |

Table II—Exp. III

| | | | | |
|---|---|---|---|---|
| 0 | 45.15 | —. | — | |
| 30 | 5.50 | .0618 | 6.78 | |
| 60 | 2.55 | .0534 | 2.60 | |
| 90 | 1.65 | .0470 | 1.37 | |
| 120 | .90 | .0506 | 90 | |
| 180 | .40 | .0527 | .40 | |
| 240 | .25 | .0605 | .25 | |
| | Av. | .0527 | | 396.0 |

Table III—Exp. XIII

| | | | | |
|---|---|---|---|---|
| 0 | 37.40 | — | — | |
| 30 | 12.25 | (.0249) | — | |
| 60 | 7.45 | .0207 | 8.71 | |
| 90 | 6.60 | .0153 | 5.49 | |
| 120 | 4.35 | .0165 | 3.78 | |
| 150 | 2.45 | .0194 | 2.76 | |
| | Av. | .0179 | | 163.0 |

Table IV—Exp. XII

| Secs. | $V_1 \times 10^{-6}$ Obs. | $\beta$ | $V_1 \times 10^{-6}$ Calc. | $\frac{R}{r}$ |
|---|---|---|---|---|
| 0 | 33.20 | — | — | |
| 30 | 2.85(.08041) | | — | |
| 60 | 1.60 | .05925 | 1.89 | |
| 90 | 1.00 | .05291 | .99 | |
| 120 | .75 | .04711 | .61 | |
| | Av. | .05309 | | 542.5 |

Table V—Exp. XI

| | | | | |
|---|---|---|---|---|
| 0 | 46.40 | — | — | |
| 30 | 7.45 | .0498 | 8.52 | |
| 60 | 2.75 | .0518 | 3.45 | |
| 90 | 2.35 | .0382 | 1.85 | |
| 120 | 1.60 | .0365 | 1.16 | |
| 150 | .75 | .0458 | .77 | |
| | Av. | .0445 | | 325.3 |

## The Experiments

In Series I single cells only were counted. Fig. 2 shows the manner in which the number of single cells decreases with time; the logarithms of the number of cells per ccm. are used as ordinates and time in seconds as abscissae. In the Tables I-V the constant 1/T or $\beta$ was calculated from the formula $\beta = 1/T \left( \sqrt{\frac{V_o}{V_1}} - 1 \right)$. The calculated values for the number of single cells were obtained by applying the formula $V_1 = V_o/(1 + \beta t)^2$. In each case the $\beta$ used is the average for the experiment with the exclusion of those

enclosed by brackets. These are omitted as obviously too large, since it is impossible to stop the progress of agglutination promptly at this point. The same difficulty was observed by Zsigmondy and others who worked with colloidal solutions. The $\beta$ for each experiment is fairly constant and the calculated numbers of single cells agree approximately with the actual counts.

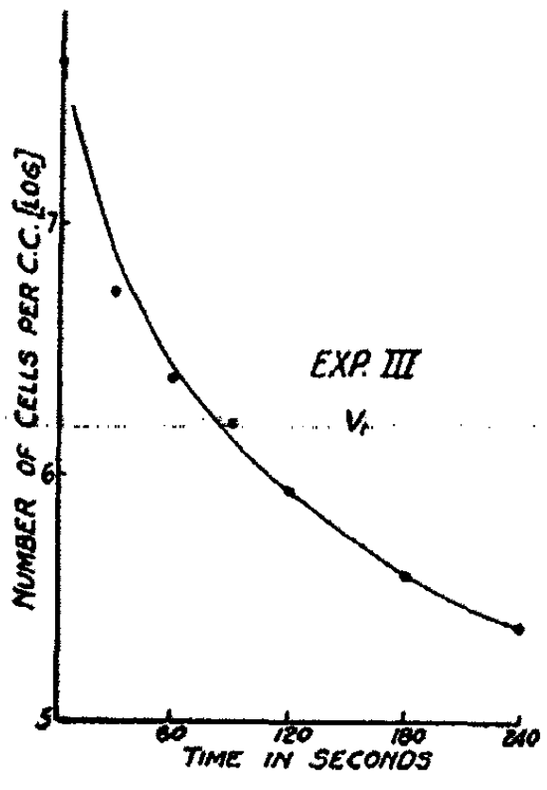



FIG. 2

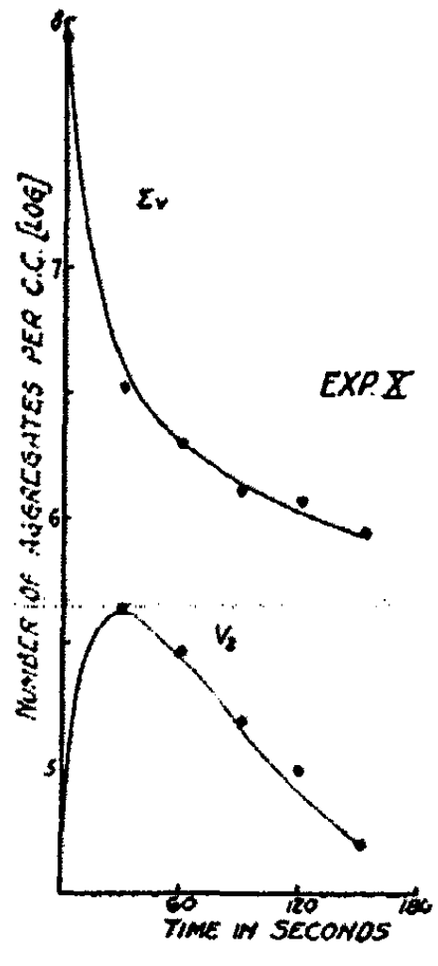



FIG. 3

## SERIES II

### Table VI—Exp. IX

| Secs. | $\Sigma_v \times 10^{-5}$ Obs. | $\beta$ | $\Sigma_v \times 10^{-6}$ Calc. | $\frac{R}{r}$ |
|---|---|---|---|---|
| 0 | 22.60 | — | — | |
| 30 | 4.70 | (.1273) | — | |
| 60 | 3.80 | .0826 | 4.03 | |
| 90 | 2.65 | .0838 | 2.86 | |
| 120 | 2.60 | .0627 | 2.21 | |
| | | Av. .0769 | | 1152.0 |

### Table VII—Exp. X

| | | | | |
|---|---|---|---|---|
| 0 | 84.10 | — | — | |
| 30 | 3.35 | (.803) | — | |
| 60 | 2.45 | .631 | 2.17 | |
| 90 | 1.35 | .681 | 1.47 | |
| 120 | 1.25 | .551 | 1.11 | |
| 150 | .90 | .630 | .89 | |
| | | Av. .623 | | 2513.0 |

Table VIII—Exp. VI

| | | | |
|---|---|---|---|
| 0 | 29.10 | — | — |
| 30 | 4.50 | .1820 | 5.24 |
| 60 | 2.20 | .2040 | 2.88 |
| 90 | 1.85 | .1670 | 2.03 |
| 120 | 1.50 | .1530 | 1.52 |
| 150 | 1.70 | .1073 | 1.23 |
| 180 | 1.60 | .0955 | 1.03 |
| | | Av. .1516 | 1832.0 |

In Series II the total number of cells and aggregates was counted and similar calculations made with the formulae

$$\beta = 1/t \cdot V_o/\Sigma_v - 1$$

and

$$\Sigma_v = V_o/1 + \beta t$$

Tables VI-VIII and the upper curve in Fig. 3 illustrate experiments of this type. Agreement between the theoretical and observed values is not as close as observed in Series I, but is approximate.

## Series III

Table IX—Exp. XII

| Secs. | $V_2 \times 10^{-6}$ Obs. | $\beta$ | $V_2 \times 10^{-6}$ Calc. | $\frac{R}{r}$ |
|---|---|---|---|---|
| 0 | .00 | — | — | |
| 30 | .80 | (.162) | — | |
| 60 | .50 | .110 | .571 | |
| 90 | .30 | .099 | .294 | |
| 120 | .20 | .094 | .178 | |
| | Av. .101 | | | 1032.0 |

Table X—Exp. XI

| | | | | |
|---|---|---|---|---|
| 0 | .00 | — | — | |
| 30 | 1.60 | .127 | 2.20 | |
| 60 | .70 | .110 | .82 | |
| 90 | .50 | .090 | .42 | |
| 120 | .40 | .077 | .26 | |
| 150 | .20 | .092 | .17 | |
| | Av. .099 | | | 723.8 |

Table XI—Exp. X

| | | | | |
|---|---|---|---|---|
| 0 | 0.0 | | — | |
| 30 | 0.45 | (.408) | — | |
| 60 | 0.30 | .253 | .31 | |
| 90 | .15 | .246 | .15 | |
| 120 | .10 | .228 | .09 | |
| 150 | .05 | .265 | .06 | |
| | Av. .248 | | | 1001.0 |

Table XII—Exp. IX

| Secs. | $V_2 \times 10^{-6}$ Obs. | $\beta$ | $V_2 \times 10^{-6}$ Calc. | $\frac{R}{r}$ |
|---|---|---|---|---|
| 0 | .00 | — | — | |
| 30 | .85 | (.120) | — | |
| 60 | .60 | .076 | .62 | |
| 90 | .35 | .072 | .33 | |
| 120 | .35 | .074 | .21 | |
| | Av. .074 | | | 1108.0 |

Table XIII—Exp. XIII

| | | | | |
|---|---|---|---|---|
| 0 | .00 | — | — | |
| 30 | 1.90 | (.095) | — | |
| 60 | 1.30 | .063 | 1.64 | |
| 90 | 1.00 | .051 | .93 | |
| 120 | .65 | .050 | .60 | |
| 150 | .50 | .047 | .42 | |
| | Av. .053 | | | 478.9 |

TABLE XIV

Valves of $\beta$ obtained in same experiment by different methods.

| Exp. | From $\Sigma_v$ | | From $V_1$ | | From $V_2$ | |
|---|---|---|---|---|---|---|
| | $\beta$ | R/r | $\beta$ | R/r | $\beta$ | R/r |
| VIII | .046 | 345.2 | .0269 | 206.3 | — | |
| IX | .0769 | 1152.0 | — | | .074 | 1108.0 |
| X | .623 | 2513.0 | — | | .246 | 1001.0 |
| XI | — | | .0445 | 325.3 | .099 | 723.8 |
| XII | — | | .0531 | 542.5 | .101 | 1032.0 |
| XIII | — | | .0179 | 163.0 | .0528 | 478.9 |

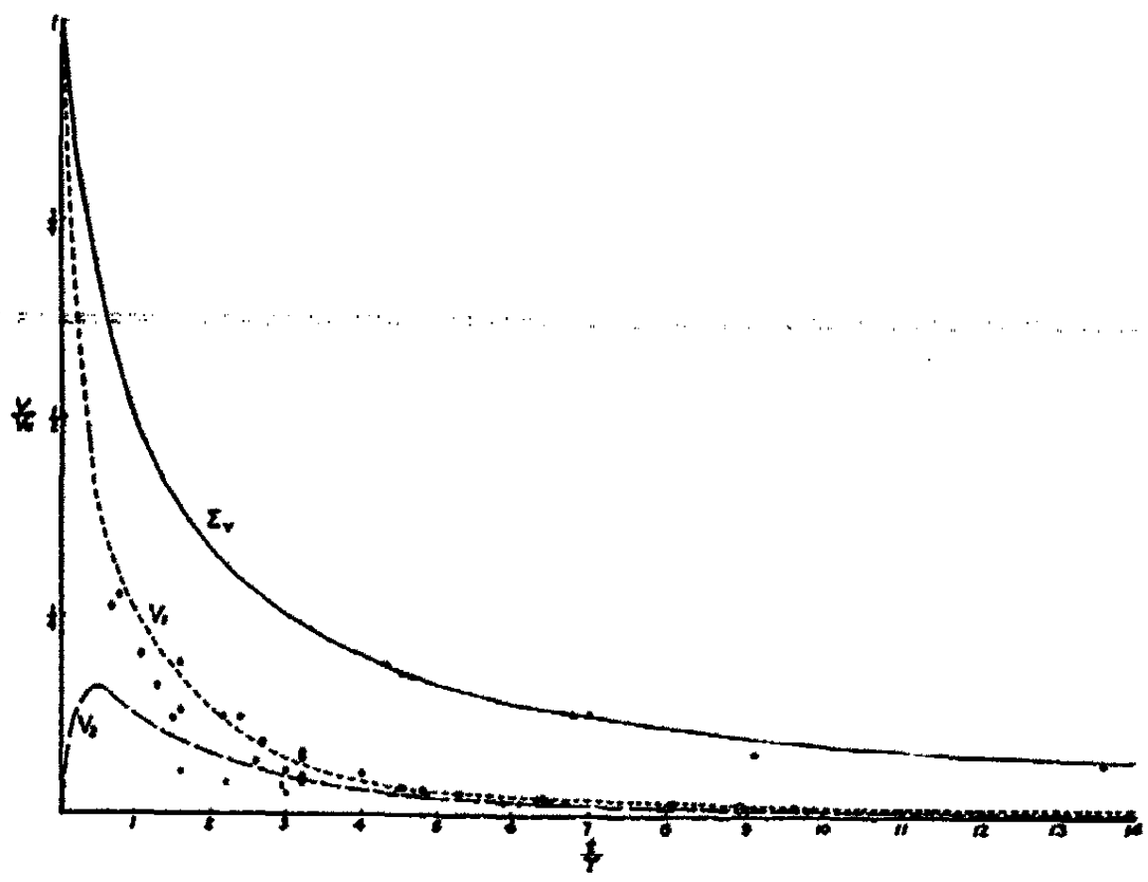



FIG. 4

In Series III, two-celled aggregates were counted and calculations of the values of $\beta$ and of $V_2$ made by the use of the equation,

$$V_2 = V_0 \beta t/(1 + \beta t)^3.$$

The data obtained are shown in Tables IX-XIII, and the type of curve is illustrated by the lower curve in Fig. 3.

In Series IV two different kinds of counts were made from each tube to see if the values for $\beta$ would be the same for the two counts. There is considerable variation in the $\beta$ of some of the experiments as is shown by Table XIV. In others the agreement is as satisfactory as can be expected in such a rigorous test of the theory.

Two methods have been devised to give a graphic comparison between the theoretical and experimental values. Von Smoluchowski constructed curves showing the theoretical progress of coagulation based on equations (1) to (4) using $v/v^\circ$ as ordinates and $t/T$ as abscissae. Such a set of theoretical curves, together with the experimental data is shown in Fig. 4.

The second method in which the theoretical values are represented by straight lines was used by Ehringhaus and Wintgen[1]. By the rearrangement of the equation $\Sigma_v = \frac{V_o}{1 + t/T}$ the equation $1/\Sigma_v = 1/V_o + \left(\frac{1/T}{V_o}\right)t$ is obtained and since $1/V_o + \frac{1/T}{V_o}$ is constant for a given experiment, plotting $1/\Sigma_v$ against t should give a straight line. The results are shown in Figs. 5-7.

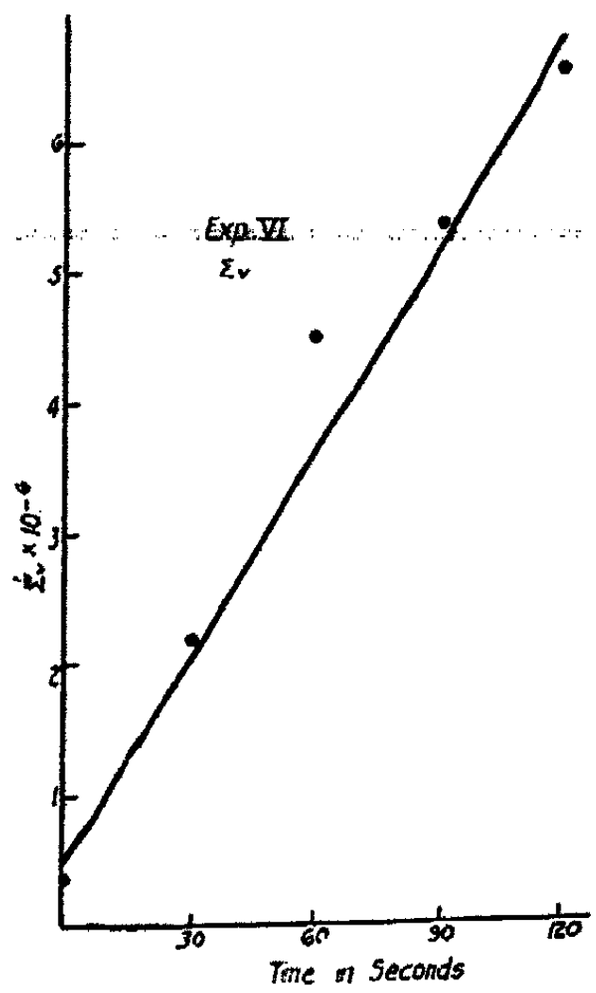



FIG. 5

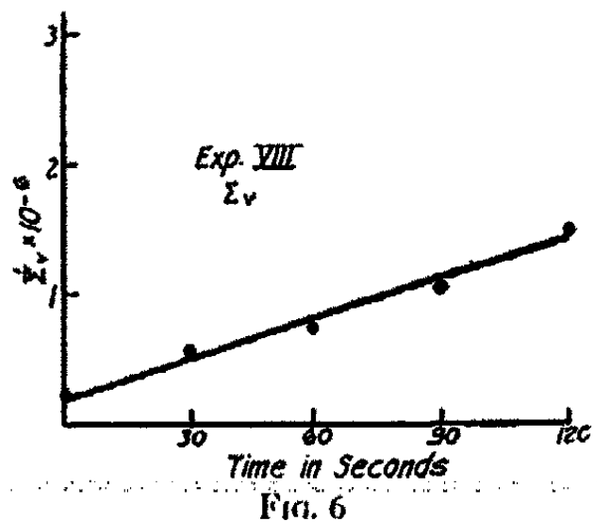



FIG. 6

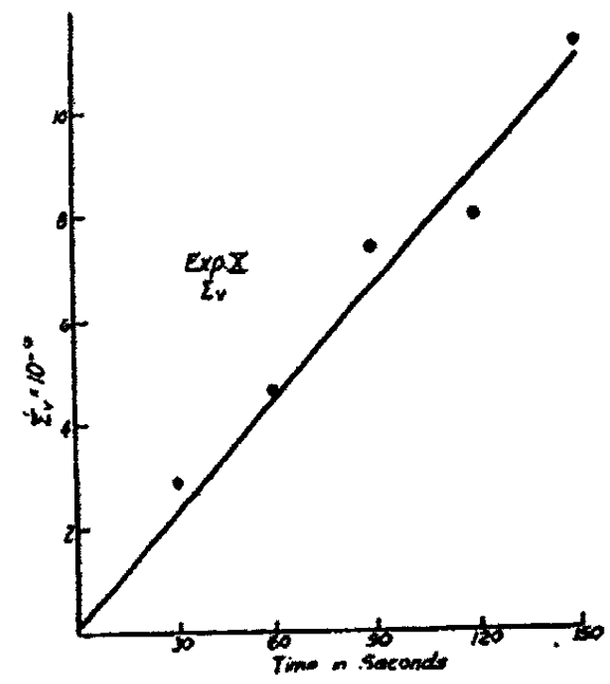



FIG. 7

Similarly the equation $V_1 = \frac{V_o}{(1 + t/T)^2}$ was rearranged, giving $\sqrt{\frac{1}{V_1}} = \frac{1}{\sqrt{V^o}} + \left(\frac{1/T}{\sqrt{V_o}}\right)t$ and $\sqrt{\frac{1}{V_1}}$ plotted against t. The results are illustrated by Figs. 8-10. Considering the difficulties of the experiment the agreements between the theoretical and observed values are quite satisfactory.

## Discussion

Certain differences between the mechanism of chemical reactions and of coagulation have been pointed out by v. Smoluchowski. In chemical union

[1] Z. physik. Chem. **104**, 301 (1923).

only a definite number of atoms or atom groups unite to form a molecule while in coagulation successive complexes are formed whose size has theoretically no limit. In Figures 11 and 2 the usual kinetic formulae of chemical reactions are applied to the observed rate of agglutinations as expressed by the decrease in the number of single particles, the concentration $V_1$ being plotted as log $V_1$ (Fig. 2), and $1/V_1$ and $1/V_1^2$ (Fig. 11). It is seen that the process of agglutination does not follow the course of a mono-, bi- or trimolecular reaction.

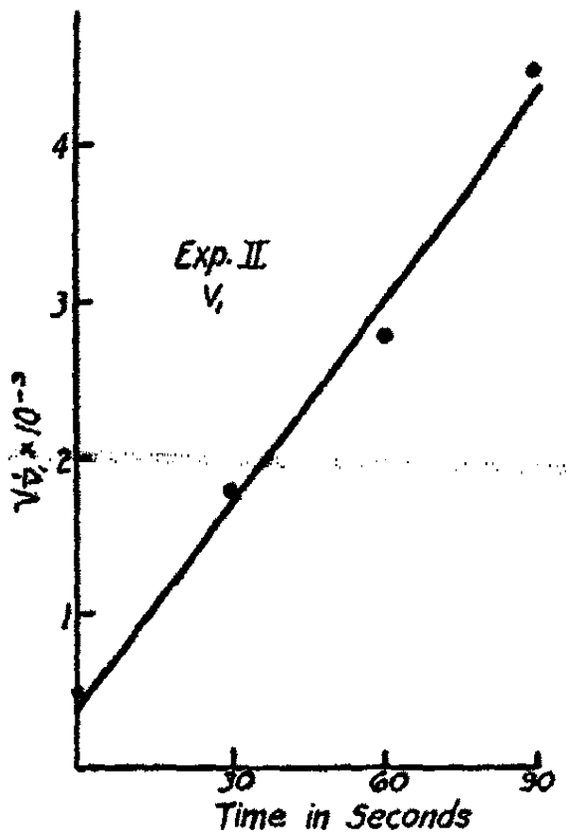



FIG. 8

The experimental data on the rate of rapid agglutination of red blood cells are therefore in fairly good agreement with the reported results with colloids and with v. Smoluchowski's theory. But when we come to the calculation of R/r i.e., the ratio of the radius of the cell to its sphere of attraction, a striking difference appears. Whereas the largest values

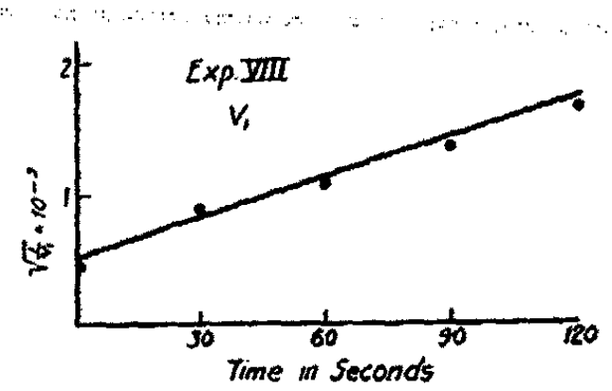



FIG. 9

heretofore obtained is 13.7 (Ehringhaus and Wintgen), our values range from 142.3 to 2513, the average of all experiments being 653.0. In the equation $R/r = \frac{\beta}{2/3\ H\Theta/N\eta\ V_o}$ the quantity $2/3\ H\Theta/N\eta$ is practically a constant for ordinary temperatures, so that the value of R/r depends almost wholly on the ratio $\beta/V_o$. In all of our experiments the value of $V_o$ is small as compared to the concentrations of colloids used by other investigators. Our values for $\beta$, on the contrary, do not, except in a few instances differ markedly from those obtained by others. This follows from the fact that the absolute rate of the agglutination of the weak cell suspension is almost as rapid as that of the coagulation of the concentrated colloidal solution.

In order for agglutination of the cells to proceed as rapidly as coagulation of the particles there are at least two differences in the suspensions which must be compensated for if their units are to come in contact and form aggregates at equal rates. In the first place, the red blood cells are farther apart. Comparing one of Westgren and Reitstötter's experiments with our experiment IX, their particles are $7.9 \times 10^{-4}$ cm. apart whereas the red blood cells are $35.4 \times 10^{-4}$ cm. apart. This gives a ratio,

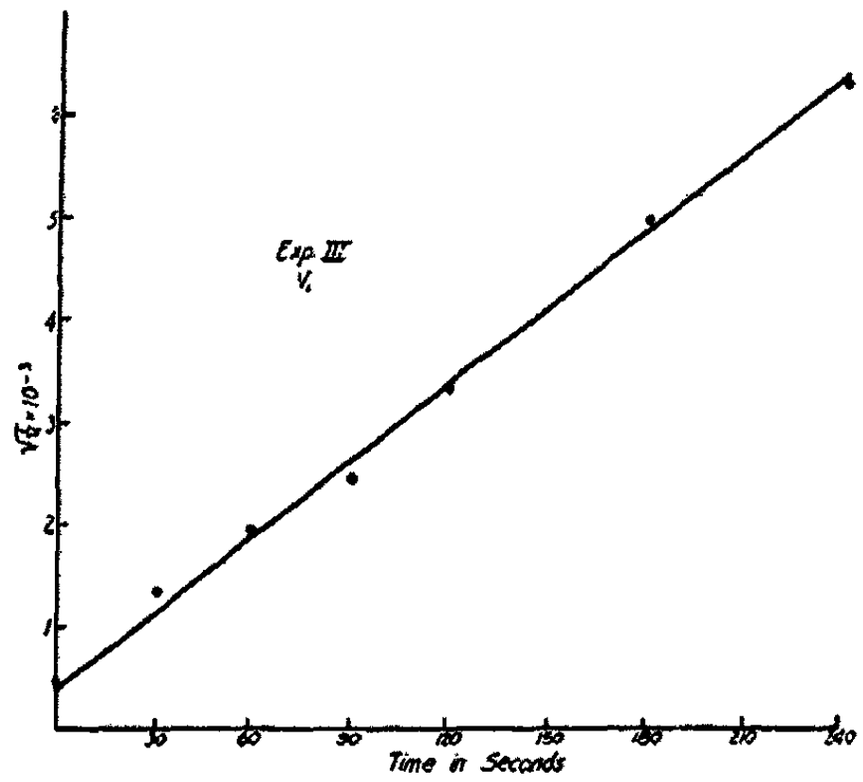



FIG. 10

$$\frac{\text{Distance between cells}}{\text{Distance between particles}} = 4.4$$

The second factor is that the Brownian movement of red blood cells is relatively slight. From the formula $\Delta^2 = RT/N \cdot 1/3\pi\eta r \cdot t$, where $\Delta$ = average distance; $R = 8.31 \times 10^7$ (gas constant); $N = 6.06 \times 10^{23}$ (Avogadro's constant); T = absolute temperature; t = time in seconds; $\eta$ = coefficient of viscosity; r = radius of particle. The Brownian movement of the gold particles in the experiment cited above which have a radius of $96\mu\mu$ is $19.2 \times$

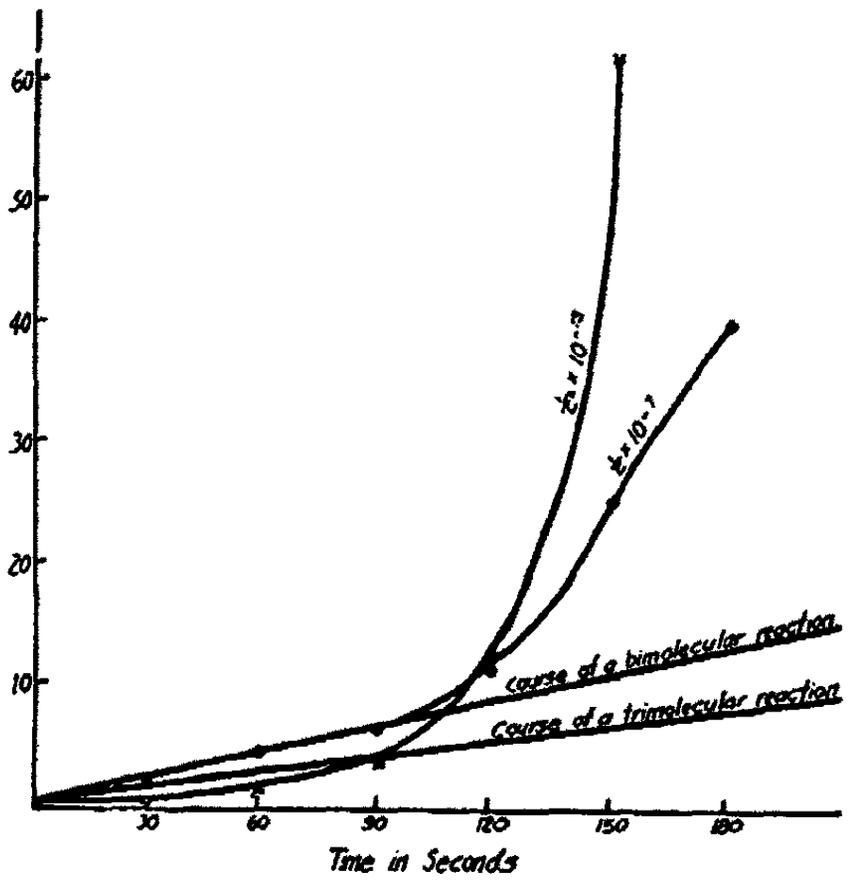



FIG. 11

$10^{-5}$ cm. per second. The Brownian movement of the red blood cells used, which have a radius of 2600$\mu\mu$ is *theoretically* $4.05 \times 10^{-5}$ cm. per cc. This gives a ratio

$$\frac{\text{Brownian movement of cells}}{\text{Brownian movement of particles}} = 0.21$$

and the ratio

$$\frac{\text{Distance ratio}}{\text{Brownian movement ratio}} = 20.95$$

In actual fact this ratio of discrepancy between the two types of suspensions is certainly much larger, as the red cells have even less Brownian movement

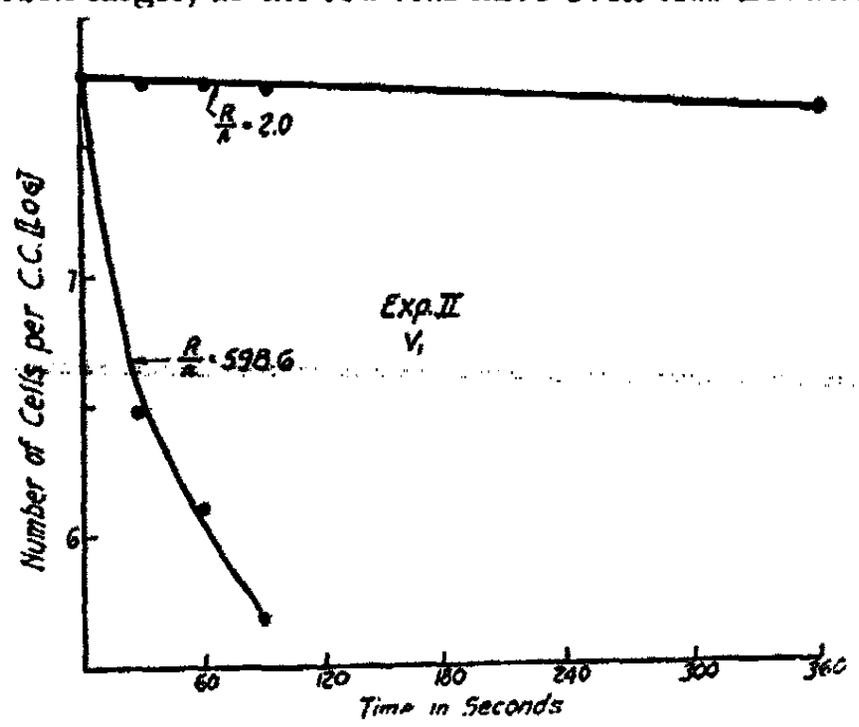



FIG. 12

than the theory would indicate. Practically speaking they have none when one considers the distance which separates them in our suspensions.

It is therefore evident that some factor must operate to enable the red blood cells to form, as they do, aggregates as rapidly as colloidal particles. This unknown factor may well be included in what is considered a larger attration sphere. This necessity for a large attraction sphere is shown graphically in Fig. 12, where the upper curve illustrates what the course of agglutination in experiment II would be if $R/r = 2.0$, and the lower curve illustrates the actual data where $R/r = 598.6$. In other words the maximum range of effective attraction between the cells in this experiment was 0.15 cm!

We have at present no explanation to offer for this remarkable difference between the cell suspensions and the colloidal solutions in regard to the "radii of attraction" of their particles. The cells and particles themselves differ in at least two ways. The cells are relatively enormous, their volume being approximately 50,000 times that of the gold particles. They also bear a different relation to the surrounding medium than does the gold particle as they are permeable to water and certain ions. Mass effects and surface energies may therefore differ considerably in the two cases and these may account for the relatively large "sphere of attraction" that is observed in the rapid agglutination of the red cells. An investigation of these problems is in progress.

# REACTIONS OF THE TYPE $Cl_2 + 2\ KOH = KCl + KClO + H_2O$ [1]

BY F. W. BERGSTROM[2]

## Introduction and Discussion

Potassium amide[3] reacts readily with strongly electropositive elements such as sodium, lithium, and calcium, more slowly with magnesium, aluminum and lanthanum, and very slowly with cerium, zinc and manganese[4].

Elements between cadmium and cobalt in the electropotential series fail to react with solutions of potassium amide. A solution of this base was found to react very slowly with lead and bismuth, more readily with tin, antimony, arsenic, and tellurium, and very readily with selenium, sulfur, and iodine. Potassium amide thus reacts most readily with strongly electropositive or strongly electronegative elements, while the rate of reaction approaches zero in the case of elements of intermediate electroaffinity, such as cadmium, iron, and cobalt.

The reactions with these classes of elements were found to differ in type. Strongly electropositive elements react initially with basic amides with the formation of solutions of the more electropositive metal:

$$(1)\ Al + 3\ NaNH_2 \rightleftharpoons Al(NH_2)_3 + 3\ Na.$$[5]

Subsequent reactions of sodium upon the solvent and of sodium amide on the amphoteric base, aluminum amide, lead to the formation of sodium ammono-aluminate, $Al(NH_2)_2NHNa \cdot NH_3$:

The initial reaction of an electronegative element with potassium amide is similar to that of chlorine with a cold dilute solution of potassium hydroxide in water:

$$(2)\ Cl_2 + 2\ KOH = KCl + KClO + H_2O.$$

Some other reactions of this type[6] that have been recognized in aqueous solution are the following:

---

[1] The Action of Solutions of Ammono Bases in Liquid Ammonia on Elements more Electronegative than Nickel.

[2] National Research Fellow.

[3] Potassium amide is a base in ammonia, just as potassium hydroxide is a base in water. Franklin: J. Am. Chem. Soc. **46**, 2139 (1924).

[4] Franklin: J. Am. Chem. Soc. **35**, 1463 (1913); J. Phys. Chem. **23**, 41 (1919); J. Am. Chem. Soc. **37**, 2300 (1915); Fitzgerald; **29**, 660 (1907); Bergstrom, **45**, 2788 (1923); **46**, 1548, 1552. (1924); **47**, 1836 (1925).

[5] In general terms, $M^n + nANH_2 \rightleftharpoons M(NH_2)n + nA$, where M is a metal, such as aluminum, of positive valence, n, and A is an alkali metal. See Kraus and Kurtz: J. Am. Chem. Soc., **47**, 45 (1925); Bergstrom: **45**, 2788 (1923); **47**, 1836 (1925)

[6] Mellor: "A Comprehensive Treatise on Theoretical and Inorganic Chemistry," vol. 2, p.50 (1922); Tartar and Draves: [J. Am. Chem. Soc. **46**, 574(1924)]. Arsenic, phosphorus, and silicon react with alkali hydroxides to give as one of the reaction products, respectively, arsine, phosphine, and hydrogen. Winter [J. Am. Chem. Soc., **26**, 1509 (1904)] correctly considers that sodium phosphide is one of the primary products of the action of sodium hydroxide on phosphorus. Sodium phosphide is readily converted by hydrolysis to phosphine and sodium hydroxide. Undoubtedly, sodium arsenide is one of the primary products of the reaction of sodium hydroxide upon arsenic. Arsine is, of course, readily formed by hydrolysis of sodium arsenide.

(3) $F_2 + 2\ KOH = 2\ KF + H_2O + 1/2\ O_2$

(4) Iodine and bromine react initially as in (2)

(5) $(2x + 2)S + 6\ KOH = 2\ K_2S_x + K_2S_2O_3 + 3\ H_2O.$

(6) $(2x + 1)Se + 6\ KOH = 2\ K_2Se_x + K_2SeO_3 + 3H_2O.$

(7) $(2x + 1)Te + 6\ KOH = 2\ K_2Te_x + K_2TeO_3 + 3\ H_2O.$

It is the purpose of the present investigation to examine in detail reactions of this type occurring in liquid ammonia as solvent.

It was found that elements more electronegative than nickel react with solutions of potassium amide, and, to a less extent, with solutions of other ammono bases, provided that the alkali metal salts of that element are soluble in ammonia.[1,2] $Na + NH_3 \longrightarrow \frac{1}{2}H_2 + NaNH_2$, a reaction catalyzed by Al and $Al(NH_2)_3$; $NaNH_2 + Al(NH_2)_3 \longrightarrow Al(NH_2)NHNa{\cdot}NH_3$.

Tin reacts with sodium or potassium hydroxide to form a stannite and hydrogen, while phosphorus reacts with this base to form a hypophosphite and phosphine. In view of the fact that potassium amide reacts with these elements in ammonia initially according to the type reaction illustrated by equation (2), it is probable that the reactions of these elements and arsenic with bases in water all take place in an analogous manner. Due to hydrolysis, the alkali stannides formed by the action of sodium or potassium hydroxide on tin are converted to stannane, $SnH_4$, which is unstable and decomposes to give tin and hydrogen.[3]

No satisfactory mechanism has heretofore been proposed for the action of aqueous solutions of bases upon tin.[4]

### The Reaction between Potassium Amide and Iodine

Iodine reacts very rapidly with potassium amide at $-33°$ with the formation of potassium iodide and nitrogen, according to the equation (8) $6\ I + 6\ KNH_2 = 6\ KI + 4\ NH_3 + N_2$. Obviously, this reaction is analogous to the action of fluorine on a solution of potassium hydroxide.(3). Calculated from (8), 29.4 cc. of nitrogen (standard conditions) would be liberated by the action of potassium amide upon one gram of iodine. Experimentally there was collected 38.6 and 37.8 cc. nitrogen (reduced to standard conditions) when 1.160 and 1.118 g. iodine reacted with an excess of potassium amide. This corresponds respectively to 33.3 and 33.9 cc. nitrogen per gram of iodine. The apparatus used for collection of gas was not altogether satisfactory. Iodine was melted into glass tubes of 5 mm. diameter, convenient lengths of

---

[1] Potassium and sodium form soluble salts of homo-atomic anions containing lead, tin, bismuth, antimony, arsenic, phosphorus, tellurium, selenium, sulfur, iodine. Kraus; J. Am. Chem. Soc. **44**, 1220 (1922). E.g, $K_4Pb_9$, $Na_3Sb_7$, $Na_2Te_4$, $K_2Se_5$, $K_2S_x$, etc.

[2] The initial reactions may be expressed by the general equation

$$(1 + m/n)M + nANH_2 = m/nM(NH_2)_n + AmM$$

where m is the negative and n the positive valence of the element M. In general, one or both of the products on the right hand side of the equation react further with those on the left hand side. Kraus: Trans. Am. Electrochem. Soc. **45**, 185 (1924).

[3] Kraus: J. Am. Chem. Soc. **44**, 179 (1922). The alkali stannides are analogous to the KCl of equation (2), while the stannites are analogous to KClO.

[4] Cf. Mellor: "A Comprehensive Treatise, etc"., Vol. 2, p. 509 (1922).

this tube were cut off and introduced rapidly into a reaction vessel, cooled by a bath of liquid ammonia at $-33°$. Gases evolved in the reaction were passed through a mercury trap into a large tube filled with water to absorb ammonia, thence being drawn through phosphorus pentoxide tubes by a Töpler pump, and so transferred to an apparatus for gas analysis. By the action of sodium amide on iodine at very low temperatures, Ruff[1] prepared a substance of the composition $Na_2NI_3$, which probably consisted in part of a sodium ammonohypoiodite. Substances have been prepared[2] which may be regarded as salts of ammono hypoiodous acid, $INH_2$ or $I_2NH$.( = $NI_3 \cdot xNH_3$).

### The Reaction between Basic Amides and Sulfur

Sulfur reacts very readily and without evolution of gas with a solution of potassium amide at $-33°$ initially to form a yellow precipitate, which subsequently goes into solution because of further reaction with sulfur. Sulfur readily reacts with the amides of lithium, calcium, barium and magnesium while a solution of sulfur in liquid ammonia at 20° more slowly reacts with cobaltous and mercuric nitrides and lead imide. It appears from this work that there are obtained derivatives of ammonosulfurous acid, $S(NH)_2$, of ammonothiosulfuric acid, $S_2(NH)_2$, and perhaps of other ammono sulfur acids.[3]

### The Reaction between Ammono Bases and Selenium

Selenium reacts readily with potassium amide solution at $-33°$ or room temperature initially with the formation of a white precipitate which contains a very explosive substance, probably a potassium salt of selenium amide or imide, and potassium monoselenide. Further reaction with an excess of selenium leads to the formation of highly colored solutions containing polyselenides of potassium and a soluble, non-explosive potassium salt of a complex ammono acid containing selenium.[4] Selenium was found to react readily with the amides of sodium, lithium, and barium. Calcium amide attacks selenium at a very slow rate, probably because of the low solubility of the products of the reaction. No gas was evolved in the reaction between selenium and potassium amide at $-33°$, although small amounts were obtained when the reaction was carried on at room temperature.[5]

### The Reaction between Potassium Amide and Tellurium

Tellurium reacts fairly readily with potassium or sodium amides at room temperature, although only very slowly at $-33°$. In the presence of an excess of tellurium, soluble alkali polytellurides are formed, the insoluble product of the reaction probably being an ammonotellurite or tellurate. Attempts to analyze this substance resulted in violent explosions.

---

[1] Ber. **33**, 3025 (1900).

[2] Szuhay: Ber. **26**, 1933 (1893); Silberrad: J. Chem. Soc. **87**, 68 (1905).

[3] Derivatives of ammonosulfurous and ammonothiosulfuric acids have been prepared by Ruff and Geisel: Ber., **37**, 1573 (1904). A more complete discussion of the ammono acids of sulfur will appear in a forthcoming paper.

[4] This salt may possibly bear some analogy to the thiosulfates.

[5] For method of determining this gas, see J. Am. Chem. Soc. **47**, 2320 (1925).

### The Reaction between Basic Amides and Arsenic, Antimony, and Bismuth

Arsenic and antimony react slowly with a solution of potassium amide at room temperature with the production of red solutions indicative of the presence of complex anions containing these two elements.[1] Sodium amide reacts slowly with arsenic and very slowly with antimony. Potassium amide, and more particularly sodium amide, react with extreme slowness with bismuth.

### The Reaction between Basic Amides and Phosphorus

Red and yellow phosphorus both react readily with potassium amide at room temperature to form a solution containing a polyphosphide of potassium and a light yellow precipitate, perhaps a potassium ammonophosphite. Sodium amide reacts in a similar manner with red phosphorus.

### The Reaction between Basic Amides and Tin

Tin was found to react slowly with sodium amide and with a dilute solution of potassium amide with the formation of deep red solutions containing sodium or potassium ammonostannites and polystannides, in accordance with the equation:[2,3,4]

(9) $10Sn + 6\ KNH_2$ (or $NaNH_2$) $= 2SnNK\cdot 2NH_3$ (or $SnNNa\cdot 2NH_3$) $+ K_4Sn_8$ (or $Na_4Sn_8$)

The stannites may be alternately formulated as $Sn(NH_2)_2\cdot KNH_2$, $Sn(NH_2)_2\cdot NaNH_2$ or as $K(Sn(NH_2)_3)$, $Na(Sn(NH_2)_3)$. Tin, while dissolved at a very slow rate by lithium amide, fails to react appreciably with barium or calcium amides at room temperature.

Potassium and sodium ammonostannites are white solids, very readily soluble in liquid ammonia and are thus easily distinguished from potassium ammonostannate, which is only very slightly soluble.[5] The stannites react very vigorously with water without the formation of appreciable quantities of nitrogen or hydrogen. That potassium and sodium ammonostannites are derivatives of divalent tin was verified by preparing the potassium salt by the action of potassium amide on stannous chloride.

Although potassium amide in dilute solution at room temperature reacts slowly with tin, the reaction in the more concentrated solutions is practically negligible, owing to the formation of passive coating over the metal. (See Fig. 1) This passive coating could be removed by the action of a solution of ammonium chloride—an acid in ammonia—or even by the long continued

---

[1] Peck: J. Am. Chem. Soc. 40, 335 (1918).

[2] It is not certain, although it is very probable, that the ammono salt first formed is a derivative of divalent tin, for potassium ammonostannate was found to react very slowly with tin to form potassium ammonostannite. Thus, a tin rod in contact with an excess of crystals of potassium ammonostannate in liquid ammonia for three weeks at room temperatures lost 7 mg. in weight.

[3] For a discussion of intermetallic compounds of this type, see Kraus: J. Am. Chem. Soc., 44, 1216 (1922).

[4] Kraus: J. Am. Chem. Soc., 44, 179 (1922).

[5] Fitzgerald: J. Am. Chem. Soc. 29, 1692 (1907).

action of the pure solvent, so was probably a very slightly soluble potassium tin alloy. Sodium amide was found to react more smoothly and readily with tin without the formation of a passive coating over the metal. The formation of this coating evidently depends upon the initial concentration of the reacting base. Sodium amide is soluble only to the extent of about a gram per liter in liquid ammonia at ordinary temperatures, while potassium amide is very soluble.

*Experimental Work:*

The equations given for the reactions between tin and the amides of sodium and potassium have been verified (1) by determination of the amount of tin dissolved by weighed quantities of potassium or sodium amides at room temperature; (2) by the approximate determination of the ratio of alkali metal in the ammono salt formed to the total quantity of alkali metal used in the reaction; (3) by analysis of the ammono salt.

The solubility of tin in potassium or sodium amide solutions was determined by allowing a known amount of the ammono base to react with a weighed tin rod, the weight of the rod again being determined after the attainment of equilibrium. Sodium and potassium amides were prepared by the action of liquid ammonia, in the presence of iron wire, which acts as a catalyst, upon weighed quantities of the corresponding alkali metal.[1] Tin was used in the form of slender rods, obtained by melting the metal in a vacuum and allowing it to flow into a glass tube of 5-6 mm. internal diameter, which served as a mold. The glass was readily removed from the tin by suddenly chilling the still hot tube in water.[2]

It was found convenient to use a three-legged glass reaction tube, the legs containing respectively alkali metal plus iron wire catalyst, the weighed rod of tin, and mercury. The alkali metal amide was transferred quantitatively to the leg containing the tin and allowed to react with this metal from two to twelve months. In order to remove the alkali metal polystannide, the deep red solution resulting from this reaction was washed into the leg containing the mercury, in which this alloy is soluble.[3] The leg of the reaction tube containing the tin was opened[4] the tin removed and weighed, and the leg cleaned and sealed up again. Into this leg was then decanted the colorless solution of the stannite, which was evaporated to dryness, the resulting solid being dried in a vacuum and submitted to analysis. The ammonia in the reaction tube was evaporated into a tared flask of water and so determined.

The solubilities of tin in sodium and potassium amide solutions, as thus determined, are plotted in Fig. 1. against the concentration. The average

---

[1] Kraus and Chiu: J. Am. Chem. Soc. **44**, 2001 (1922) give directions for preparing sealed glass capsules containing weighed quantities of sodium or potassium.

[2] Compare method of Kraus and Chiu for preparing sticks of tellurium. ibid, p. 2002.

[3] Bergstrom: J. Am. Chem. Soc. **47**, 1506 (1925).

[4] The manipulations required for the preparation of substances in liquid ammonia solution will readily be understood from previous articles. Franklin and others: J. Am. Chem. Soc. **27**, 832 (1905); **29**, 1694 (1907); **35**, 1460 (1913); **46**, 1545 (1924); J. Phys. Chem. **15**, 915 (1911); **16**, 694 (1912). In these reactions, the stopcock of the reaction tube was sealed off to prevent gradual loss of ammonia.

atomic ration of tin to alkali metal in the case of tin–sodium amide is 1.65. The maximum ratio in the case of tin–potassium amide is 1.70. These values would indicate $Na_4Sn_8$ or $K_4Sn_8$ to be formed in the reactions represented by equation (9). It is possible that some alkali ammonostannate is formed simultaneously with the stannite, for a very small amount of white matter, very slightly soluble in ammonia, is invariably present at the end of a reaction.

In the reactions between sodium or potassium amides and tin amalgam, nearly the theoretical amount of alkali metal initially used (33.3%, according to equation 9) was recovered in the sodium or potassium ammonostannite. In the reactions between tin and the alkali metal amides, the percentage of

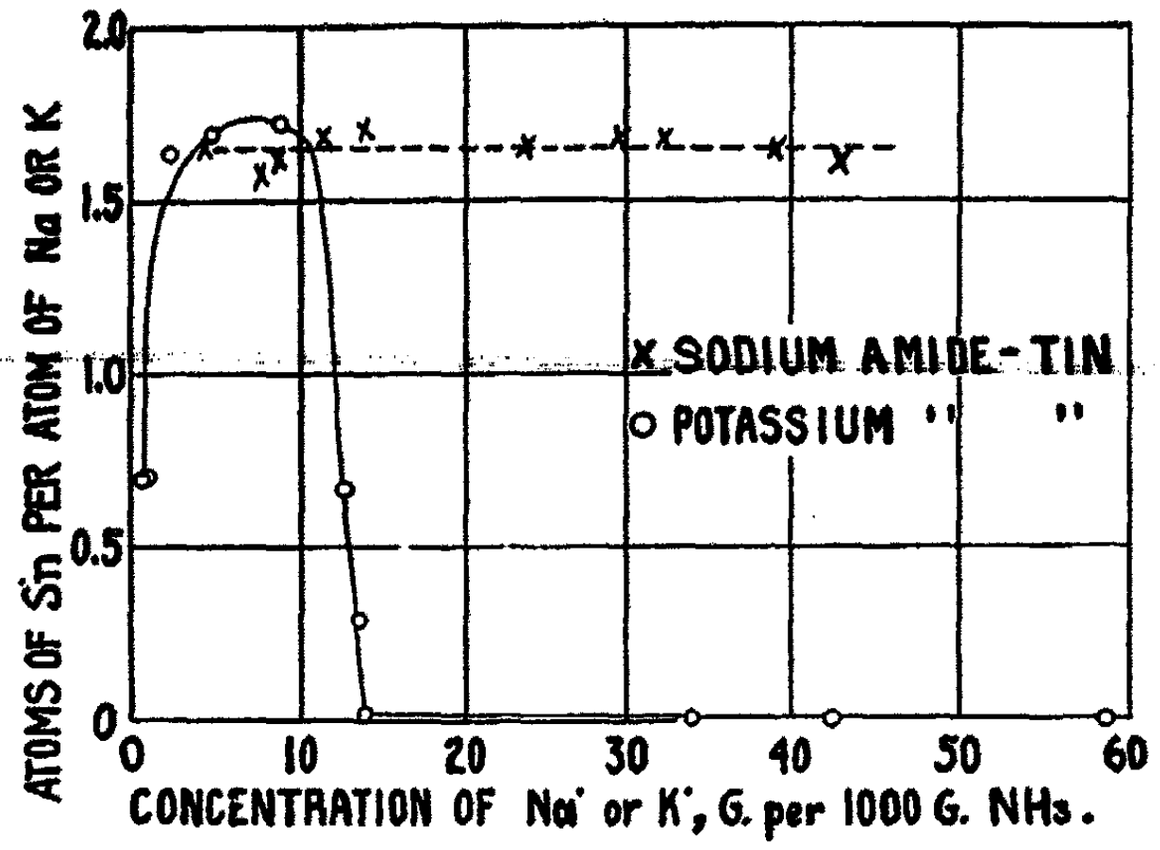



FIG. 1

the alkali metal found in the ammono salt was frequently close to 33%, and at times several percent lower, due chiefly to experimental error.

*Preparations of Potassium Ammonostannite.*

Specimen (1) was prepared by the action of mercury on the product of reaction of tin with potassium amide, specimens (2) and (3) by the action of potassium amide upon an excess of tin amalgam, and (4) and (5) by the action of potassium amide upon stannous chloride: $3KNH_2 + SnCl_2 = 2KCl + SnNK \cdot 2NH_3$. If potassium amide is not used in excess of the quantity demanded by the equation, the only soluble product of the reaction is potassium ammonostannite. Potassium chloride is only slightly soluble in ammonia. Some reduction of the stannous chloride evidently takes place, the resulting tin reacting with potassium amide to give a light red solution containing a potassium polystannide, which decolorizes slowly in contact with the precipitate in the reaction tube.

Preparatory to analysis, the specimens were dried in a vacuum, hydrolyzed rapidly by water and dissolved in dilute hydrochloric acid. All of the nitro-

gen present in the preparations was thereby converted to ammonium chloride, in which form the nitrogen was readily determined by the customary acidimetric method. Tin was precipitated as sulfide and weighed as dioxide, but the method was not satisfactory, giving low results for tin. Potassium was determined as sulfate in the filtrate from the tin sulfide.

| No. | Wt. subs. dried in vacuo at (°). | | Wt. of $SnO_2$ in () of subs. | | Wt. of nitrogen in () of subs. | | Wt. of $K_2SO_4$ in () of subs. | |
|---|---|---|---|---|---|---|---|---|
| 1 | (20°) | 0.1118g | | | (1/2) | 0.01090g. | (1/2) | 0.0248g. |
| 2 | (20°) | 0.5454 | | | (1/4) | 0.02839 | (1/2) | 0.1160 |
| 3 | (20°) | 0.5967 | (3/4) | 0.3232g | (1/4) | 0.02968 | (3/4) | 0.1855 |
| 4 | (-40°) | 0.4684 | | | | | | |
| | (20°) | 0.4677 | (1/4) | 0.0838 | (1/4) | 0.02375 | (1/2) | 0.1031 |
| 5 | (20°) | 0.2827 | (1/4) | 0.0513 | (1/4) | 0.01459 | (1/2) | 0.0629 |

*Preparations of Sodium Ammonostannite.*

Specimen (1) was prepared from sodium amide and tin amalgam. The remainder of the preparations were made by the action of mercury on the product of reaction of sodium amide and tin. Sodium ammonostannite was analyzed in the same manner as the potassium salt.

| No. | Wt. subs. dried in vacuo at ()° | | Wt. of $SnO_2$ in () of subs. | | Wt. of nitrogen in () of subs. | | Wt. of $Na_2SO_4$ in () of subs. | |
|---|---|---|---|---|---|---|---|---|
| 1 | (20°) | 0.5042g | (3/4) | 0.2977g | (1/4) | 0.01757g | (3/4) | 0.1451g |
| 2 | (20°) | 0.6507 | (1/4) | 0.1265 | (1/4) | 0.03617 | (1/2) | 0.1244 |
| 3 | (20°) | 0.7334 | (1/4) | 0.1446 | (1/4) | 0.04077 | (1/4) | 0.0701 |
| 4 | (20°) | 0.1979 | (1/2) | 0.0766 | | | (1/2) | 0.0377 |

**Summary of Analyses**

(Dried in a vacuum at 20°)

| | Calc. for $SnNK{\cdot}2NH_3$ | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| Sn | 57.7 | | | 56.9 | 56.5 | 57.2 |
| N | 20.4 | 19.5 | 20.8 | 19.9 | 20.3 | 20.6 |
| K | 19.0 | 19.9 | 19.1 | 18.6 | 19.8 | 20.0 |
| | Calc. for $SnNNa{\cdot}NH_3$ | | | | | |
| Sn | 62.6 | 62.0 | 61.3 | 62.2 | 61.8 | |
| N | 22.1 | 22.1 | 22.2 | 22.3 | | |
| Na | 12.1 | 12.4 | 12.4 | 12.2 | 12.3 | |

The analyses are satisfactory, considering the fact that the salts were too soluble in ammonia to be purified by crystallization from this solvent.

*The Reaction between Solutions of the Basic Amides and Lead.*

Lead was found to behave in a very erratic manner. At times this metal reacted very slowly with a solution of potassium amide with the formation of a green solution containing potassium polyplumbide, and, presumably, potassium ammonoplumbite; while, at other times, apparently under the

identical experimental conditions reaction failed to take place. This is probably due to the condition of the surface of the lead. Sodium amide, in two experiments, failed to react with lead over a period of several months.

*The Reactions between Solutions of Potassium Amide and Others of the more Electronegative Elements and Their Amalgams.*

A 0.6 normal solution of potassium amide failed appreciably to attack gold in four months, or copper in nine months at room temperature. Germanium, either in powder or lump form was not appreciably attacked in two months. Mercury, which had been distilled in a vacuum, but not in a current of air[1] was attacked at an extremely slow rate. Lead, bismuth, silver amalgams were not appreciably attacked by a solution of potassium amide, while the amalgams of copper and gold were attacked very slowly, and tin amalgam was attacked much more rapidly.

In conclusion, the author wishes to express his thanks to Dr. C. A. Kraus for his kind and helpful interest in this work.

## Summary

(1) Potassium amide reacts with lead and all elements more electronegative than lead, provided the alkali metal salts containing these elements in homo-atomic anions are soluble in liquid ammonia. These reactions are all of the type of the reaction between chlorine and a cold dilute solution of potassium hydroxide: $Cl_2 + 2KOH = KClO + KCl + H_2O$. Thus, the equation for the reaction of potassium amide with an excess of tin is $10Sn + + 6KNH_2 = K_4Sn_8 + 2SnNK \cdot 2NH_3$.

(2) The reactions between aqueous solutions of bases and tin, arsenic or phosphorus are likewise of the type $Cl_2 + 2KOH = KClO + KCl + H_2O$ The hydrogen obtained in the first instance, and the arsine and phosphine in the second and third undoubtedly result from secondary reactions of water on potassium stannide potassium arsenide, and potassium phosphide.

(3) Potassium and sodium ammonostannites have been prepared. The constitution of these salts may be represented by the alternate formulas:

$Sn(NH_2)_2 \cdot KNH_2$, $SnNK \cdot 2NH_3$ or $K[Sn(NH_2)_3]$;

$Sn(NH_2)_2 \cdot NaNH_2$, $SnNNa \cdot 2NH_3$, or $Na[Sn(NH_2)_3]$.

[1] Hulett: Phys. Rev. **33**, 397 (1911) states that mercury prepared in this manner is not quite pure.

# THE ANTAGONISTIC ACTION OF IONS IN THE NEUTRALIZATION OF SOLS

BY HARRY B. WEISER

In the precipitation by electrolytes of sols stabilized by preferential adsorption of ions, it is usually considered that only anions count in the case of positive sols and only cations count in the case of negative sols. However, it was recognized by Freundlich[1] a score of years ago that the critical precipitation concentration of electrolytes for sols may be influenced by the ion having the same charge as the sol; and a decade ago Bancroft[2] pointed out that the amount of electrolyte required to precipitate any given suspension will vary with the nature of the cation, the anion and the disperse phase. This point of view does not seem to have been taken seriously by many people; but in 1920, attention was called[3] to the fact that the influence of the ions having the same charge as the sol cannot be disregarded entirely in any case, and may be quite marked if the electrolyte precipitates only in high concentration. The precipitation value of electrolytes for sols was therefore defined as that concentration which results in sufficient adsorption of the precipitating ion to neutralize the combined adsorption of the original stabilizing ion and the stabilizing ion added with the precipitating solution. There is thus an antagonistic action between the oppositely charged ions of a precipitating electrolyte in the sense that the greater the adsorption of the stabilizing ion the greater must be the adsorption of the precipitating ion to effect neutralization. Hence the precipitation value of an electrolyte with a strongly adsorbed stabilizing ion is necessarily higher than that of an electrolyte with a weakly adsorbed stabilizing ion.

Recognition of the importance of the stabilizing ion in the precipitation of sols by electrolytes lead directly to a plausible explanation of the manner in which the precipitation value varies with the concentration of sol and furnished a partial explanation of the behavior of certain mixtures of electrolytes with certain sols. Within the past year there has appeared a number of papers by Dhar, Sen and Ghosh[4] more than 150 pages to date, which further emphasize the action of ions having the same charge as the sol. Since the relation of this work to the work of the author is not always clear, particularly in the later papers, it seems advisable to consider the phenomena studied earlier by the author in the light of the observations of Dhar and his collaborators, Of these phenomena, the influence of dilution of sols on their stability toward electrolytes and the "acclimatization" of sols will be discussed briefly;

[1] "Kapillarchemie", 352 (1909); Z. physik, Chem., **44**, 104 (1903).

[2] J. Phys. Chem., **19**, 363 (1915).

[3] Weiser: J. Phys. Chem., **24**, 30 (1920).

[4] J. Phys. Chem., **28**, 313, 457, 1029 (1924); **29**, 435, 517, 659 (1925); Kolloid-Z., **34**, 262 (1924); **36**, 129 (1925); Z. anorg. Chem., **142**, 345 (1925). See also Mukherjee and Ghosh: Quart. J. Indian. Chem. Soc., **1**, 213 (1924).

while the action of mixtures of electrolytes on sols will receive detailed consideration.

### Effect of Dilution of Sols on their Stability toward Electrolytes

From an investigation of the influence of the concentration of sols on their precipitation by electrolytes the following conclusions were formulated:[1]

(1) The manner in which the precipitation value of an electrolyte varies with the concentration of colloid is determined to a large extent by the relative adsorbability of the precipitating ion and the stabilizing ion.

(2) If the adsorption of the stabilizing ion of an electrolyte is negligible and the adsorption of the precipitating ion is very large, the precipitation value varies almost directly with the concentration of the colloid. This condition may be realized experimentally with electrolytes having trivalent and tetravalent precipitating ions which precipitate in extremely low concentration.

(3) If the adsorption of the stabilizing ion of an electrolyte is appreciable, the precipitation value is increased. This effect is more pronounced the greater the dilution of the colloid, since the decreased opportunity both of collision and coalescence of particles combines to render the colloid proportionately more stable so that proportionately more of the precipitating ion must be added for complete coagulation. The influence of adsorption of the stabilizing ion is more marked with electrolytes having univalent precipitating ions which precipitate only in very high concentration. Under these conditions, the precipitation value falls off much less sharply than under the conditions given in (1) and may even increase as the concentration of the colloid is decreased.

A survey of the work of the Allahabad laboratory dealing with this subject, discloses merely an extension of the number of cases studied, without contributing anything to the general principles formulated above. The confirmatory data are, of course, valuable; but it is too bad that an attempt at classifying the data leads to the enunciation of a "general dilution rule, that the greater the concentration of a sol, the greater is the amount of electrolyte necessary for coagulation irrespective of the valence of the precipitating ion." This qualitative statement holds whenever the adsorption of the stabilizing ion is small relatively to that of the precipitating ion; but there are necessarily many exceptions to it. Some of these are mentioned; but it is obvious that the list could be extended greatly if there were any point in doing so. Since the precipitation value of an electrolyte depends on the nature of the anion, and of the cation and on the nature of the sol, one might expect the same sol to behave differently with different electrolytes having the same precipitating ion and a different stabilizing ion. Indeed Ghosh and Dhar[2] found that the "rule" was followed with positive ferric oxide sol using potassium chloride[3] but was "abnormal" if aluminum nitrate was the precipitating electrolyte;

[1] Weiser and Nicholas: J. Phys. Chem., 25, 742 (1921).

[2] J. Phys. Chem., 29, 659 (1925).

[3] Note: The results with potassium nitrate are similar to those with potassium chloride.

a result that might be expected from (3) above. Such a rule as Dhar has set down seems to me to be a positive menace rather than a help, if its limitations and the principles on which it is based are not recognized clearly; and if these are recognized, the qualitative rule is superfluous, particularly when one can find exceptions whenever one looks for them.

It was somewhat disconcerting to find Dhar and his collaborators accepting in principle, the author's explanation of the influence of dilution of sols on their stability toward electrolytes, when the former were laboring under the mistaken idea that the most readily adsorbed ion precipitates in highest concentration, the converse of which is that the least adsorbed ion having the same charge as the sols is the strongest stabilizing ion. It is gratifying, however, to find Ghosh and Dhar[1] at last attributing the higher precipitation values for arsenious sulfide sol of potassium sulfate, potassium citrate and potassium ferrocyanide as compared with potassium chloride, to stronger adsorption of the multivalent ions than of univalent chloride. Other advocates of Freundlich's adsorption theory of the stabilization and precipitation of sols had reached this conclusion many years ago.

## The Acclimatization Phenomenon

The amount of electrolyte which will cause complete precipitation when added rapidly, frequently will not do so when it is added dropwise through a long interval of time. In attempting to arrive at the cause of this phenomenon of "acclimatization"[2], it was noted that the slow addition was always accompanied by fractional precipitation of the sol, and I attributed the excess required on slow addition to the continuous removal of ions owing to adsorption by neutralized particles. On this basis the factors which determine the excess of electrolyte required for a given slow rate of addition are: (1) the extent to which the colloid undergoes fractional precipitation; (2) the adsorbing power of the precipitated colloid; and (3) the adsorbability of the precipitating ion. At the time this communication was written I had not studied the effect of dilution of sols on their stability toward electrolytes and so did not know enough to call attention to the fact that the effect is greatest when the precipitation value of the electrolyte increases with decreasing concentrations of sol, such as obtains in the precipitation of arsenious sulfide sol with potassium chloride. In this case, the fractional precipitation accompanying the dropwise addition of potassium salt produces sols that are successively more and more stable, so that a relatively larger amount of electrolyte is necessary for complete precipitation. Recognizing this fact, it was only necessary to modify the third factor in my original paper to read: (3) the relative adsorbability of the precipitating and stabilizing ions. This modification was made in a chapter on adsorption written two years ago for a book being compiled by J. Alexander.

[1] Kolloid-Z., 36, 129 (1925).

[2] Weiser: J. Phys. Chem., 25, 399 (1921).

Dhar, Sen and Ghosh have repeated and extended the experiments on the acclimatization phenomenon and attribute it to adsorption of the stabilizing ion without entering into the mechanism of the action. Had they done so, they would have recognized that strong adsorption of the stabilizing ion is not essential in case there is strong adsorption of the precipitating ions during fractional agglomeration. On the other hand, strong adsorption of the stabilizing ion is important, if not essential, in case the successive dilutions of the sol by fractional precipitation is the determining factor. In either case, acclimatization to a greater or lesser degree is a necessary concomitant of fractional precipitation.

It should be pointed out, in passing, that acclimatization of hydrous ferric oxide precipitated by aluminum nitrate would be expected in view of the increasing precipitation value of this electrolyte with decreasing concentration of sol; however, one should not overlook the stabilizing effect of colloidal hydrous aluminum oxide formed by hydrolysis of the diluted electrolyte. I should not be surprised if this were the more important factor in increasing the precipitation value on slow addition of the electrolyte.

## The Precipitation of Sols by Mixtures

From a study of the precipitation of sols by mixtures of electrolytes, the following conclusions were drawn in 1921:[1]

(1) The precipitating action of mixtures of pairs of electrolytes is approximately additive if the precipitating power of each is of the same order of magnitude; but may be far from additive if the electrolytes have widely varying precipitating power. In the latter case the action of the electrolytes is "antagonistic", in the sense that relatively more of each is necessary than if the other were absent.

(2) In the simultaneous adsoption by solids from mixtures of two electrolytes having no ion in common, the most strongly adsorbed cation and anion are taken up most and the other pair least readily; from mixtures having one ion in common, the oppositely charged ions are each adsorbed less than if the others were absent but the most readily adsorbed ion is displaced the least.

(3) Factors which influence the precipitating action of mixtures of electrolytes are (1) the effect of the presence of each precipitating ion on the adsorption of the other and (2) the stabilizing action of the ions having the same charge as the colloid. The second factor is of minor importance with mixtures of electrolytes that have similar precipitation values and have stabilizing ions in common.

In discussing the action of potassium chloride on colloidal arsenious sulfide it was noted "that the sol probably owes its stability to preferential adsorption of $HS'$ ion derived from the primary dissociation of hydrogen sulfide. If enough potassium chloride is added to this colloid, the adsorption of potassium ion will neutralize the combined adsorption of the stabilizing ions, $HS'$ and $Cl'$. In this particular case the high precipitation value of potassium

[1] Weiser: J. Phys. Chem., 25, 665 (1921).

chloride may be due to the adsorption of Cl′ being comparable at certain concentrations to the adsorption of potassium ion. Indeed it is possible, but not proven, that at certain concentrations of potassium chloride considerable below the precipitation value, the adsorption isotherm for Cl′ may coincide with or even fall below that of potassium ion. Within this region the addition of a small amount of the strongly adsorbed barium or strontium ions may so decrease the adsorption of potassium ion that the isotherm for the latter will fall appreciably below that for Cl′." Almost exactly the same reasoning has been used by Ghosh and Dhar[1]. I represented diagramatically the relative position of the adsorption isotherms for potassium ion and chloride ion which would account for the experimental results; but pointed out that the diagram must be looked upon merely as representing a possibility that has not been verified experimentally so far. Indeed when I returned to this problem, three years later[2], I concluded from a study of adsorption during the precipitation of sols by mixtures, that the first factor mentioned under (3) above was the more important in raising the precipitation values of certain mixtures above the additive value. Thus the greater precipitation value of barium chloride in the presence of lithium chloride or potassium chloride was thought to be due chiefly to the cutting down of the adsorption of each precipitating ion by the presence of the other. Ghosh and Dhar in the first papers dealing with this phenomenon give both factors mentioned in my original paper about equal prominence but in their latest paper,[3] the influence of the stabilizing ion is looked upon as the only factor of importance, largely because the sols which show "abnormal" behavior on dilution and the phenomenon of acclimatization are "abnormal" toward mixtures of electrolytes; and since the first and second phenomena are attributed to adsorption of the stabilizing ion, the third must be. By plotting the logarithms of the concentration of one of the electrolytes added to a negative sol against the logarithms of the difference between observed and calculated values, "more or less straight lines" were obtained. This was cited as conclusive evidence of stabilization by anion adsorption; but, unfortunately, such a qualitative result would be expected if the behavior with mixtures were attributed to cationic antagonism between ions of varying adsorbability.

Sen[4] arrives at the same conclusion as Dhar and Ghosh; and his experimental evidence is distinctly convincing for the case investigated. Thus, with copper ferrocyanide sol, he found an increase in precipitation value of potassium chloride and of barium chloride in the presence of potassium ferrocyanide. With mixtures of potassium chloride and potassium ferrocyanide, it is quite obvious that cationic antagonism can not come in since both precipitating cations are the same. For the first time, this raises the question whether the antagonistic action between ions of the same charge ever plays

[1] J. Phys. Chem., 29, 453 (1925).
[2] Weiser: J. Phys. Chem., 28, 232 (1924).
[3] J. Phys. Chem., 29, 659 (1925).
[4] Z. anorg. Chem., 142, 345 (1925); J. Phys. Chem., 29, 517 (1925).

an important role in raising the precipitation value of mixtures above the additive value.

Consider the case of Graham's ferric oxide sol which owes its stability to preferential adsorption of hydrogen ion derived from hydrolysis of ferric chloride. It is too well known to need comment, that the stability of the sol falls off as the hydrogen ion concentration is decreased by dialysis and if the dialysis is continued long enough, all of the sol will precipitate. Conversely, if we add hydrochloric acid to a highly purified sol, the stability toward all electrolytes will increase. Similar stabilization would be expected on adding ferric chloride, aluminum chloride or lanthanum nitrate, as Freundlich and Wosnessensky[1] have shown. With the relatively insoluble Péan de St. Gilles sol, a maximum in the stability is reached on adding hydrochloric acid; and at a suitable concentration, the adsorption of the precipitating chloride ion neutralizes the adsorption of hydrogen ion and precipitation takes place[2] Similarly, colloidal copper ferrocyanide and Prussian blue are stabilized by preferential adsorption of ferrocyanide ion. The lower the concentration of the ferrocyanide ion the less the stability. On adding potassium ferrocyanide to a highly purified ferrocyanide sol, the stability toward all electrolytes should be increased until the concentration is high enough for the adsorption of the precipitating potassium ion to decrease the stability of the sol below the critical value. This is exactly what Sen observed with two electrolytes of widely varying precipitating power as shown by the data given in Table I and shown graphically in Figure 1. The precipitation value of both potassium chloride and barium chloride is increased to a maximum that lies above the value for either electrolyte alone.

TABLE I

Precipitation of Colloidal Prussian Blue by Mixtures. (Sen.)
(Precipitation values in millieq. per liter.)

| $K_4Fe(CN)_6$ | + | $BaCl_2$ | $K_4Fe(CN)_6$ | + | KCl |
|---|---|---|---|---|---|
| 0.0 | | 0.38 | 0.0 | | 40.0 |
| 15.0 | | 0.44 | 5.0 | | 51.0 |
| 25.0 | | 0.50 | 25.0 | | 50.0 |
| 40.0 | | 0.56 | 50.0 | | 43.8 |
| 100.0 | | 0.60 | 75.0 | | 35.0 |
| 110.0 | | 0.54 | 100.0 | | 23.8 |
| 140.0 | | 0.00 | 140.0 | | 0.0 |

Turning to arsenious sulfide sol, we are confronted with the problem of determining whether the addition of potassium chloride, say, stabilizes the sol in the same way as potassium ferrocyanide stabilizes ferrocyanide sols. This, it will be remembered, was suggested in my original paper; but some

[1] Kolloid-Z., 33, 222 (1923).
[2] Weiser: J. Phys. Chem., 25, 665 (1921).

experiments of Linder and Picton[1] are not in accord with this assumption. The latter prepared an arsenious sulfide sol with particles sufficiently fine to pass through a clay plate. On adding a few drops of a dilute solution of sodium chloride, the stability appeared unchanged but the smaller particles agglomerated so that they no longer passed through the filter. This definite evidence of agglomeration is indicative of decreased stability since, in general, stability falls off with increasing size of particles. Moreover, it is not easy to see how preferential adsorption of chloride ion would bring about agglomeration of the particles. Accordingly, the experiments recorded in the next section were undertaken.

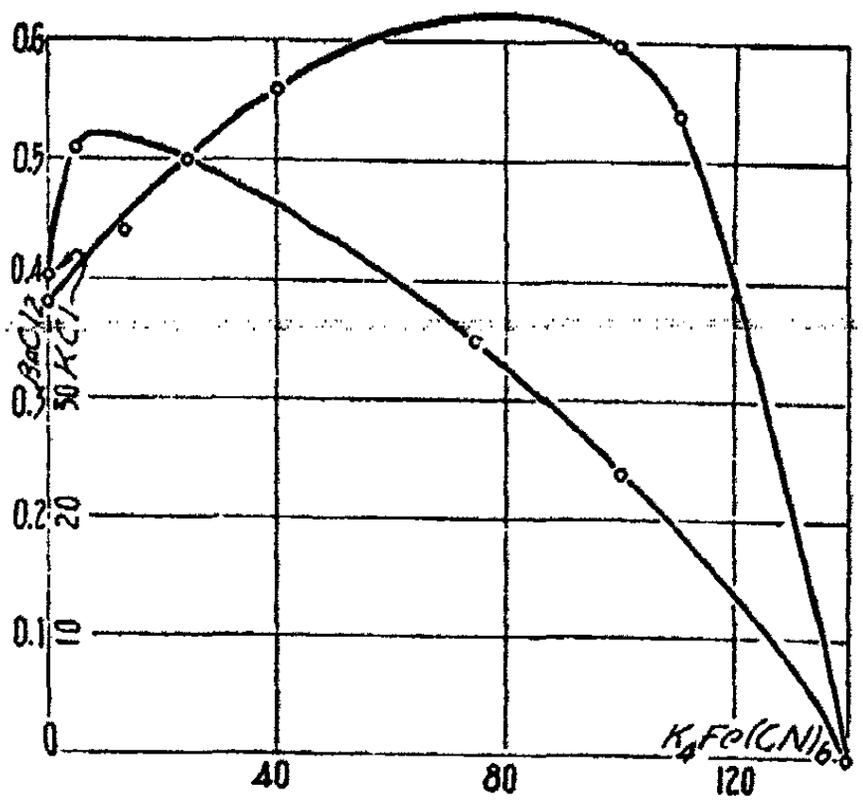



FIG. 1

## Experimental

In a recent communication[2] it was shown that the same concentration of different alkali chlorides cuts down the adsorption of barium ion to widely different degrees. At the same time, barium ion doubtless cuts down the adsorption of the alkali cations to different degrees. It seemed probable, therefore, that the precipitation value of barium chloride would vary in the presence of approximately the same concentration of chloride ion but with different alkali cations. That such is the case is shown clearly by observations recorded in Table II and shown graphically in Figure 2. The precipitation values were determined exactly as described in earlier papers, by mixing 10 cc. of sol containing 0.1 g. arsenious sulfide with a definite amount of standard electrolyte diluted to 10 cc. The time of standing was 2 hours, the mixtures being shaken every one-half hour.[3] All the observations were made within two

[1] J. Chem. Soc., 67, 73 (1895).
[2] Weiser: J. Phys. Chem., 29, 955 (1925).
[3] Cf. Freundlich and Baser: Z. physik. Chem., 115, 203 (1925).

TABLE II

Precipitation of $As_2S_3$ by Mixtures of $BaCl_2$ and Alkali Chlorides
(Precipitation values in millieq. per liter)

| LiCl | + $BaCl_2$ | NaCl | + $BaCl_2$ | KCl | + $BaCl_2$ | HCl | + $BaCl_2$ |
|---|---|---|---|---|---|---|---|
| 0.0 | 1.60 | 0.0 | 1.60 | 0.0 | 1.60 | 0.0 | 1.60 |
| 12.5 | 2.02 | 12.5 | 1.93 | 12.0 | 1.88 | 12.5 | 1.98 |
| 25.0 | 2.18 | 25.0 | 1.98 | 25.0 | 1.92 | 25.0 | 1.93 |
| 43.7 | 2.13 | 43.7 | 1.82 | 43.7 | 1.62 | 37.5 | 1.65 |
| 62.5 | 1.78 | 62.5 | 1.30 | 62.5 | 1.05 | 50.0 | 1.00 |
| 81.2 | 1.23 | 95.0 | 0.00 | 83.0 | 0.00 | 61.5 | 0.00 |
| 111.2 | 0.00 | | | | | | |

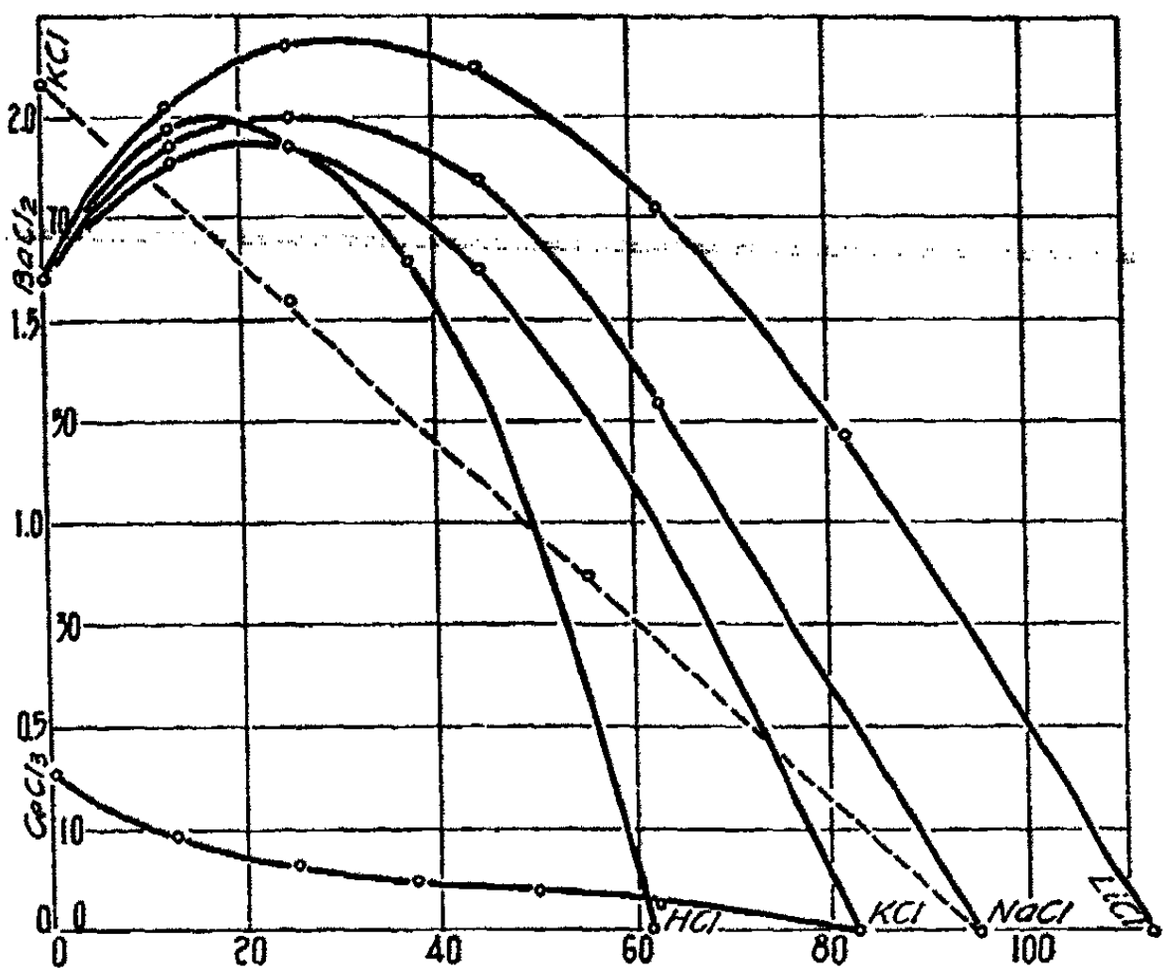



FIG. 2

days after the preparation of the sol. It will be noted that the precipitation value of barium chloride is increased by like amounts of alkali chlorides in the order LiCl > NaCl > KCl; while in the presence of HCl, the precipitation value of barium salt first rises to a point just below that in the presence of a like amount of lithium chloride and then drops off rather sharply. Since the adsorbability of the alkalis is in the order K > Na > Li,[1] it may be reasoned that the stabilizing action of chloride ion will be greater in the presence of lithium ion than of potassium ion thus accounting for the higher precipitation values of barium chloride in the presence of lithium chloride than of potassium chloride. This would not account for the behavior of mixtures of

[1] Weiser: J. Phys. Chem., 29, (1925).

hydrochloric acid and barium chloride for, at certain concentrations of chloride, the precipitation value in the presence of the relatively strongly adsorbed hydrogen ion is similar to that in the presence of lithium ion and greater than that in the presence of either sodium or potassium ion.

Another explanation suggests itself: For a given alkali chloride concentration, precipitation will take place when the combined adsorption of the two cations neutralizes the combined adsorption of chloride and hydrosulfide ions. The combined adsorption will be equivalent for different pairs of cations; but the relative amounts of each that make up this equivalent adsorption will vary, depending as it does on the relative adsorbability of the two cations. If one may disregard for the moment the slight variation in the amounts of chloride added with barium chloride as compared with the relatively large amount of this ion added with the alkali chloride, it follows that, for a given concentration of different alkali chlorides, the varying amounts of barium that must be added will depend on the effect of each cation on the adsorption of the other. Thus the adsorption of barium is cut down by lithium ion less than by potassium ion, tending to make the precipitation concentration of barium chloride less in the presence of lithium chloride than of potassium chloride. Hand in hand with this is the decrease in the adsorption of alkali by barium, which will tend to make the precipitation concentration of barium chloride higher in the presence of lithium. From this point of view the latter factor appears to predominate with the alkali chlorides. With hydrochloric acid however, the cutting down of the adsorption of barium by hydrogen ion is the determining factor with lower concentration of hydrochloric acid while with higher concentrations of acid the second factor appears to predominate.

To give some further indication of the influence of the stabilizing ion on the behavior of mixtures of electrolytes, some experiments were carried out on the precipitation of arsenious sulfide sol with mixtures of barium ferrocyanide with potassium ferrocyanide. The results are given in Table III and shown graphically in Figure 3. Comparing these results with those for chlorides given in Figure 2 it will be seen that the variation from additive relationships is greater with ferrocyanide than with chlorides. This is unquestionably

TABLE III

Precipitation of $As_2S_3$ by Mixtures of $Ba_2Fe(CN)_6$ and Alkali Ferrocyanides
(Precipitation values in millieq. per liter.)

| $Na_4Fe(CN)_6$ | + | $Ba_2Fe(CN)_6$ | $K_4Fe(CN)_6$ | + | $Ba_2Fe(CN)_6$ |
|---|---|---|---|---|---|
| 0.0 | | 2.25 | 0.0 | | 2.25 |
| 25.0 | | 7.10 | 25.0 | | 5.75 |
| 50.0 | | 7.75 | 50.0 | | 6.20 |
| 75.0 | | 7.50 | 75.0 | | 5.60 |
| 125.0 | | 5.25 | 100.0 | | 4.40 |
| 187.0 | | 0.00 | 155.0 | | 0.00 |

due to the difference in the adsorbability of the stabilizing ions; but how this difference brings about the observed results is not altogether obvious. Of course, one may say that a given amount of potassium ferrocyanide stabilizes the sol more than the same amount of potassium chloride, hence the amount of barium salt necessary to precipitate the sol in the presence of potassium ferrocyanide will be greater than in the presence of potassium chloride. But there is another factor which must not be overlooked: One should expect the adsorption of both barium ion and potassium ion to be greater in the presence of ferrocyanide than of chloride on account of the stronger adsorption of the multivalent ion. It then becomes a question of fact, whether the cationic

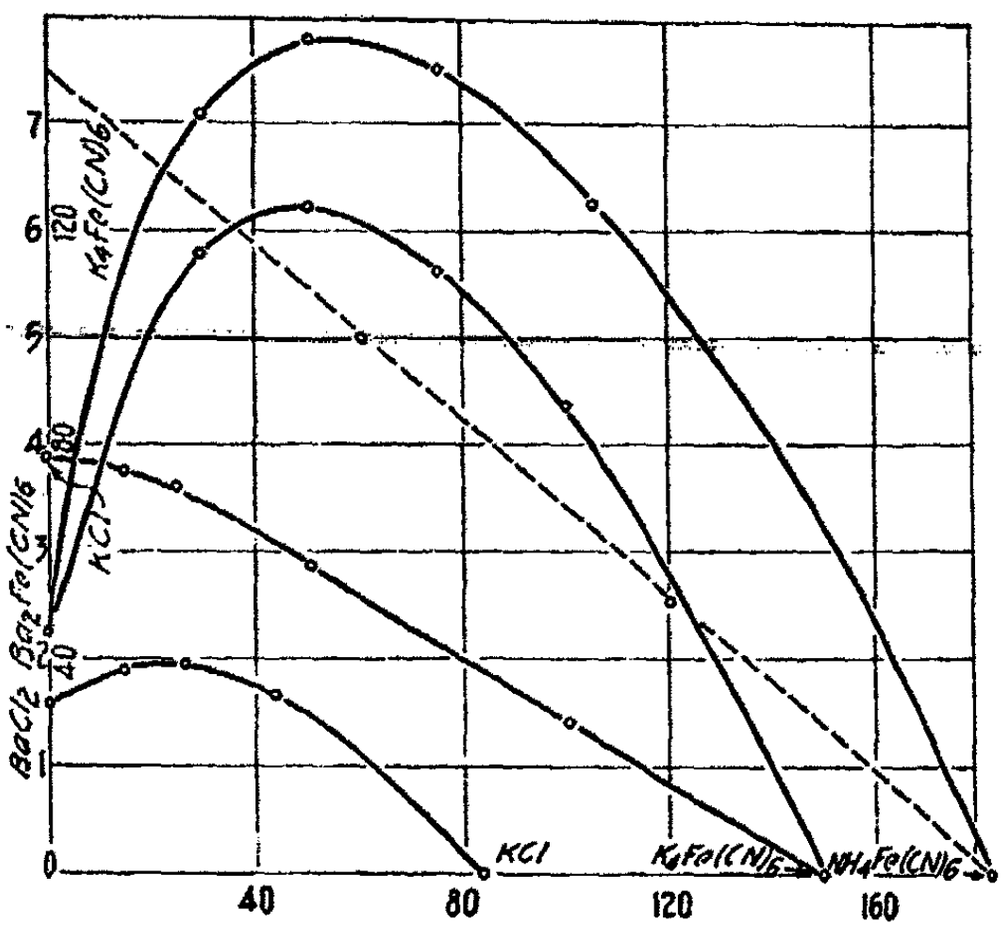



FIG. 3

antagonism will be greater in ferrocyanide solution than in chloride solution. To determine this, 100 cc. portions of sol containing 0.95 g. arsenious sulfide were precipitated in a mixing apparatus with definite amounts of electrolyte as shown in Table IV and the adsorption determined by analysis of the supernatant solution exactly as described in earlier communications. Particular precautions were taken to secure accurate results. To avoid errors arising from adsorption of ferrocyanide, the precipitates in each instance were dissolved in concentrated sulfuric acid and reprecipitated in the usual way by pouring into water. Just as was expected, under similar conditions the adsorption of barium from ferrocyanide solution is 28 per cent higher than from chloride solution. Moreover the presence of a given amount of potassium chloride cuts down the adsorption of barium from the chloride solution 65 per cent while the same amount of potassium ferrocyanide cuts down the adsorption 75 per cent from ferrocyanide solution. This evidence of a greater

TABLE IV

Adsorption of Barium Ion during the Precipitation of $As_2S_3$ Sol.

| Solutions mixed with 100 cc. of sol. Total volume 200 cc. | | $BaSO_4$ remaining in 150 cc. | | | Barium adsorbed millieq. per g. |
|---|---|---|---|---|---|
| | | 1 | 2 | 3 | |
| N/50 $BaCl_2$ | N KCl | | | | |
| 70 | 0.0 | 0.1146 | 0.1148 | | 0.065 |
| 70 | 20.0 | 0.1199 | 0.1197 | 0.1198 | 0.023 |
| N/50 $Ba_2Fe(CN)_6$ | N $K_4Fe(CN)_6$ | | | | |
| 70 | 0.0 | 0.1128 | 0.1126 | | 0.082 |
| 70 | 20.0 | 0.1202 | 0.1198 | 0.1202 | 0.020 |

cationic antagonism in the presence of the more strongly adsorbed ferrocyanide ion must be considered in any interpretation of the difference in behavior of mixtures of chlorides and ferrocyanides.

Another method of attack is to determine whether the presence of relatively small amounts of potassium chloride, say, increases the precipitation value for arsenious sulfide sol of chlorides other than barium chloride. Observations with mixtures of potassium chloride with sodium chloride and cerium chloride respectively are given in Table V and plotted in Figure 2.

TABLE V

Precipitation of $As_2S_3$ Sol by Mixtures

| KCl | + | NaCl | KCl | + | $CeCl_3$ |
|---|---|---|---|---|---|
| 0.0 | | 91.0 | 0.0 | | 0.388 |
| 25.0 | | 64.0 | 12.5 | | 0.230 |
| 50.0 | | 25.0 | 25.0 | | 0.162 |
| 83.0 | | 0.0 | 37.5 | | 0.132 |
| | | | 50.0 | | 0.105 |
| | | | 62.5 | | 0.067 |
| | | | 83.0 | | 0.000 |

The results are quite conclusive that the addition of potassium chloride does not increase the stability of arsenious sulfide sol toward all other chlorides. Thus the relationship is approximately additive with sodium chloride whereas the precipitation value of cerium chloride is decreased unmistakably by the presence of potassium chloride. It hardly seems probable that the latter result would obtain if potassium chloride in small concentration actually stabilized the sol in the same way that a highly purified ferric oxide sol is stabilized by the addition of a small amount of hydrogen ion or ferrocyanide sols by a small amount of ferrocyanide. I have previously pointed out that in the absence of marked ionic antagonism between ions of the same sign, one might expect the precipitation values of mixtures to fall below the additive value on account of the relatively greater adsorbability of the precipitating ions at low concentrations. This was actually observed in a number of instan-

ces with hydrous oxide sols.[1] To account for the difference in the results with barium chloride and cerium chloride one should expect to find the adsorption of barium cut down much more strongly than cerium by the presence of proportionate amounts of potassium chloride. That such is the case is shown by the results recorded in Table VI on the adsorption of barium and of cerium, respectively, in the presence of 50 times the concentration of potassium chloride. Cerium was determined by the colorimetric method of Benz

TABLE VI

| Solutions mixed with 100 cc. sol. Total volume 200 cc. | | N/200 $CeCl_3$ remaining cc. | | Ce adsorbed millieq. per g. |
|---|---|---|---|---|
| N/200 $CeCl_3$ | N/2 KCl | | | |
| 20 | 0 | 5.4 | | 0.073 |
| 20 | 5 | 9.0 | | 0.058 |
| N/50 $BaCl_2$ | N/2 KCl | $BaSO_4$ remaining in 180 cc. | | Ba adsorbed millieq. per g. |
| 30 | 0 | 0.0537 | 0.0537 | 0.064 |
| 30 | 30 | 0.0614 | 0.0615 | 0.010 |

previously used sucessfully by Freundlich[2] in measuring the adsorption of this element by arsenious sulfide. The method was found to be entirely satisfactory when all the usual precautions in quantitive colorimetric analysis are observed. It will be noted that, under similar conditions, the adsorption of cerium is cut down less than 25 percent, while the adsorption of barium is cut down almost 85 percent.

In accord with my earlier conclusions, the presence of potassium chloride does not raise the precipitation concentration of sodium chloride above the additive value as would be expected if the sol was stabilized by preferential adsorption of chloride ion. The precipitation values of such mixtures having a common anion, are additive since the adsorption of the precipitating cations are similar and so the adsorption of each is affected but slightly by the presence of the other within the limits of the precipitation concentration. On the other hand, with mixtures having precipitating cations in common and different anions, one should expect variations from additive values in proportion to the difference in adsorbability of the anions. Thus, the precipitation concentrations for mixtures of potassium and sodium ferrocyanide are additive whereas the critical concentrations for mixtures of potassium chloride and ferrocyanide rise slightly above the additive values[3], because of the greater adsorbability of ferrocyanide ion than of chloride ion. (See Table VII and Figure 3.) It is of interest to note, however, that the precipitation values of potassium chloride are raised but little above the additive values by the presence of potassium ferrocyanide; and are never greater than the value for potassium chloride alone, as was observed with ferrocyanide sol. Evidently, the

[1] Weiser: J. Phys. Chem., 28, 232 (1924).
[2] Z. physik. Chem., 37, 407 (1910).
[3] Sen: J. Phys. Chem., 29, 517 (1925).

TABLE VII

Precipitation of $As_2S_3$ Sol by Mixtures
(Precipitation values in millieq. per liter)

| $K_4Fe(CN)_6$ | + | $Na_4Fe(CN)_6$ | $K_4Fe(CN)_6$ | + | KCl |
|---|---|---|---|---|---|
| 0 | | 187 | 0.0 | | 77.5 |
| 50 | | 120 | 12.5 | | 75.0 |
| 100 | | 60 | 25.0 | | 71.0 |
| 150 | | 0 | 50.0 | | 57.0 |
| | | | 100.0 | | 28.0 |
| | | | 150.0 | | 0.0 |

stabilizing action of ferrocyanide ion on arsenious sulfide sol is much less than on ferrocyanide sols. Since the stabilizing action of chloride on arsenious sulfide sol is much less even than ferrocyanide, it seems very doubtful whether the addition of a small amount of alkali chloride increases the stability of the sol owing to stronger adsorption of anion than of cation. As I have mentioned before, this latter view is incompatible with the filtration experiments of Linder and Picton and my precipitation experiments with mixtures of the chlorides of potassium and cerium. On the other hand, one cannot disregard the influence of the stabilizing ion as evidenced by the greater variation from additive values with mixtures of the ferrocyanides than of the chlorides of barium and potassium. We thus arrive once more at my original conclusion, formulated four years ago, that two factors may influence the precipitating action of mixtures of electrolytes: The effect of the presence of each precipitating ion on the adsorption of the other; and the stabilizing action of the ions having the same charge of the sol. The antagonistic action between precipitating ions of the same charge may influence precipitation of salt pairs only in case they show a marked difference in adsorbability. Under certain conditions, the critical values for mixtures of two electrolytes may rise above the additive values even when the precipitating ions of the two are identical, thus eliminating antagonism between precipitating ions of the same charge (Sen). For such a result there must be an appreciable difference between the adsorbability of the stabilizing ions, the magnitude of the variations from an additive relationship being determined by this difference in adsorbability.

## Summary and Conclusions

1. The precipitation values for sols of mixtures of two electrolytes may be additive, may be greater than the additive values or may be less than the additive values.

2. The factors which determine the precipitation concentration of mixtures are: (1) The effect of each precipitating ion on the adsorption of the other. (2) The stabilizing action of ions having the same charge as the sol. (3) The relatively greater adsorbability of ions at lower concentrations.

3. The antagonistic action between precipitating ions of the same charge is important in raising the critical concentrations above the additive value,

only in case the ions show a marked difference in adsorbability. This effect comes in when arsenious sulfide sol is precipitated by mixtures of salts of barium and potassium.

4. Although the stabilizing action of ions having the same charge as the sol can not be eliminated, the critical values for mixtures of two electrolytes may rise above the additive value even when the precipitating ions of the two are identical, thus eliminating antagonism between precipitating ions. (Sen).

5. Variation from the additive relationship with mixtures of salt pairs having a common precipitating ion, results only when there is an appreciable difference in the adsorbability of the stabilizing ions, the magnitude of the variation from an additive relationship being determined by this difference in adsorbability.

6. If the first and second factors referred to in (2) are not too pronounced, the precipitation values of mixtures may fall below the additive value on account of the relatively greater adsorbability of precipitating ions at low concentrations. An example of this phenomenon is the precipitation of arsenious sulfide sol by mixtures of the chlorides of potassium and cerium.

7. The influence of dilution of sol on the precipitation values of an electrolyte is determined by the nature of the anion, the nature of the cation and the nature of the sol. The "general dilution rule" enunicated by Ghosh and Dhar fails to take all of these factors into account and so is necessarily limited in its applicability.

8. Strong adsorption of the stabilizing ions of the precipitating electrolytes is not essential for the "acclimatization" of sols in case there is strong adsorption of the precipitating ions during fractional agglomeration; on the other hand, strong adsorption of the stabilizing ion is essential in case the successive dilutions of the sol by fractional precipitation is the determining factor. In either case acclimatization to a greater or lesser degree is a necessary concomitant of fractional precipitation.

*Department of Chemistry,*
*The Rice Institute,*
*Houston, Texas.*

# PHOTOSENSITIZATION BY OPTICALLY EXCITED MERCURY ATOMS, THE HYDROGEN OXYGEN REACTION

BY ABRAHAM LINCOLN MARSHALL

Kinetic studies of gas reactions have played a very important role in the development of theories concerning the mechanism of chemical reactions. There are, however, very few such reactions occurring in the gas phase free from disturbances due to the walls of the containing vessel. Bodenstein and his co-workers have made many comprehensive studies regarding the behavior of thermal gas reactions and have accumulated a large amount of valuable data. In all of this work remarkably few truly homogeneous reactions have been found, by far the greater number taking place at some solid surface. Hinshelwood and Hughes[1] have shown that the data on the thermal decomposition of nitrous oxide, hydrogen iodide and chlorine monoxide can be completely interpreted in terms of simple thermal activation by collision, with every collision between two molecules of joint energy exceeding an amount Q leading to reaction. The thermal decomposition of nitrogen pentoxide studied by Daniels and Johnston[2] has been shown to be a unimolecular homogeneous gas reaction[3].

The studies on heterogeneous gas reactions have thrown a great deal of light[4] on the influence of the physical condition and chemical nature of the surface on the course of the reaction but have yielded practically no information on the mechanism by which the reaction proceeds at the surface.

Photochemical studies of gas reactions have given us considerable additional information on reaction mechanism in the gas phase. The number of such reactions available for exact quantitative study has in the past been limited, however, by the small absorption coefficient of many of the reactants in the wave length range available. Other complications have been secondary reactions induced in the primary products due primarily to the lack of intense sources of monochromatic radiation.

The Einstein Law of Photochemical Equivalence between quanta absorbed and molecules reacting has been of the greatest value in correlating the results of experiment. In a number of cases approximate equivalence has been found[5] and in quite a few others wide divergence. But in all these cases it has served as a starting point in studying the mechanism of these reactions. The hydrogen chlorine combination is one of the cases of wide divergence; in this case a million molecules react per quantum absorbed. It has, however,

[1] J. Chem. Soc. 125, 1841 (1924);
See however H. A. Taylor; J. Phys. Chem. 28, 984 (1924).

[2] J. Am. Chem. Soc. 43, 53 (1921).

[3] White and Tolman; J. Am. Chem. Soc. 47, 1240 (1925); Hirst: J. Chem. Soc. 127, 657 (1925).

[4] Rideal and Taylor: Catalysis in Theory and Practice; Taylor: "Treatise on Physical Chemistry", Chap XV.

[5] "Treatise on Physical Chemistry", p. 1212.

been possible to evolve a quite satisfactory mechanism for this reaction. Recently Bodenstein and Lütkemeyer[1] have studied the photochemical reaction between hydrogen and bromine and confirmed the mechanism[2] previously postulated to account for the thermal reaction[3]. They have also obtained valuable data on the rate of combination of bromine atoms: all this from an interpretation based on the Photochemical Equivalence Law.

Weigert[4] has shown that a number of gas reactions can be sensitized to light in a spectral region easily available. By the addition of chlorine to the reaction mixture, he has studied the decomposition of ozone and the combination of hydrogen and oxygen in visible light.

One must remember that in all photochemical gas reactions conditions are considerably simplified over those obtaining in purely thermal reactions. The reactions are homogeneous and the method of activation is known. If the primary action of the light can be interpreted it is usually possible to obtain a fairly complete idea of the mechanism of the reaction.

A large number of workers, since the time of Davy, have investigated the thermal reaction between hydrogen and oxygen. This work has clearly shown that the controlling influence for this reaction is the nature of the surface exposed, the reaction being hetereogeneous. Bodenstein[5] has investigated the reaction over a glazed porcelain surface in the temperature range 482°-689°C and at ordinary temperatures with a platinum catalyst. Bone and Wheeler[6] have made a very complete study with a large variety of catalytic material and have demonstrated that the reaction depends primarily on the condensation of one or the other of the reactants on the heated surface. Langmuir[7] has shown that with platinum as a catalyst in the temperature range 300°-600°K the reaction velocity is proportional to the oxygen pressure and inversely to that of the hydrogen. He interprets this as meaning that adsorbed oxygen atoms on the platinum surface are very reactive towards hydrogen, every collision between a hydrogen molecule and an oxygen atom resulting in combination. Under certain conditions, he states, adsorbed hydrogen atoms are relatively inactive towards oxygen molecules.

Direct photochemical investigation of this reaction is very difficult since oxygen does not commence to absorb appreciably above 195$\mu\mu$ and hydrogen is diactinic down to 103$\mu\mu$. Any photochemical reaction observed must be due to activation of the oxygen present. Andreew[8] has observed that under the influence of ultraviolet light the rate of reaction is independent of the concentration of the reacting gases. Cochn and Grote[9] have studied this reaction

[1] Z. physik. Chem. 114, 208 (1924).
[2] Christiansen: Dansk. Vid. Math. Phys. Med. 1, 14 (1919); Polanyi; Z. Elektrochem. 26, 50 (1920); Herzfeld: 25, 301 (1919).
[3] Bodenstein and Lind: Z. physik. Chem. 57, 118 (1906).
[4] Ann. Physik, (4) 24, 55, 243 (1907).
[5] Z. physik. Chem. 29, 665 (1899).
[6] Phil. Trans. 206A, 1 (1906).
[7] Trans. Faraday Soc. 17, 621 (1921).
[8] J. Russ. Phys. Chem. Ges. 43, 1342 (1911).
[9] "Nernst Festschrift", p. 136.

in the temperature range 150°-240°C. They obtain a velocity constant of the first order from their kinetic studies. Also they report a trace of hydrogen peroxide in the initial stages of the reaction. The temperature coefficient is given as 1.04. They put forward a reaction mechanism of the type

$$H_2 + O_2 = H_2O_2$$
$$H_2O_2 + H_2 = 2H_2O$$

Weigert[1] has observed that the reaction can be sensitized by chlorine and Norrish and Rideal[2] have investigated this reaction in detail and suggested a possible mechanism. The reaction is completed by the formation of hydrogen chloride but they have shown that the rate of reaction is independent of the hydrogen concentration and can be represented by the equation

$$\frac{d[H_2O]}{dt} = K\,[Cl_2]\,[O_2]$$

Griffith and Shutt[3] have studied the photochemical reaction between hydrogen and ozone-oxygen mixture in visible light. They find that the presence of hydrogen causes the reaction

$$2O_3 \longrightarrow 3O_2$$

to take place many times faster. In a mixture 6% $O_3$, 40% $H_2$, 54% $O_2$ it goes five times as fast as in the absence of hydrogen. The secondary reactions may be either

$$O + H_2 \longrightarrow H_2O \quad \text{or}$$
$$O_3\ (\text{activated}) + H_2 \longrightarrow H_2O + O_2$$

depending on the mechanism postulated for the primary action of the light. They suggest some sort of a chain mechanism involving energy-rich water molecules to explain the effect of the hydrogen.

Taylor and Marshall[4] have observed that a large number of hydrogenation reactions will proceed in the gas phase when the mixture contains mercury vapor and is illuminated by the light of a cold mercury arc. This paper will give an account of a more complete investigation of the reaction between hydrogen and oxygen. The method of sensitization by mercury has already been described. In our previous experiments a pressure decrease of thirty millimeters per hour was the maximum rate observed.

The apparatus now to be described was designed to enable one to utilize completely all the radiation, from the quartz mercury arc, that is absorbable by mercury vapor. A compartment for a light filter has been provided and it is possible to control the temperature of the reaction system independently from that of the arc. A diagram of the cell is given in Fig. 1. The inner compartment contains the quartz mercury arc C which is cooled by a flow of tap water from A to B; electrical connections are made as indicated. The compartment D is evacuated and enables one to control the temperature of E

[1] Ann. Physik, (4) **24**, 55, 243 (1907).
[2] J. Chem. Soc. **127**, 787 (1925).
[3] J. Chem. Soc. **123**, 2752 (1923).
[4] J. Phys. Chem. **29**, 1140 (1925).

and F independently from C. The compartment E is 6 mm. in thickness and in some of the experiments contained chlorine at two atmospheres pressure together with about 60 mm. pressure of bromine. The compartment F is 55 mm. inside diameter and 71 mm. outside giving a thickness of 6 mm; it is 100 mm. long. The capillary G connects to gas holders and a manometer. The whole apparatus was placed in a thermostat to give accurate temperature control. The arc is 90 mm. long between the tungsten spiral and the mercury surface and is centered in the tube by quartz lugs fused to it.

Wood[1] gives the following table for the relative intensity of the lines in the cold mercury arc.

TABLE I

Relative Intensities of Lines in Cold Mercury Arc

| λ | Intensity | λ | Intensity |
|---|---|---|---|
| 2536 | 400 | 3131 | 50 |
| 2652 | 8 | 3341 | 8 |
| 2753 | 2 | 3650 | 64 |
| 2805 | 1 | 3654 | 30 |
| 2894 | 4 | 3663 | 30 |
| 2967 | 12 | 4046 | 100 |
| 3023 | 10 | 4077 | 30 |
| 3125 | 30 | 4358 | 200 |
| | | 5461 | 400 |

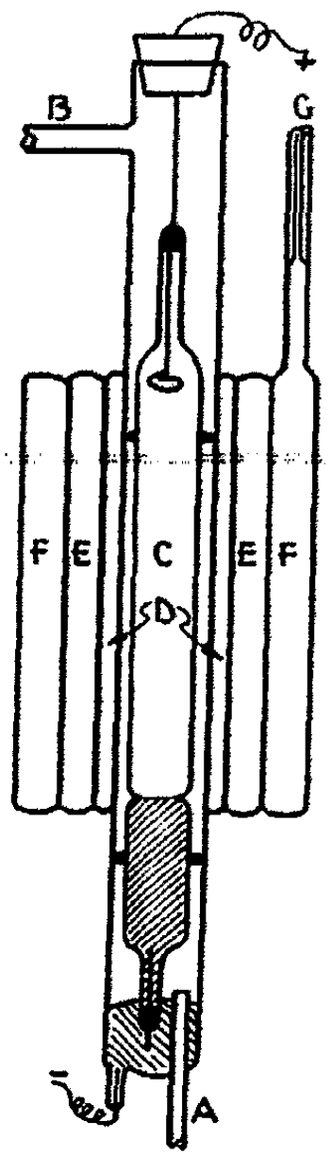



FIG. 1

The chlorine-bromine light filter absorbs all the radiation in the range 2900–5000 A° so that apart from the yellow and green lines the only light of any intensity reaching the vessel is 2536 A° which is the wave length employed.

The volume of the reaction chamber was about 120 c.c. and the capillary connecting to the manometer which was external to the thermostat has a volume of 2 c.c. Experiments were carried out in the temperature range 25—70°C. The hydrogen and oxygen were prepared electrolytically, passed over heated palladized asbestos and dried over phosphorous pentoxide. In some cases the mixtures used were prepared directly by electrolysis by the use of auxiliary electrodes. This ensured complete mixing before introducing into the reaction chamber. This factor was of importance since the reactions proceeded so rapidly. Some seventy-five experiments in all have been performed and the results of these will be given in a series of tables and curves.

A number of experiments at 50°C with gas mixtures ranging in composition from 406 mm. $H_2$ and 148 mm. $O_2$ to 572 mm. $H_2$ and 156 mm. $O_2$ gave reactions taking place at the same rate, the pressure decrease being 24.7 mm.

[1] Proc. Roy. Soc. 106A, 679 (1924).

per minute. The pressure-time curves showed an initial break at a point corresponding to saturation with water vapor and the curve was then linear till the reaction was complete, the rate thus being independent of the total pressure to a partial pressure of hydrogen or oxygen of the order of a few millimeters. In all these cases there was an excess of hydrogen over the amount required to combine with all the oxygen present. Fig. 2 (a) illustrates the type of curve obtained. The curves were quite different in character when oxygen was present in excess. The rate of combination decreased rapidly as the reaction proceeded. Typical results are given in Fig. 2 (b) and (c).

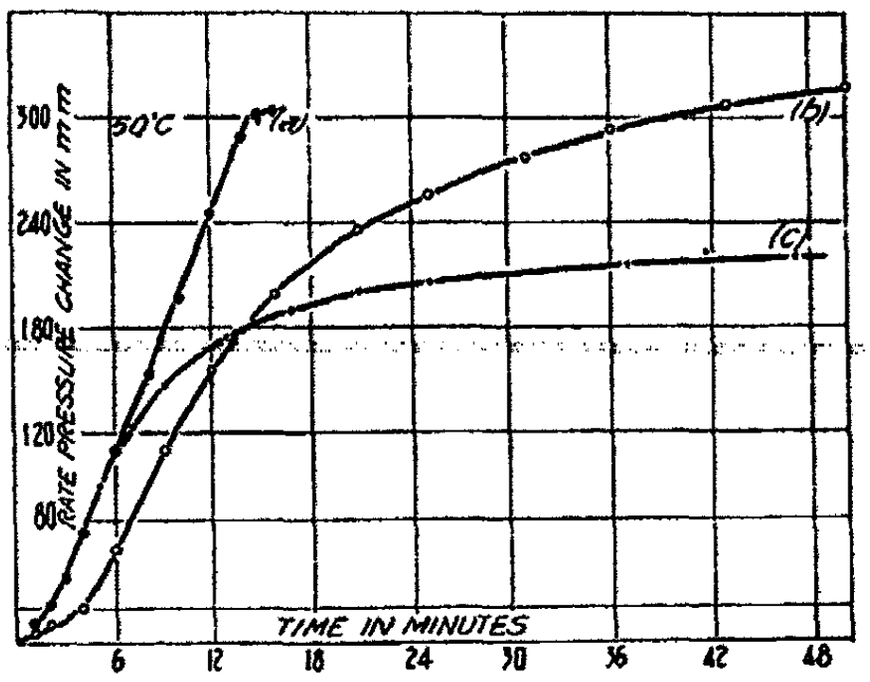



FIG. 2

The Compositions of the Reacting Mixtures are

(a) 520 mm $H_2$
131 mm $O_2$
(b) 294 mm $H_2$
481 mm $O_2$
(c) 208 mm $H_2$
229 mm $O_2$

A large number of experiments were made with mixtures containing approximately two volumes of hydrogen to one of oxygen in the temperature range 25°–70°C. Table II summarizes these results. The rate of pressure change was that determined after saturation had been reached.

TABLE II

| Temperature | Rate of Pressure Change mm./min. |
|---|---|
| 50° | 38.3 |
| 60° | 45 |
| 70° | 48 |

Table III gives similar results where the experiments had been sandwiched in order to obtain some idea of the reproducibility of the results. The numbers in brackets give the order in which the experiments were performed.

TABLE III

| Temperature | 60° | 40° | 25° |
|---|---|---|---|
| | 36.8 one | | |
| | | 18.6 two | |
| | | | 2.72 three |
| 39.0 four | | 24.0 five | |
| | | 25.7 six | |

In the first five of these experiments a chlorine-bromine light filter was used. For experiment (6) this was removed and the results show that it exerted no appreciable influence.

The results in these two tables indicate that the temperature coefficient obtained in this way is a very involved quantity. There seem to be at least two factors entering; firstly the increased vapor pressure of mercury at the higher temperatures giving an increased light absorption and secondly the increased yield per quantum absorbed. Table IV gives the vapor pressures of mercury in the temperature range under consideration.

TABLE IV

Vapor Pressures of Mercury

| Temperature | Vapor Pressure |
|---|---|
| 25 | .0017 mm. |
| 40 | .0057 " |
| 50 | .012 " |
| 60 | .025 " |
| 70 | .06 " |

From the measurements given by Wood[1] on the extinction coefficient of mercury vapor for $\lambda 2536.7$ A° it appears that at temperatures slightly above 25° there should be complete absorption. These values however were obtained for pure mercury vapor. Later results by the same author[2] indicate that the presence of other gases may greatly modify the width of the absorption band and very probably the magnitude of the extinction coefficient as well. In pure helium at 14 cm. pressure and room temperature the resonance radiation is enormously enhanced and the width of the line is broadened. Wood estimated a thirty fold increase in intensity. From this work it is evident that it will be necessary to obtain exact experimental evidence on the quantum yield at the various temperatures before any definite evidence can be given on the temperature coefficient of this reaction. The fact that the values at 60° and 70° agree so closely seems to indicate that the true temperature coefficient will be found to be very close to unity. Another complication enters at the higher temperatures from the fact that the reaction mixture cannot be completely homogeneous. The energy absorption will be very high at the inner

[1] Phil. Mag. **23**, 689 (1912).
[2] Wood: Proc. Roy. Soc. **106**, 674 (1924).

surface of the reaction vessel and decrease rapidly as the light progresses thru the chamber. Hence the rate of reaction will be different in various parts of the vessel and this will cause concentration differences to be set up.

At the end of experiment (28) the apparatus was dismantled and the reaction chamber was found to be heavily coated with yellow mercuric oxide. This will undoubtedly account for some of the variability in rate between successive experiments. It was later observed that the mercuric oxide was formed to the greatest extent in experiments using excess of oxygen and more particularly towards the end of these runs. This point will be discussed in more detail later. Another factor of importance in causing variability is the gradual deterioration of the quartz mercury arc. In later experiments with a new arc rates twice as great as those mentioned so far were obtained.

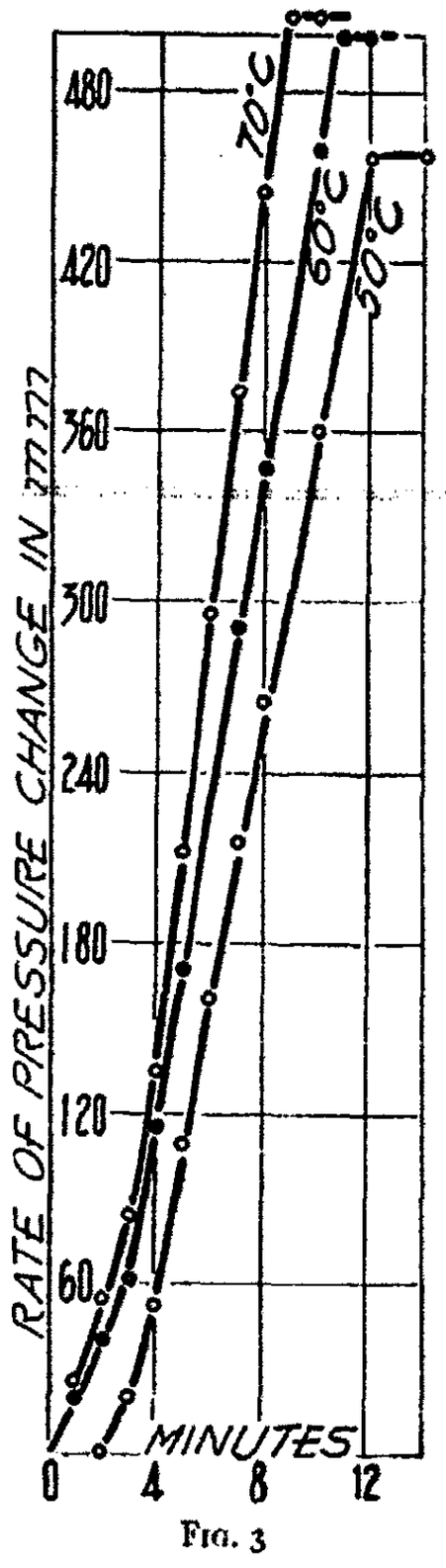


FIG. 3

Fig. 3 illustrates some of the results obtained in later experiments. In these cases the reaction mixture ($2H_2:1O_2$) was prepared by direct electrolysis of caustic soda solution and dried over phosphorous pentoxide. The reaction proceeded at a constant rate until the very end, the final pressure in every case being the vapor pressure of water at the temperature of the experiment. Table V gives a more complete list of the experiments. The experiments are numbered in the order of their occurrence. Experiments 1–9 and 10–32 were carried out on consecutive days. After experiments 21, 23, 25, 27, 28 and 30 pure hydrogen was admitted to the reaction chamber and illuminated for about half an hour in order to remove any mercuric oxide from the vessel walls. After experiment 31, the vessel was thoroly cleaned. From these experiments it is evident that a considerable portion of the variability is due to the coating of mercuric oxide on the walls, which apparently cuts down the transmission of the active radiation.

Figs. 4 and 5 illustrate experiments with mixtures containing approximately equal amounts of hydrogen and oxygen. Tangents have been drawn to these curves at a number of points to determine the rate at these points. Table VI presents the values obtained. The first column gives the $H_2$ pressure in mm., the second the oxygen, the third, fourth and fifth the ratios $H_2/O_2$, $H_2/(H_2 + O_2)$ and $H_2/(H_2 + O_2 + H_2O)$ the sixth the rate of reaction in

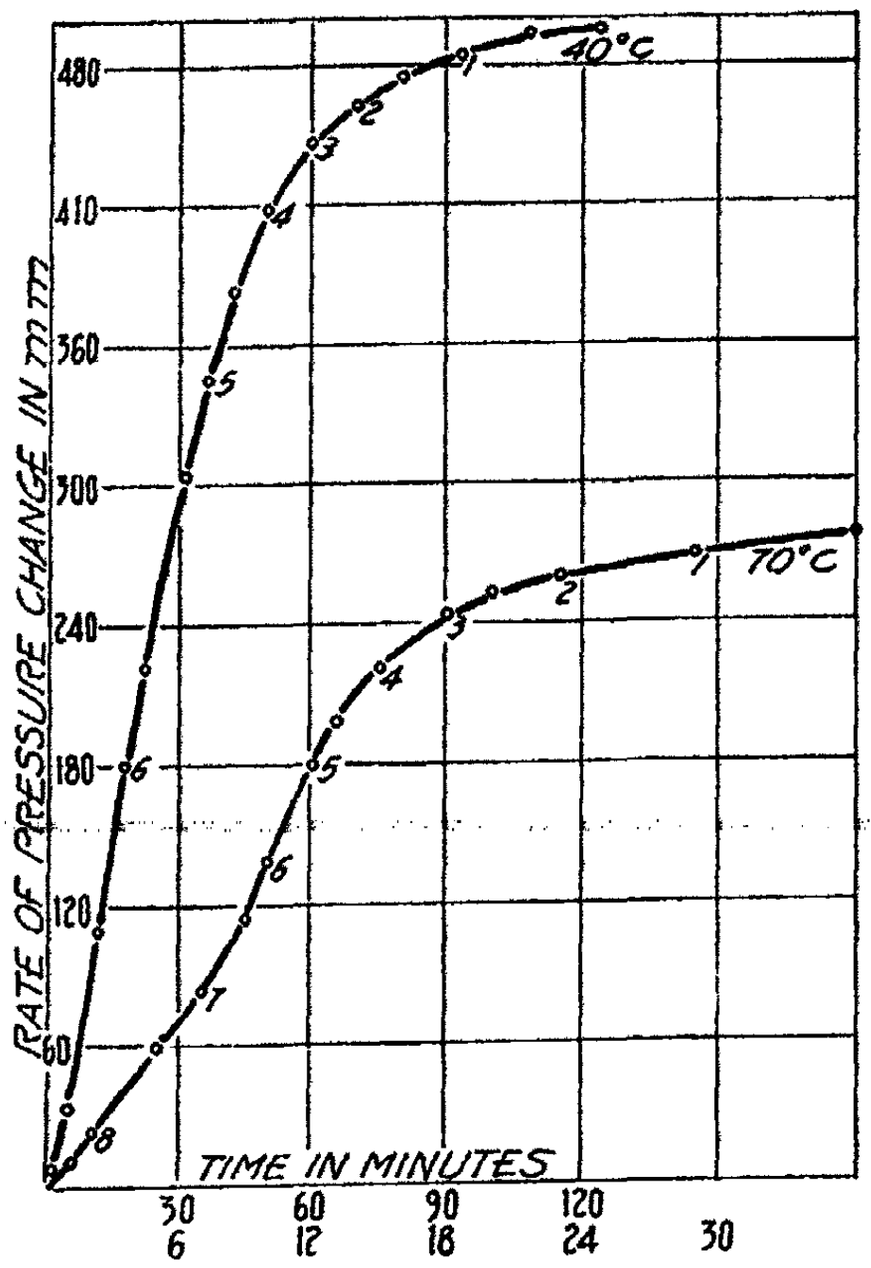



FIG. 4

Composition of Gas
40° = 359 mm $H_2$, 364 mm $O_2$
70° = 336 mm $H_2$, 341 mm $O_2$

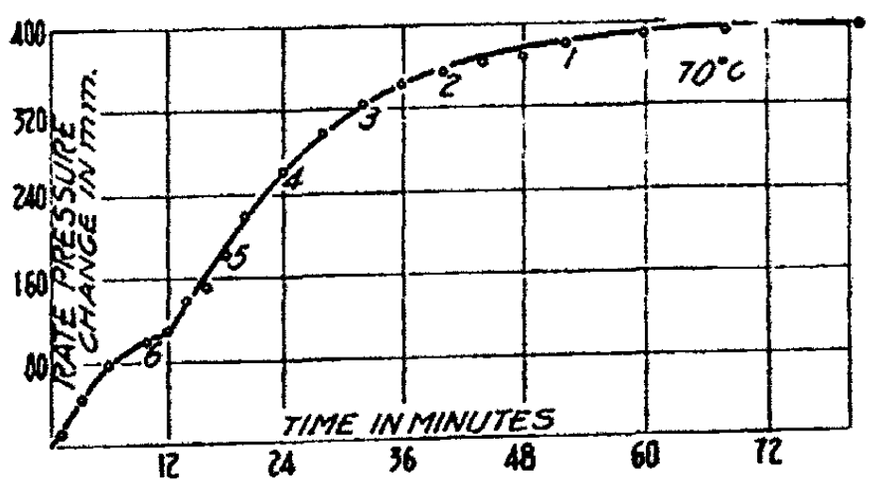



FIG. 5

TABLE V

Rate of Reaction in mm./ min.

| Temperature 70° | 60° | 50° | 40° | 25° |
|---|---|---|---|---|
| | 67.3 (2) | | 51.1 (1) | |
| | 80.0 (3) | | | |
| | 85.0 (4) | 71. (6) | | 14.9(5) |
| | | 77.5 (7) | | |
| 87.2 (8) | | | | |
| 86.4 (9) | | | | |
| 77.5 (10) | | | | |
| 79.0 (11) | | | | |
| 77.5 (12) | | | | |
| 72.4 (13) | | | | |
| 71.4 (14) | | | | |
| | | | 43 (15) | |
| | | | 32.1 (16) | |
| | | | 28 (17) | |
| | 57 (18) | | | |
| | 51.1 (19) | | | |
| | 52.6 (20) | | | |
| 57.8 (21) | | | | |
| 73 (22) | | | | |
| 65.6 (23) | 70 (24) | | | |
| 65 (27) | 65.2 (25) | | | |
| | | | | 35.3 (26) |
| 57.2 (31) | | 47.9 (29) | | 41.5 (28) |
| 70 (32) | | 50.5 (30) | | |

mm. pressure change per minute and the remaining columns this rate divided by the above ratios.

The numbers in brackets refer to the points on the curves in Figs. 4 and 5. The last three columns give the constants for the kinetic equations

$$\frac{d[H_2O]}{dt} = K_1 \frac{[H_2]}{[O_2]} \qquad (1)$$

$$= K_2 \frac{[H_2]}{[H_2]+[O_2]} \qquad (2)$$

$$= K_3 \frac{[H_2]}{[H_2]+[O_2]+[H_2O]} \qquad (3)$$

The degree of constancy is about the same in each case so that the data from this type of experiment with excess of oxygen will not permit us to differentiate between these three equations. The method used to determine the hydrogen pressure—calculation from point to point on the curve assuming no side reactions—makes all the errors cumulative. It is proposed to repeat these experiments with a modified apparatus, employing a circulatory system which will enable samples to be taken from time to time during the course of the reaction. This will enable one to obtain a much more accurate idea regarding

TABLE VI

| | $H_2$ | $O_2$ | $H_2/O_2$ | $H_2/H_2+O_2$ | $H_2/H_2+O_2+H_2O$ | Rate | rate $H_2/O_2$ | rate $H_2/H_2+O_2$ | rate $H_2/H_2+O_2+H_2O$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 70°C (Fig. 4) | | | | | |
| (2) | 10.6 | 178 | .059 | .056 | .025 | 1.9 | 32 | 34 | 76 |
| (3) | 21.2 | 184 | .115 | .103 | .048 | 5.3 | 46 | 51 | 110 |
| (4) | 36.5 | 191 | .19 | .16 | .079 | 9.4 | 49 | 59 | 119 |
| (5) | 64 | 205 | .31 | .24 | .127 | 18 | 58 | 75 | 140 |
| (6) | 93 | 219 | .42 | .29 | .17 | 22 | 52 | 76 | 130 |
| (7) | 150 | 248 | .61 | .37 | .24 | 32 | 53 | 87 | 130 |
| (8) | 271 | 308 | .88 | .47 | .43 | 37 | 42 | 79 | 86 |
| | | | | 40°C (Fig. 4) | | | | | |
| (1) | 6.6 | 187 | .035 | .034 | .026 | 0.65 | 18 | 19 | 26 |
| (2) | 22 | 195 | .113 | .101 | .081 | 1.4 | 12 | 14 | 17 |
| (3) | 32 | 200 | .16 | .14 | .11 | 2.1 | 13 | 15 | 19 |
| (4) | 52 | 210 | .25 | .20 | .16 | 3.6 | 14 | 18 | 23 |
| (5) | 100 | 234 | .43 | .30 | .26 | 7.3 | 17 | 24 | 28 |
| (6) | 144 | 256 | .56 | .36 | 32 | 10 | 18 | 28 | 31 |
| | | | | 70°C (Fig. 5) | | | | | |
| (1) | 10 | 195 | .051 | .049 | .023 | 1.2 | 24 | 25 | 52 |
| (2) | 26.6 | 203 | .13 | .115 | .057 | 2.7 | 21 | 24 | 47 |
| (3) | 47 | 214 | .22 | .18 | .094 | 5.6 | 26 | 31 | 60 |
| (4) | 90 | 235 | .38 | .28 | .16 | 9.0 | 24 | 32 | 56 |
| (5) | 141 | 260 | .54 | .35 | .22 | 13 | 24 | 37 | 59 |
| (6) | 196 | 288 | .68 | .40 | .30 | 16 | 24 | 40 | 54 |

the value of K. The degree of constancy obtained is all one can expect under present conditions.

The results obtained at the higher temperature with the $2H_2 + 1O_2$ mixtures seem to rule out equation (3). In these cases the water vapor pressure was as high as 250 mm. but in no case did the reaction rate show any decrease until the very end. Some of the earlier experiments at 50°C using excess hydrogen over that necessary for a two to one mixture showed practically no increase in rate towards the end of the reaction as predicted by equation (1). So it can be said that the results at present available favor the kinetic equation (2).

$$\frac{d\,[H_2O]}{dt} = K_2 \frac{[H_2]}{[H_2] + [O_2]}$$

Experiments by H. A. Stuart[1] on the quenching of resonance fluorescence in mercury vapor by various gases indicate that hydrogen, oxygen and water vapor all have a very strong effect in quenching the fluorescence. In the light of this knowledge, it seems that these gases are all able to take energy from excited mercury atoms by collisions of the "second kind," and in amounts proportional to their concentration. Cario and Franck[2] have shown that hydrogen atoms are formed by collisions between molecular hydrogen and excited mercury molecules. Apparently the energy absorbed by the oxygen is degraded as heat. The probability of the collision of a hydrogen molecule with an excited mercury atom is proportional to the hydrogen pressure divided by the sum of the hydrogen and oxygen pressures and it is this probability which determines the rate of the reaction.

It is possible to put forward several suggestions concerning possible mechanisms but the thermal data are entirely lacking to test these thermodynamically. The first step is of course the dissociation of hydrogen then

$$H_2 + Hg\ (\text{excited}) = 2H + Hg \qquad (1)$$
$$H + O_2 = HO_2 \qquad (2)$$
$$HO_2 = HO + O \qquad (3)$$
$$HO_2 + H_2 = H_2O_2 + H \qquad (4)$$
$$O + H_2 = H_2O \qquad (5)$$
$$OH + H_2 = H_2O + H \qquad (6)$$
$$H_2O_2 = H_2O + O \qquad (7)$$

Such a series of reactions would give a "chain mechanism." If (4) is one of the steps in the reaction it should be possible by use of a rapid circulatory system to remove the hydrogen peroxide from the reaction chamber and obtain sufficient quantities for a qualitative test. There is a distinct possibility also of ozone taking part in the reaction. If hydroxyl is present in one stage it might be possible to show its presence by a study of the reactions in a mixture of ethylene, hydrogen and oxygen. There is one other possible factor

[1] Z. Physik, 33, 262 (1925).

[2] Z. Physik, 11, 162 (1922).

that has not been discussed so far. There is at present no experimental evidence on the intensity of the 1849 A° line in the water cooled arc altho Wood[1] has evidence of its presence. This light also excites resonance radiation, of greater energy, in mercury and the quantum (150 Kg. cals.) may be sufficient to dissociate oxygen. Further work will be necessary to settle this point.

It has been mentioned that at times considerable amounts of mercuric oxide are formed. The rate of formation is greatest at 70°C, where there is a relatively high concentration of mercury vapor. A high mol fraction of oxygen greatly favors its formation. Under these conditions it is possible for the reaction

$$Hg + O = HgO$$

to proceed to a considerable extent and this may be the mechanism of its formation.

A very rough calculation shows that a considerable portion of the energy of λ 2536 emitted by the arc must be absorbed in the reaction system to obtain equivalence between quanta absorbed and molecules reacting. The lamp was burning on 20 volts and 10 amps. The intensity of the visible radiation is very much less than with the arc burning at 60 volts and 3 amps. Let us assume that 10% of the energy, some 20 watts is radiated and that 25% of this is in the 2536 A° line. This amounts to 5 watts with a quantum of $7.8\ (10)^{-12}$ ergs or $3.8\ (10)^{20}$ quanta. The maximum rate observed was 8 cm. pressure change per minute in a volume of 120 c.c. which corresponds to

$$2/3 \times 8/760 \times 120/22400 \times 6\ (10)^{23} = 2.2\ (10)^{19}$$

molecules of water formed per minute.

This calculation shows that it is necessary for large absorption of the 2536 A° line to obtain equivalence. Unless the width of the absorption band of mercury is very greatly increased by the presence of the reacting gases such equivalence is impossible. In a previous communication[2] it has been pointed out that the reaction between hydrogen and ethylene does not take place when the mixture is illuminated by a hot mercury arc. This is attributed to self-reversal of the resonance line in the arc. Such reversal, however, cannot be detected with an ordinary quartz spectrograph. This seems to indicate that in this case at least only a very small fraction of the energy in the line 2536 A° is useful in exciting the mercury atoms. At present it seems necessary to postulate a "chain mechanism," such as that given, to account for the rate of reaction observed.

## Summary

Photochemical studies of gas reactions should yield valuable information on the mechanism of chemical reactions.

[1] Proc. Roy. Soc. 106, 687 (1924).

[2] This Journal 29, 1140 (1925).

A quartz reaction system has been developed to study reactions sensitized by optically excited mercury atoms.

A more complete study of the reaction between hydrogen and oxygen has been made. The kinetic equation has been shown to be of the form

$$\frac{d[H_2O]}{dt} = K \frac{[H_2]}{[H_2] + [O_2]}$$

It seems probable from energy considerations that we are dealing with a "chain reaction" and several possible mechanisms are advanced.

*Research Laboratory*
*General Electric Company*
*Schenectady*
*New York*

# THE HEAT CAPACITIES OF SOME METALLIC OXIDES

BY GEORGE S. PARKS AND KENNETH K. KELLEY

The past fifteen years have witnessed a rather extensive study of the heat capacities of substances at low temperatures. In this connection the elements themselves and certain classes of compounds, notably the halogen salts, have been investigated to a considerable extent. On the other hand, only scanty data on metallic oxides have been published, although such information is of importance from both the theoretical and the industrial standpoint. In view of this situation, about two years ago there was initiated in this laboratory a systematic investigation of the heat capacities of oxides at low temperatures. The present paper records the results of measurements made upon the oxides of magnesium, calcium, and aluminum and upon the two iron compounds, hematite and magnetite.

## Experimental Part

*Method.*—The method was essentially the same as that recently employed by one of us[1] in an investigation of the specific heats of aliphatic alcohols.

In every case the sample of oxide studied was either in the form of a powder or of small crystals, never exceeding 3 or 4 mm. in dimensions. Such a sample was placed in a gas-tight, cylindrical copper can, 8 cm. long and 2.5 cm. in diameter, with a capacity of approximately 40 cc. To facilitate the attainment of thermal equilibrium the inside of this container was fitted with perforated disks, spaced 2 to 4 mm. apart along a small copper tube which ran through the center of the cylinder and served as a holder for the thermocouple used in measuring the temperatures. These disks, even though made out of extremely thin copper foil, added considerably to the weight of the calorimeter; their use, however, was justified by the fact that in this way no portion of the oxide under investigation was more than 2 mm. from a highly conducting copper surface. A 150-ohm heating coil made from B. and S. No. 36, silk-insulated Therlo wire was wound around the outer surface of the can and baked on with electricians' enameling fluid; it had external leads of No. 40 copper wire. To reduce heat losses through radiation thin silver foil was then wrapped tightly around the container. The bottom of the can, sealed in with soft solder and easily removable, provided a means of introducing and removing the sample of oxide. The finished calorimeter, constructed with these features, weighed about 35 grams. Its heat capacity in the unfilled state represented, on the average, about a quarter of the total heat input during a specific heat determination on the oxides and was measured in a separate series of experimental runs.

The calorimeter was suspended by silk thread within a larger copper cylinder weighing about 600 gm. This sheath, fitted with a top and bottom and silvered on both its inner and outer surfaces, provided a relatively uniform tempera-

[1] Parks: J. Am. Chem. Soc., **47**, 338 (1925).

ture environment for the heat capcity determinations. In order to control its temperature it was equipped with a heating-coil and thermocouple. The cylinder and contents rested on small wooden legs in a vacuum-tight brass can, 5 cm. in diameter and 15 cm. high. A German-silver tube 1 cm. in diameter and 50 cm. long, soldered into a hole in the top of the brass can, served the three-fold purpose of connecting the system to the charcoal evacuating tube, of providing an exit path for the electrical connections and of serving as a support, the entire apparatus being suspended in a 1000 cc. Dewar jar. Details of electrical wiring, bringing out the connections, etc. were similar to those recently described by Rodebush[1] in his work upon cadmium and tin and will not be repeated here.

A satisfactory vacuum was obtained by a preliminary evacuation with a Nelson oil-pump, followed by the use of activated charcoal immersed in liquid air. The desired temperatures were attained with the aid of various baths such as liquid air, crystalline ethyl alcohol (melting point, 158° K.), solid carbon dioxide in alcohol, ice, and water at approximately the temperature of the room.

Single-element copper-constantan thermocouples, constructed from B. and S. No. 40 silk-insulated copper and No. 30 silk-insulated constantan wire were used with a White potentiometer in measuring the temperatures of the calorimeter and copper sheath. For these thermocouples the temperatures and the rates of change of e. m. f. with change of temperature, dE/dT, were obtained by means of the two equations of Eastman and Rodebush,[2] since the wire used was evidently similar to theirs. From a careful study of this Eastman-Rodebush temperature scale we have concluded that its use involves an error of less than 0.2% above 200° K. and probably not more than 0.5% in any region below this point.

The actual procedure in making the measurements was as follows. The system was first evacuated and an appropriate bath was placed around the external brass can. When the calorimeter and surrounding copper sheath had attained the desired temperature (a process which often required a day or more in the case of the lower temperatures), the reading of the calorimeter thermocouple was carefully recorded. Heat was then supplied to the calorimeter for a period of four to eight minutes by means of an electric current from an 8-volt storage battery. During this interval the energy input was measured with an accuracy of 0.1% by a calibrated stop-watch and a potentiometric evaluation of the current and voltage. In general it was such as to cause a temperature rise of about 4°. After switching off the heating current, the readings of the calorimeter thermocouple were recorded at one minute intervals for about half an hour. As a rule a very regular cooling rate was attained within the first four to six minutes of this period, indicating that heat equilibrium had been reached. The remaining thermocouple readings sufficed for an accurate evaluation of the cooling correction during and im-

[1] Rodebush: J. Am. Chem. Soc., 45, 1413 (1923).

[2] Eastman and Rodebush: J. Am. Chem. Soc., 40, 492 (1918).

mediately following the heating period. This correction was but a small percentage of the total temperature rise.

As a typical example of the way in which the results were obtained, the calculations from the data for one of the magnesium oxide runs are given in detail.

Time, 361.4 seconds.
Voltage at terminals of heating coil, 7.958 volts.
Current through heating coil, 0.05270 amperes.
Total heat supplied, (361.4) (7.958) (0.05270) (.2391) = 36.250 cal.
Initial thermocouple reading, 5586.1 microvolts
Final thermocouple reading, corrected for cooling, 5449.3 microvolts
Difference 136.8 "
Temperature corresponding to average thermocouple reading, 94.1° K.
Corresponding dE/dT, 19.63 microvolts
Heat supplied to calorimeter and contents per degree,.

$$36.250\ (19.63 \div 136.8) = 5.201 \text{ cal.}$$

Heat capacity of calorimeter at 94.1° K., 2.130 cal.
Heat supplied to magnesium oxide per degree,

$$5.201 - 2.130 = 3.071 \text{ cal.}$$

Weight of magnesium oxide, 76.40 gm.
$C_p$ of magnesium per gram, 3.071/76.40 = .0402 cal.
$C_p$ per mean gm. atom, 0.81 cal.

## Materials

*Magnesium Oxide.*—A high-grade sample of fused magnesium oxide was employed. On examination it gave no tests for any of the common impurities, such as silica or calcium, and seemed to be 100% pure within the limits of analytical error. It had been given to Professor D. L. Webster of the Physics Department of Stanford University by the Norton Company.

*Calcium Oxide.*—Kahlbaum's calcium oxide was used. An analysis of this material gave 98.8% CaO, 0.4% $H_2O$ and no $SiO_2$.

*Aluminum Oxide.*—Small, almost colorless sapphires from Ceylon were employed in the measurements. An analysis made upon them gave 99.3% $Al_2O_3$.

*Ferric Oxide.*—Two samples of ferric oxide were studied. The first, consisting of large crystals of specular hematite from the Island of Elba, gave on analysis 99.2% $Fe_2O_3$, 0.5% $H_2O$ and 0.5% $SiO_2$.

The second sample was Kahlbaum's product, prepared from the oxalate. It gave 99.5% $Fe_2O_3$, the remaining 0.5% being presumably moisture. This material consisted of a fine, smooth powder and on X-ray analysis[1] yielded much fainter lines than did a powered crystal of the specular hematite. A rough estimate of the relative intensities would place them, perhaps, in the

[1] For advice and assistance in making this X-ray analysis, the authors wish to acknowledge their great indebtedness to Professor P. A. Ross of the Physics Department of Stanford University.

ratio of 1 to 10. Apparently, then, this Kahlbaum sample contained a large amount of amorphous substance.

*Magnetite.*—The magnetite used was similar to that employed by Sosman and Hostetter[1] in an earlier investigation and was in the form of remarkably perfect, large crystals. The Sosman-Hostetter analysis gave 99.00% $Fe_3O_4$ 0.63% $Fe_2O_3$, and 0.37% impurities (chiefly quartz.)

## Heat Capacity Data

The results of the measurements appear in Tables I-VI inclusive. In each case the first column contains the temperatures in degrees absolute; in the second column appear the corresponding heat capacities at constant pressure per gram of the material and in the third column are the resulting values for the mean atomic heat. These specific and atomic heats are expressed in terms of the 15° C. calorie, which is used throughout the present paper.

As to the accuracy of the results, it is very hard to state definitely. In general the measurements themselves are reproducible to 0.5% or better and probably in no region of the temperature scale involve an absolute error of more than 1.0%. On the other hand, the impurities, which in certain instances are of the order of 1%, may affect the results to some extent, although the magnitude of their influence is rather problematical. For this reason no attempt to correct for the effect of impurities has been made is presenting the data.

In the studies with magnetite a region of marked heat absorption was noted in the short temperature interval, 113°-117° K. A rough measurement of this heat effect gave 0.69 cal. per gram or 23 cal. per mean gram atom. In the case of no other substance was a heat absorption or transition point observed.

TABLE I

The Heat Capacity of Magnesium Oxide

| Temperature °K | $C_p$ per gram | $C_p$ per gram atom |
|---|---|---|
| 94.1 | 0.0402 | 0.81 |
| 97.9 | 0.0442 | 0.89 |
| 98.5 | 0.0450 | 0.91 |
| 100.0 | 0.0470 | 0.95 |
| 151.8 | 0.1101 | 2.22 |
| 188.4 | 0.1452 | 2.93 |
| 193.4 | 0.1502 | 3.03 |
| 275.3 | 0.2096 | 4.22 |
| 278.0 | 0.2137 | 4.30 |
| 288.3 | 0.2170 | 4.37 |
| 291.0 | 0.2184 | 4.40 |

[1] Sosman and Hostetter: J. Am. Chem. Soc., 38, 812 (1916). Dr. Sosman very kindly loaned us this material for our investigation.

TABLE II

The Heat Capacity of Calcium Oxide

| Temperature °K | $C_p$ per gram | $C_p$ per gram atom |
|---|---|---|
| 87.2 | 0.0535 | 1.50 |
| 87.7 | 0.0536 | 1.50 |
| 91.1 | 0.0579 | 1.62 |
| 92.2 | 0.0591 | 1.66 |
| 150.3 | 0.1158 | 3.25 |
| 194.0 | 0.1446 | 4.06 |
| 197.1 | 0.1474 | 4.13 |
| 275.4 | 0.1762 | 4.94 |
| 277.8 | 0.1772 | 4.97 |
| 282.1 | 0.1794 | 5.03 |
| 292.7 | 0.1808 | 5.07 |

TABLE III

The Heat Capacity of Aluminum Oxide

| Temperature °K | $C_p$ per gram | $C_p$ per gram atom |
|---|---|---|
| 91.1 | 0.0249 | 0.51 |
| 91.7 | 0.0255 | 0.52 |
| 93.0 | 0.0260 | 0.53 |
| 95.6 | 0.0286 | 0.58 |
| 150.6 | 0.0768 | 1.57 |
| 193.3 | 0.1155 | 2.35 |
| 197.2 | 0.1190 | 2.43 |
| 200.1 | 0.1218 | 2.48 |
| 275.1 | 0.1726 | 3.52 |
| 276.4 | 0.1743 | 3.55 |
| 288.6 | 0.1800 | 3.67 |
| 291.3 | 0.1813 | 3.70 |

TABLE IV

The Heat Capacity of Ferric Oxide (Specular)

| Temperature °K | $C_p$ per gram | $C_p$ per gram atom |
|---|---|---|
| 89.8 | 0.0404 | 1.29 |
| 90.3 | 0.0414 | 1.32 |
| 90.5 | 0.0410 | 1.31 |
| 95.5 | 0.0445 | 1.42 |
| 148.4 | 0.0827 | 2.64 |
| 186.9 | 0.1082 | 3.46 |
| 192.8 | 0.1109 | 3.54 |
| 196.3 | 0.1128 | 3.60 |
| 275.9 | 0.1477 | 4.72 |
| 278.1 | 0.1488 | 4.75 |
| 289.1 | 0.1534 | 4.90 |
| 291.9 | 0.1539 | 4.92 |

TABLE V

The Heat Capacity of Ferric Oxide (Kahlbaum's)

| Temperature °K | $C_p$ per gram | $C_p$ per gram atom |
|---|---|---|
| 88.3 | 0.0412 | 1.32 |
| 91.8 | 0.0442 | 1.41 |
| 95.2 | 0.0465 | 1.48 |
| 98.3 | 0.0485 | 1.55 |
| 150.3 | 0.0858 | 2.74 |
| 194.3 | 0.1141 | 3.65 |
| 198.5 | 0.1162 | 3.71 |
| 274.9 | 0.1521 | 4.86 |
| 276.7 | 0.1529 | 4.88 |
| 286.9 | 0.1551 | 4.96 |
| 289.4 | 0.1561 | 4.99 |

TABLE VI

The Heat Capacity of Magnetite

| Temperature °K | $C_p$ per gram | $C_p$ per gram atom |
|---|---|---|
| 90.0 | 0.0488 | 1.61 |
| 90.2 | 0.0493 | 1.63 |
| 94.2 | 0.0524 | 1.73 |
| 96.9 | 0.0550 | 1.82 |
| 153.2 | 0.0968 | 3.20 |
| 193.5 | 0.1186 | 3.92 |
| 197.2 | 0.1205 | 3.99 |
| 276.3 | 0.1513 | 5.00 |
| 278.7 | 0.1525 | 5.04 |
| 292.1 | 0.1558 | 5.15 |
| 295.0 | 0.1570 | 5.19 |

## Discussion of Results

The preceding data possess several interesting features. One of these pertains to the relatively low mean atomic heat for $Al_2O_3$ in the sapphire form. At the temperature of liquid air this falls to 0.5 cal. per atom or 2.5 cal. per formula weight, a rather striking figure in view of the fact that the heat capacity of two atoms of metallic aluminum plus that of three atoms of liquid oxygen amounts to about 24.0 cal. at 90° K. Certainly this situation constitutes an excellent confirmation of the very general view that a low heat capacity is a concomitant of exceptional hardness, as corundum ranks No. 9 on the Mohr scale of hardness where diamond has the maximum value of 10.

The two samples of ferric oxide studied are approximately of the same purity, the essential difference being in the degree of subdivision. Throughout the entire temperature range the Kahlbaum powder was found to have a higher specific heat than the specular crystals, the excess amounting to 2.4% at 275° K. and 3.8% at the temperature of liquid air. Now these percentage differences, while small, we believe to be greater than any that would probably

result from the experimental errors in the two sets of determinations. Therefore, in our opinion these results indicate that a powder which is finely divided and somewhat amorphous possesses a higher heat capacity than large crystals of the same chemical composition.

The heat absorption, found in the case of the magnetite crystals at about 115° K., constitutes still another noteworthy feature. This temperature would seem to be very low for a transformation in crystal structure in a metallic oxide, the melting-point of which is above 1500° K. Moreover, after the runs the large crystals of magnetite showed no signs of alteration or disintegration, such as might conceivably be expected after a series of alternations in crystal structure. In view of these considerations we think that the observed heat effect may possibly be connected with a change in the magnetic properties of the substance. If this be the case, there might be no change in crystal structure, as Compton and Rognley[1] have failed to detect such a change in a magnetite crystal upon magnetization and demagnetization. Certainly this heat absorption phenomenon should be investigated further.

*Entropies of the Oxides.*—If we assume the validity of the third law of thermodynamics as stated by Lewis and Gibson[2], all the crystalline oxides have zero entropy at 0° K. The atomic heat values then provide a basis for a quantitative estimate of the entropies of the same substances at 298° K. or 25° C.

In a careful study of heat capacity data Lewis and Gibson[3] have shown that for a number of substances the atomic heat capacities at constant volume are expressible as functions of the absolute temperature by the equation,

$$C_v = f\left(\frac{T}{\Theta}\right)^n,$$

in which $f$ is the same function for all substances and $\Theta$ and $n$ are characteristic constants for each particular substance. For many substances crystallizing in the cubic system and for a number of monatomic elements, $n$ is equal to unity (Class I). For other substances $n$ is less than unity (Class II).

Of course in the present investigation our experimental values are for $C_p$ rather than $C_v$ but for the oxides the differences between these two quantities are relatively small at room temperature and become entirely negligible at lower temperatures.[4]

---

[1] Compton and Rognley: Phys. Rev., 16, 464 (1920).

[2] Lewis and Gibson: J. Am. Chem. Soc., 42, 1533 (1920).

[3] Lewis and Gibson: J. Am. Chem. Soc., 39, 2565 (1917).

[4] In the case of magnesium oxide there are data which permit us to calculate these differences between $C_p$ and $C_v$. Utilizing the values for the coefficients of compressibility and thermal expansion tabulated by Pease (Taylor: "Treatise on Physical Chemistry", p. 171 (1924)), we have calculated $C_p$-$C_v$ at 293° K. by the thermodynamic equation used by Lewis: J. Am. Chem. Soc., 29, 1165 (1907).

$$C_p - C_v = .0242\,\frac{\alpha^2 VT}{\beta}$$

This difference was found to be 0.04 cal. per gram atom. The empirical rule expressed by Lindemann and Magnus (Z. Elektrochem., 16, 269 (1910)) in the equation,

$$C_p - C_v = aT^{3/2}$$

then gives 0.01 cal. for $C_p$. $- C_v$ at 100° K.

Accordingly, on plotting our results for $C_p$ we have found that the data for the oxides of magnesium and calcium, the two compounds which possess a cubic structure like that of sodium chloride, agree well with the $C_v$ curve for solids of Class I. Fig. 1 shows this clearly for MgO. On the other hand, the data for the remaining oxides require a slightly flatter curve at the lower temperatures, where the experimentally determined heat capacities appear to approximate the requirements for a substance of Class II with a value of about 0.9 for $n$.. Whether the "$n$ formula" in these cases is more than a first approximation is, however, extremely doubtful. Its application nevertheless will involve only small absolute errors in instances, like the present, where the total entropy of each substance is small at the temperature of liquid air.

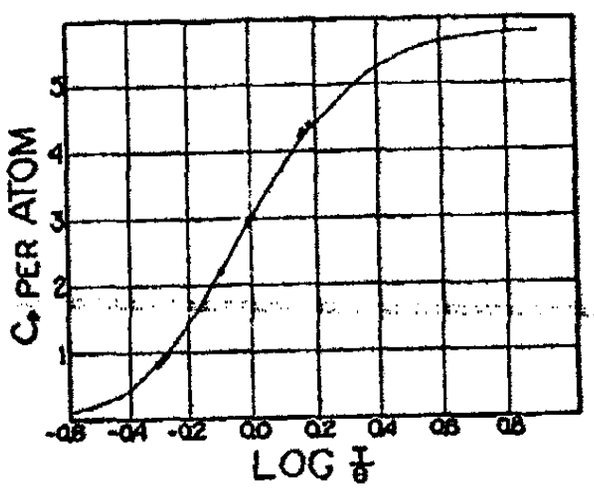



FIG. 1
$C_p$ Values for MgO and the Lewis-Gibson Curve for Class I.

Following in detail the methods of Lewis and Gibson, we have obtained the results which are given in Table VII. The entropy value for $Fe_2O_3$ is that found for the specular crystals; for the Kahlbaum powder our estimate is at least 0.4 cal. per degree above this figure. The result for magnetite includes the entropy change of 1.4 units at the heat-absorption point previously referred to.

TABLE VII

Entropies of the Oxides per Formula Weight at 298°K.

| Substance | log $\theta$ | n | Entropy in cal./degree |
|---|---|---|---|
| MgO | 2.28 | 1.00 | 6.6 |
| CaO | 2.14 | 1.00 | 9.6 |
| $Al_2O_3$ | 2.36 | .94 | 12.8 |
| $Fe_2O_3$ | 2.21 | .93 | 21.5 |
| $Fe_3O_4$ | 2.15 | .90 | 35.1 |

*Free Energies of the Oxides.*—Lewis, Gibson and Latimer[1] have calculated the entropies of the various elements at 298° K. Using their values in conjunction with our entropy results for the compounds, we have obtained the figures for $\Delta S_{298}$, the entropy of formation of each oxide from its elements, which appear in Table VIII, Column 2.

We are now in a position to calculate $\Delta F_{298}$, the free energy of formation of each oxide, by means of the fundamental thermodynamic equation,

$$\Delta F = \Delta H - T\Delta S,$$

where $\Delta H$ is the increase in heat content during the process of forming the compound from its elements and is numerically equal to the negative of the

[1] Lewis, Gibson and Latimer: J. Am. Chem. Soc., 44, 1008 (1922).

heat of formation. The values selected for $\Delta H_{298}$ in the case of each oxide appear in the third column of the following table. For MgO and $Al_2O_3$ we have employed a mean between the results of Berthelot[1] and those of Moose and Parr.[2] The figure for CaO is that obtained by Guntz and Benoit[3] in their recent investigation. For the two oxides of iron we have used the heats of formation as calculated by Tigerschioeld[4].

The resulting free energies appear in the last column. In their present form they are probably accurate to 1%. In the future, however, the accuracy of these $\Delta F$ values can be considerably increased by revision, as more reliable data for $\Delta H$ become available.

TABLE VIII

Thermal Data per Formula Weight

| Substance | $\Delta S_{298}$ Entropy units | $\Delta H_{298}$ Cal. | $\Delta F_{298}$ Cal. |
|---|---|---|---|
| MgO | −25.7 | −144,700 | −137,000 |
| CaO | −25.0 | −152,800 | −145,300 |
| $Al_2O_3$ | −72.8 | −378,000 | −356,300 |
| $Fe_2O_3$ | −63.9 | −197,500 | −178,400 |
| $Fe_3O_4$ | −81.0 | −271,000 | −246,800 |

## Summary

1. The heat capacities of magnesium oxide, calcium oxide, aluminum oxide, ferric oxide (two samples) and of magnetite have been measured over a wide range of temperatures. In the case of the last compound a heat-absorption region at 113°-117° K. has also been observed.

2. The entropies and free energies of the several compounds have been calculated.

*Department of Chemistry,*
*Stanford University,*
*September 1, 1926.*

[1] Landolt-Börnstein-Roth-Scheele: "Tabellen" (1923).
[2] Moose and Parr: J. Am. Chem. Soc., **46**, 2660 (1924).
[3] Guntz and Benoit: Ann. Chim., **20**, 33 (1923).
[4] Tigerschioeld: Chem. Abstracts **19**, 1085 (1925).

# THE EFFECT OF SOLVENTS ON THE ABSORPTION SPECTRUM OF A SIMPLE AZO DYE*

BY WALLACE R. BRODE

Before starting an extended study of the absorption spectra of a number of mon-azo dyes, a series of experiments was made to determine the effect of various solvents on the absorption spectrum of benzeneazophenol and precautions necessary in the determination of the absorption spectra of dyes of this type. The literature contains considerable theorizing and some practical data on the question of the effect of the solvent on the absorption band of dyes.[1] Kundt[2] said that the absorption band of dye is shifted towards the red end of the spectrum, i.e., to lower frequencies, with an increase in the refractive index of the solvent. This rather broad statement has since been known as Kundt's law. However, there have been nearly as many data reported in contradiction of it as in support of it.

It is certain that the refractive index of a compound is a function of its molecular constitution, and that in homologous series, the molecular refraction always increases with an increase in molecular weight. But it is not true that two isomeric substances such as methyl formate and acetic acid, or ethyl alcohol and di-methyl ether, have the same refractive index. Conversely, substances with the same refractive index do not necessarily have the same molecular constitution, and it follows that a dye dissolved in such solvents should not necessarily give the same molecular vibration. For example, benzyl alcohol and tetralin (tetrahydronaphthalene) have about the same refractive index, (1.540) which is rather high for organic solvents. Benzeneazophenol gives in benzyl alcohol a frequency of 845 f, 15 lower than in ethyl alcohol, while in tetralin the band is at a frequency of 875 f, some 15 higher than in ethyl alcohol, giving in all a difference of 30 in the center of the absorption bands in the two solvents used for the dye.

In general, little work has been done on the effect of the solvent on the absorption bands of azo dyes, and most of what has been done has been confined to the two solvents, water and alcohol. Only a few of the simple azo dyes which were to be studied in the course of this work, are soluble in water, hence it was necessary to use some organic solvent. The dye selected for the determination of the effect of the solvent on the absorption band, was benzeneazophenol. This dye was carefully prepared from purified intermediates, recrystalized repeatedly from alcohol, and dried in a vacuum oven at 60°

---

* This communication is an abstract of a portion of a thesis presented for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce. Presented before the Physical and Inorganic divisions of the American Chemical Society at Baltimore Md. April 8, 1924.

[1] Kayser: "Handbuch der Spektroscopie", 3, 80-89 (1905).

[2] Pogg. Ann. Jubelband, 615 (1874); Sitzungsber. Bayr. Akad. 7, 234 (1877); Ann. Physik, (3) 4, 34 (1878).

under reduced pressure. The dye gave a melting point of 152° corr. and analyzed 100% pure by titanous chloride titration.

In the neutral solution of benzeneazophenol in absolute ethyl alcohol there appears a very weak band near frequency 700, Fig. 1., so weak that it can scarcely be called a regular band, although the effect has been observed by a number of observers. This is followed by the principal band at a frequency 860 f, following which comes a region of fairly high transmission and then a third band at a frequency of 1280 f. The last or third band is at about the limit of the spectrophotometric measurements obtainable in the

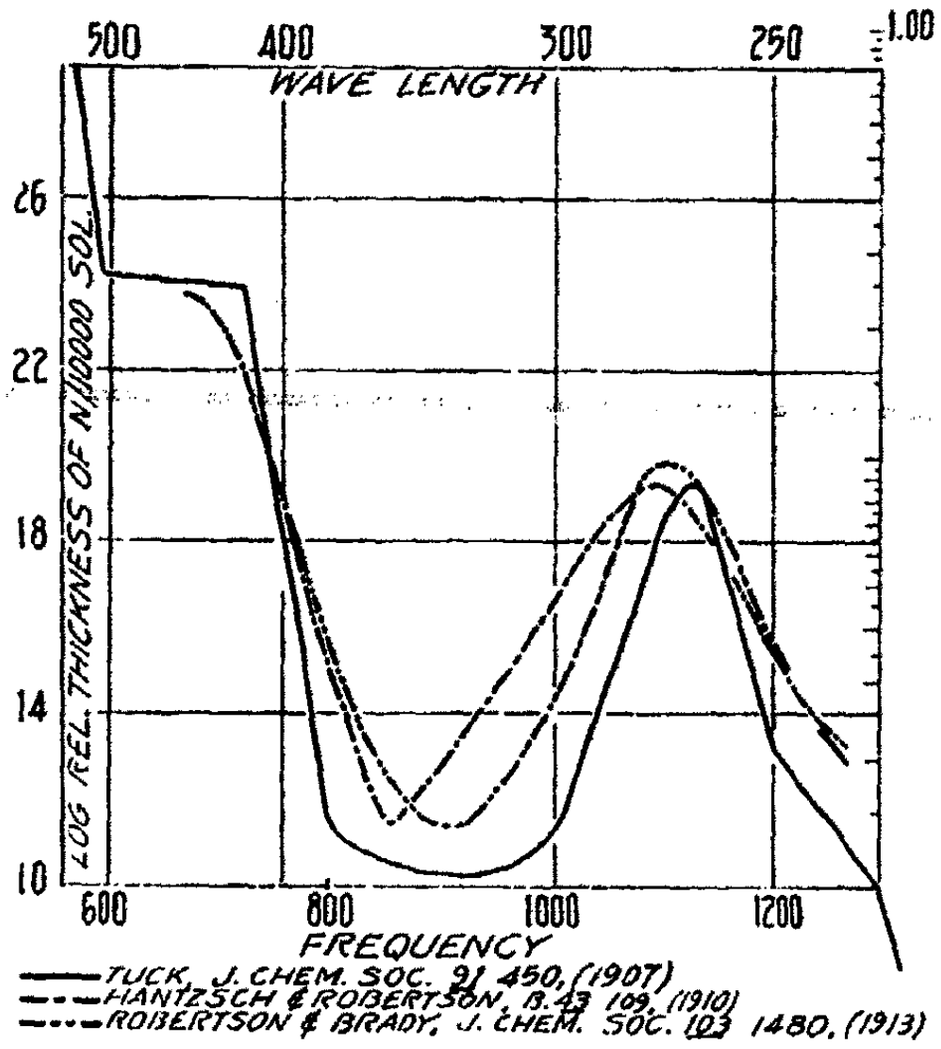



FIG. 1
Absorption Spectra of Benzeneazophenol in Alcohol.

ultra-violet. It will be noticed that the third band is an exact multiple of the second band, the third band being 3/2 of the second band, or the bands correspond to the second and third members of a series of which the first would be 430 f or the fundamental frequency and the difference between each band being 430 f on the frequency scale. In an aqueous alkaline solution there appear bands at 710 and 770 f and a third weaker one at 1150 f, which is again 3/2 of the second band; this time, however, the first band is slightly greater in intensity than the second band. In alkaline alcoholic solution there appear bands at 660 and 735 f and a weaker band at 1125 f which is 3/2 of the second band. This time the first band is somewhat weaker than the second band. In concentrated HCl a third set of bands occurs with frequencies of 630, 940 and 1200 f.

We are primarily interested in the neutral series of bands, however, and will limit this discussion to that set of bands. The first band, if it may be called such, Fig. 1, is very much weaker than any of the others, so much so that its height and center of vibration can not be accurately determined in solutions where the other bands are at a height that can be accurately measured. We will therefore disregard the first band and confine our attention to the second or principal absorption band of the dye (860 f.). One of the principal reasons for choosing this particular dye was the fact that its main absorption band, although so far out in the ultra-violet as to prohibit the use of some solvents, owing to their absorption, is very sharp and apparently consists of only one band, in contrast to the apparent double band formation present in the more complex azo dyes. No conclusions can be drawn as to the effect of solvents on the third band owing to the position it occupies in the extreme ultra-violet and the fact that nearly all the solvents used absorbed in that region so as to make observation impossible.

## Method

The Hilger sector photometer method with quartz spectograph was used in the determination of the ultra-violet spectral transmission of these solutions. The radiant energy source was an arc between tungsten electrodes under distilled water, which gave a continuous spectrum from the visible throughout the ultra-violet as far as the plates recorded. A high voltage high frequency current was used for this arc, the source of it being a large Tesla coil. The apparatus and the method of manipulation are described in detail in Scientific Paper 440 of the Bureau of Standards.

The extinction coefficient[1] which is plotted as the logarithm of the transmittancy, is shown on the accompanying graphs as a negative value and as such is plotted downwards on the ordinate. As a result the "peak" or point of maximum absorption of the band is really the lowest point rather than the highest. In this paper this point of maximum absorption will be referred to as the peak. The transmittancy is defined as the ratio of the energy passing through the cell containing the solvent and the dye, to that which passes through the cell containing only the solvent, (I/I').

The transmittancy is thus given as

$$T = 10^{bck}$$

$$\text{or } -\log T\ 1/bc = k,$$

where $b$ is the thickness in cm., $c$ the concentration in cg. per liter, and $k$ the extinction coefficient. In this paper the cell thickness was always 1 cm., while the concentration was maintained at 1.44 cg. per liter, and the extinction coefficient refers to the absorption of a solution containing 1.44 cg. per liter rather than 1. cg. per liter.

[1] Bureau of Standards Scientific Paper, No. 440; J. Opt. Soc. America, 10, 169 (1925).

The frequencies are plotted as *true* frequencies which is equivalent to $3 \times 10^6$ times the reciprocal of the wave length, rather than $10^5$ times the reciprocal of the wave length as has often been done. The unit of frequency is defined as vibrations divided by (seconds $\times 10^{12}$) = f, the fresnel.

The exposure ranged in general from about three minutes at the maximum to 10 seconds at 100% transmittancy. Each exposure resulted in two spectra, parallel and in contact with each other, the lower one representing the energy passing through the solvent containing the dye, this beam of energy being unimpeded by any absorbing agent other than the dye in the solvent. The upper band represents the energy passing through the clear solvent. In the path of this latter beam there is a rotating sector which may be set at various

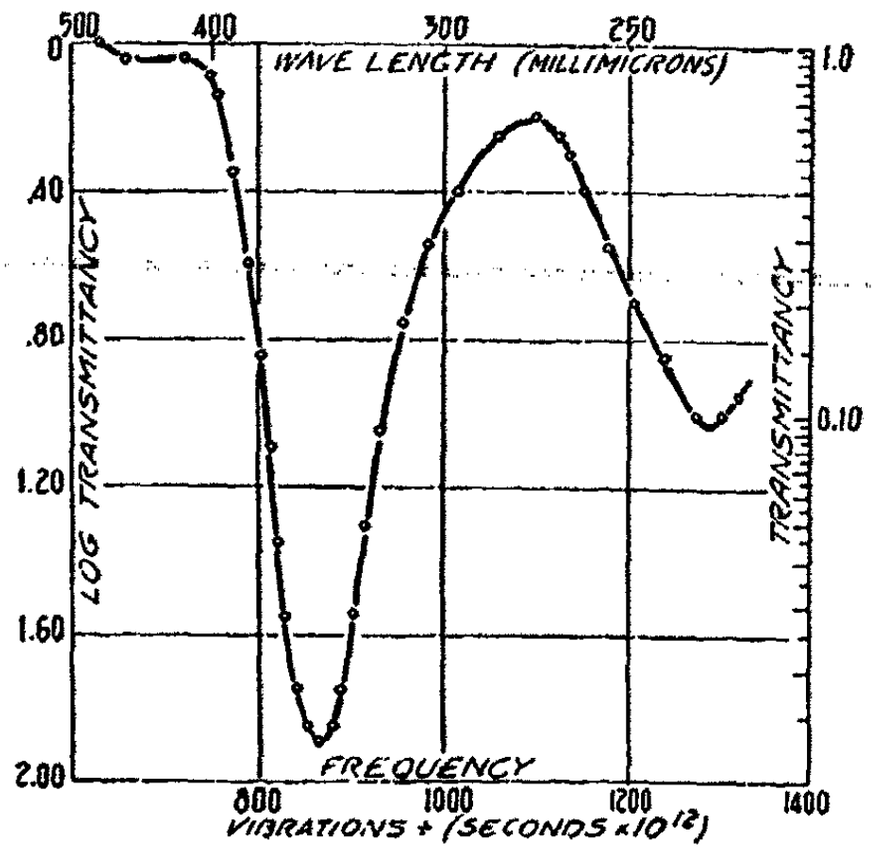



FIG. 2

Benzeneazophenol in Absolute Alcohol. Conc. = 1.44 cg per liter, thickness = 1 cm.

transmittancies. These transmittancy values are so chosen as to be equivalent to units of .05 on the log of the transmittancy scale, i.e., actual transmittances such as 100, 89.4, 79.5, 71.0, 63.1, 56.4, etc. which are equivalent to log transmittancy values of .00, .05, .10, .15, .20, .25, etc. This required from 35 to 40 sets of exposures for each solvent. These values were checked again at the maximum and at 100% transmission by some 10 more exposures on a newly made solvent solution so as to verify the previous measurements. In Fig. 2 are given curves of benzeneazophenol by various observers which have been recalculated on the basis of percentage of thickness of a solution of constant transmission and to true frequencies of vibration.

## Solvents and Preparation of Solutions

The solvents which are listed below were used for these observations. All but carbon disulfide permitted the determination of the absorption maxi-

TABLE I

Solvents and their refractive indices and dielectric constants

| No. | Solvent | MW | D | M | n | $n_c$ | ε | $\varepsilon_c$ | Quality |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Methyl Alcohol | 32.04 | .7914 | 8.34* | 1.331 | —— | 31.2 | 2.40 | Absolute |
| 2 | Ethyl Alcohol | 46.06 | .7894 | 12.9* | 1.362 | 1.125 | 27.5 | 2.36 | Absolute |
| 3 | iso Propyl Alcohol | 60.08 | .7887 | 17.5* | 1.385 | 1.131 | 22.4 | 2.27 | C. P. |
| 4 | n Butyl Alcohol | 74.10 | .8099 | 22.2* | 1.399 | —— | 19.2 | —— | Good |
| 5 | act. Amyl Alcohol | 88.11 | .816 | 26.8* | 1.409 | —— | 16.0 | —— | C. P. |
| 6 | Benzyl Alcohol | 108.1 | 1.0415 | 32.5* | 1.540 | —— | 14.0 | —— | C. P. |
| 7 | Ethyl Acetate | 88.1 | .900 | 17.7* | 1.374 | 1.128 | 6.1 | 1.82 | C. P. |
| 8 | Butyl Acetate | 116.1 | .882 | 31.6* | —— | —— | 5.0 | 1.70 | Good |
| 9 | Amyl Acetate | 130.1 | .866 | 36.2* | 1.406 | —— | 4.8 | —— | C. P. |
| 10 | Ethyl Formate | 74.1 | .9064 | 17.7* | 1.360 | 1.127 | 9.1 | 2.04 | Very Good |
| 11 | Ethyl Propionate | 102.1 | .891 | 26.9* | —— | —— | 5.6 | —— | Very Good |
| 12 | Ethyl Oxalate | 146.1 | 1.081 | 33.2* | 1.410 | —— | 8.0 | —— | C. P. |
| 13 | Ethyl Benzoate | 150.1 | 1.051 | 41.8* | —— | —— | 6.0 | —— | Very Good |
| 14 | Ethyl Ether | 74.1 | .719 | 22.3* | 1.355 | 1.113 | 4.3 | 1.71 | C. P. |
| 15 | Acetone | 58.1 | .792 | 16.1* | 1.360 | —— | 21.5 | —— | Redistilled |
| 16 | Ethyl Methyl Ketone | 72.1 | .810 | 20.7* | 1.380 | —— | 18.0 | —— | C. P. |
| 17 | Formic Acid | 46.0 | 1.190 | 8.3* | 1.372 | —— | 62.0 | —— | C. P. (85%) |
| 18 | Acetic Acid | 60.0 | 1.051 | 12.9* | 1.347 | 1.127 | 9.7 | 1.99 | C. P. (Glacial) |
| 19 | Chloroform | 119.4 | 1.499 | 21.4* | 1.449 | —— | 5.1 | —— | U. S. P. (1% Alcohol) |
| 20 | Carbon Tetrachloride | 153.8 | 1.584 | 26.3* | 1.463 | 1.165 | 2.24 | 1.34 | C. P. |
| 21 | Carbon Disulphide | 76.1 | 1.256 | —— | 1.631 | —— | —— | —— | C. P. |
| 22 | Glycerol | 92.1 | 1.266 | 20.6* | 1.472 | —— | 56.? | —— | C. P. |
| 23 | Ligroin | C-6 | .660 | 29.9* | 1.395 | 1.133 | 1.90 | 1.26 | Redistilled |
| 24 | Gasoline | C-9 | .680 | 48.3* | 1.400 | 1.132 | 1.92 | 1.26 | Redistilled |
| 25 | Petrolatum | C-15 | —— | 76.1* | 1.403 | —— | 1.84 | —— | Medicinal |
| 26 | Benzene | 78.1 | .879 | 26.3* | 1.501 | 1.174 | 2.28 | 1.35 | C. P. (Thiophene Free) |
| 27 | Toluene | 92.1 | .865 | 30.9* | 1.498 | —— | 2.37 | —— | C. P. |
| 28 | Xylene | 106.1 | .864 | 35.5* | 1.498 | —— | 2.35 | —— | C. P. |
| 29 | Tetralin | 132.1 | .974 | —— | 1.540 | —— | —— | —— | Redistilled |
| 30 | Pyridine | 79.1 | .990 | —— | 1.509 | —— | 12.4 | —— | C. P. |

MW—Molecular weight. D—density. M—molecular refraction, n—refractive index, $n_c$—refractive index at critical temperature[1], ε—dielectric constant, $\varepsilon_c$—dielectric constant at critical temperature[2], *—calculated value, not observed.

[1] Herz: Z. physik. Chem 98, 175 (1922).
[2] Herz: Z. physik. Chem. 103, 269 (1922).

mum of the dye. The solvents used were thought to be of high purity, with the possible exceptions of butyl alcohol and butyl acetate, which showed indications of impurities in their ultra-violet spectrum. A number of the solvents used were redistilled in the laboratory. It is entirely possible that the carbon disulfide used although of c.p. grade contained a small amount of free sulfur, which would have increased the absorption of the solution.

The black portion in Fig. 3 indicates the region where total absorption takes place as determined through a 1 centimeter cell on exposure of not over

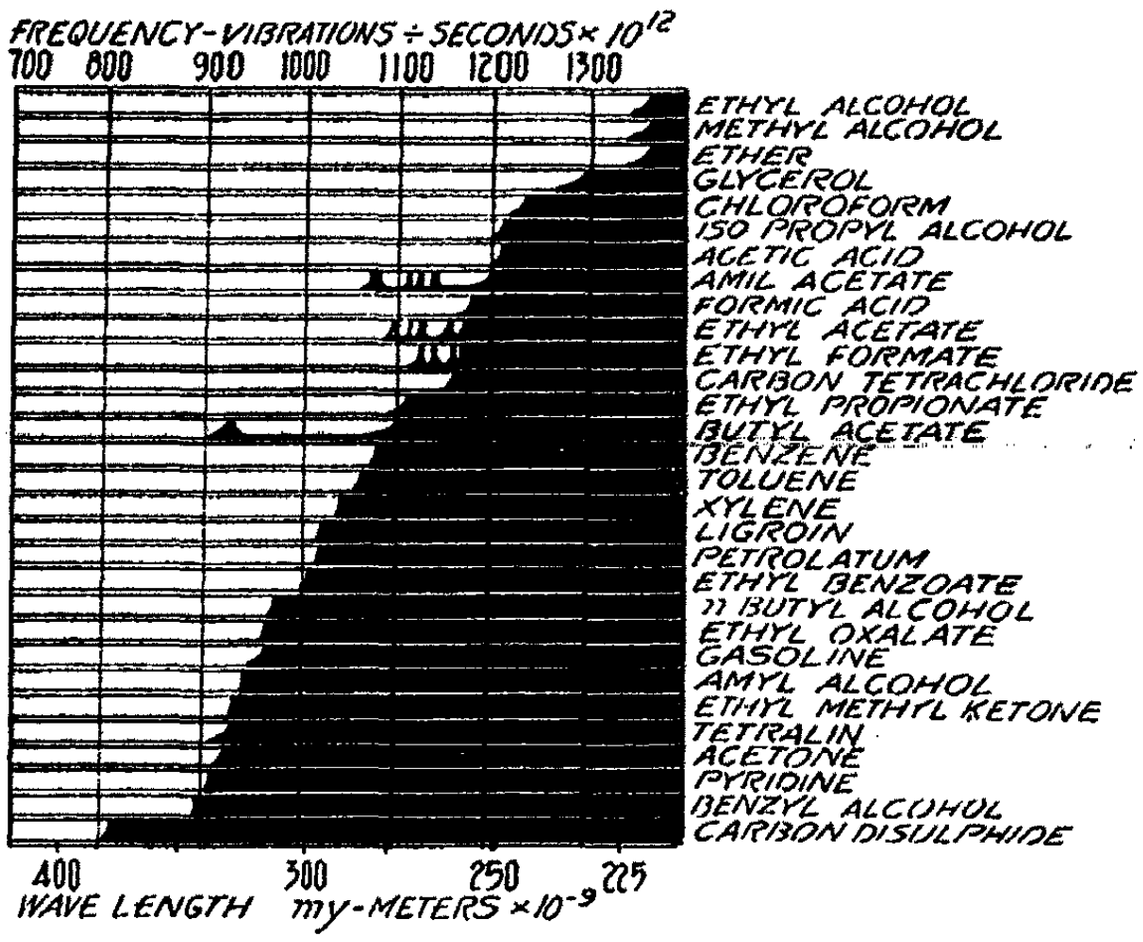



FIG. 3

Absorption of solvents used for 1 cm. thickness. Slope of start of band indicates whether the absorption is sharp or gradual.

3 minutes nor less than 2 minutes. The slope of the start of the absorption strip indicates whether the absorption commences abruptly or gradually, as determined by a series of exposures varying from 10 seconds to more than two minutes. The accuracy of the determination of the limit of transmission of these solvents can better be determined by direct examination of the plates (not reproduced in this paper). The esters were the only solvents which showed satellite bands. In all probability the other solvents would have shown bands if the cell thickness had been reduced, as it requires a relatively weak band to exhibit anything but total absorption in a thickness of 1 cm.

The graph of the absorption limits of these solvents gives a series of solvents with gradual absorptions from 1350 to 800 f and in practically all cases, except where indicated, the absorption is very sharp so that they may be used conveniently as radiant energy filters. The limit of the spectrograph used was about frequency 1360 to 1380 so that values in the neighborhood of this limit do not have as high an accuracy as those of lower frequencies.

By experiment it was found that a concentration of 1.44 centigrams per liter would give a curve with a maximum extinction coefficient of about 1.80, which was a convenient value to work with. The solutions used were made up in two ways, first, by dissolving .1900 g. of the dye in 500 cc, pipetting off 40 cc of this and making it up to 200, and pipetting off 40 cc of this solution and making it up to 200 cc. This procedure was followed when the dye dissolved with difficulty or the solvent was easily obtainable in large quantities. The second method was to dissolve .1440 g. in 100 cc of solvent, pipette off

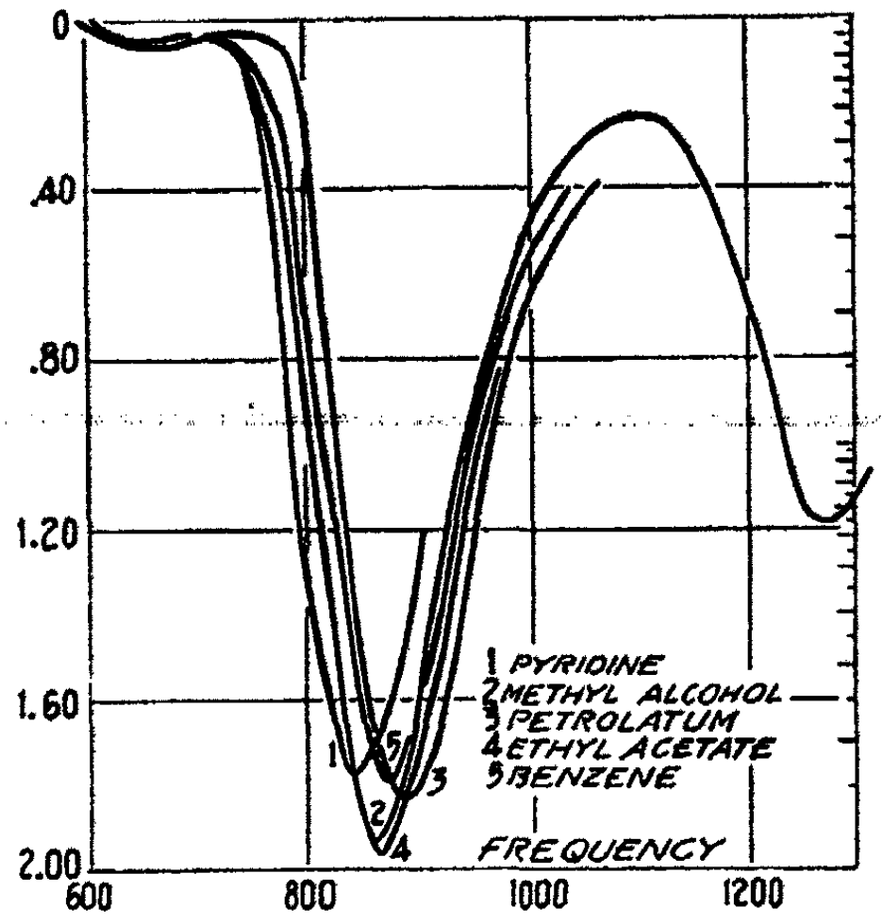



FIG. 4

Absorption Spectra of Benzeneazophenol in Pyridine (1), Methyl Alcohol (2), Petrolatum (3), Ethyl Acetate (4), Benzene (5).

10 cc of this and make up to 100 cc and pipette off 10 cc of this solution and make it up to 100 cc. The solutions were made up at 20° and samples of the clear solvent removed at the same time.

In the case of glycerol, considerable error was possible, owing to the viscosity of the solvent, so that it was necessary to wash the pipette out several times with the diluting solvent so as to insure as complete a draining of the pipette as possible. In the case of the other solutions the pipettes were simply allowed to drain. The dye dissolved with difficulty in the petroleum solvents and glycerol, it dissolved quite readily in the other solvents. The temperature of the cells when the observations were made was between 21° and 23°.

## Results

The results obtained are best illustrated graphically. In Fig. 4 are given curves for the dye in methyl alcohol, pyridine, benzene, petrolatum and ether. In the following table are given values for the extinction coefficient and frequency at the peak, for all the solvents used.

## TABLE II

Frequency and height of the absorption band of benzeneazophenol in the solvents used.

| | Solvent | F. | Extinction Coefficient |
|---|---|---|---|
| 1 | Methyl Alcohol | 862 | 1.90 |
| 2 | Ethyl Alcohol | 860 | 1.90 |
| 3 | iso Propyl Alcohol | 859 | 1.88 |
| 4 | n Butyl Alcohol | 854 | 1.91 |
| 5 | act. Amyl Alcohol | 853 | 1.92 |
| 6 | Benzyl Alcohol | 859 | 1.90 |
| 7 | Ethyl Acetate | 862 | 1.98 |
| 8 | Butyl Acetate | 861 | 1.90 |
| 9 | Amyl Acetate | 865 | 1.95 |
| 10 | Ethyl Formate | 866 | 1.98 |
| 11 | Ethyl Propionate | 864 | 1.86 |
| 12 | Ethyl Oxalate | 866 | 1.89 |
| 13 | Ethyl Benzoate | 855 | 1.84 |
| 14 | Ethyl Ether | 861 | 1.95 |
| 15 | Acetone | 865 | 2.00 |
| 16 | Ethyl Methyl Ketone | 860 | 1.90 |
| 17 | Formic Acid | 863 | 1.15* |
| 18 | Acetic Acid | 870 | 1.85 |
| 19 | Chloroform | 871 | 1.85 |
| 20 | Carbon Tetrachloride | 880 | 1.80 |
| 21 | Carbon Disulfide | — | —— |
| 22 | Glycerol | 856 | 1.60 |
| 23 | Ligroin | 885 | 1.92 |
| 24 | Gasoline | 884 | 1.92 |
| 25 | Petrolatum | 883 | 1.84 |
| 26 | Benzene | 871 | 1.80 |
| 27 | Toluene | 868 | 1.70 |
| 28 | Xylene | 871 | 1.74 |
| 29 | Tetralin | 865 | 1.74 |
| 30 | Pyridine | 840 | 1.64 |

*See Fig. 5.

From the above data it can be seen that as far as the height of the band is concerned, with a few exceptions, the band is lower in non-polar solvents. The measurements on the height of the band, however, are not as accurate as the frequency measurements and allowance must be made for instrumental errors involved in the photographing and in the reading of the plates after photographing. This is in part due to the fact that the band is flat for a very short distance at the maximum, or rather gives the appearance of such, and in such cases the greater accuracy is obtained by changing the transmission

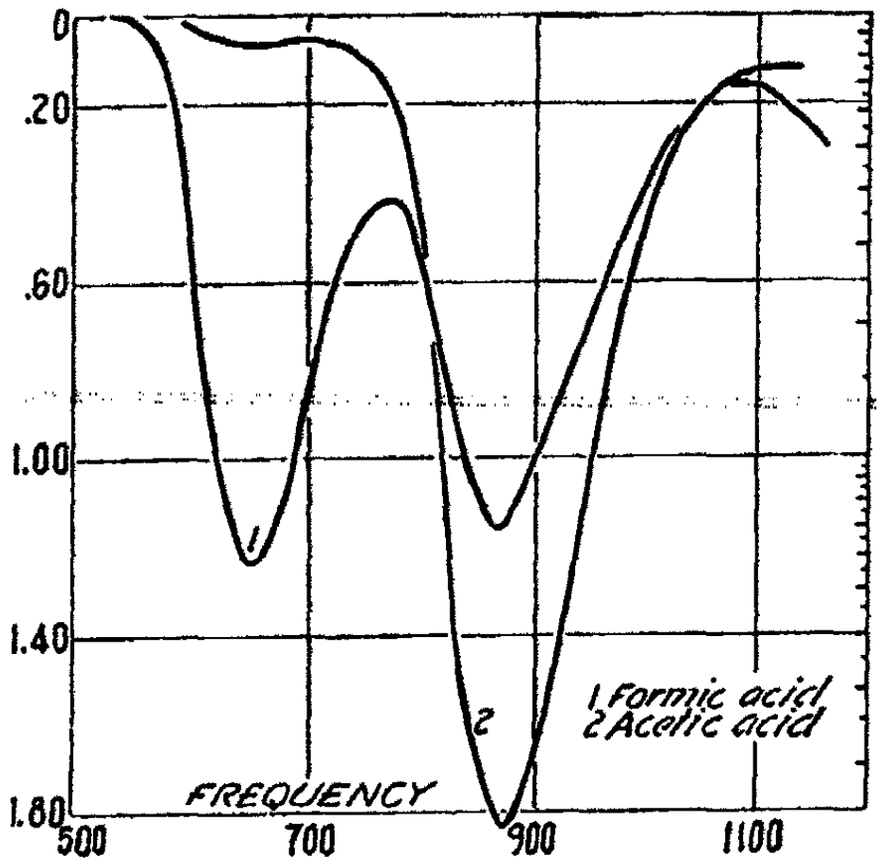



FIG. 5

Absorption Spectra of Benzeneazophenol in 85% Formic Acid (1) and Glacial Acetic (2). Note acid band which is produced by formic acid.

valves gradually, a process which is impossible photographically. The error involved in the determination of the frequency does not amount to more than ± 2 in most of the cases observed except where the absorption of the solvent was near enough to the peak of the band to decrease the intensity.

The general shape of the band is the same for all of the solvents, indicating a general shift of the entire band rather than the increasing of certain frequency amplitudes within the band structure with the decreasing of others, as it is highly improbable that if the latter were the case the change would be exactly analogous in all cases so as to give the same shaped band but with a different vibrational center.

From Fig. 6 it is evident that there is very little if any relation between the refractive indices of the various solvents used and the frequency of the absorption maximum, although in the case of certain homologous series such as the alcohols there seems to be a general shift with an increasing molecular weight. It is also to be noticed that similar solvents in general group together

although the order in which they arrange themselves is not consistent with the increase of their refractive indices. Although there are a large number of exceptions, in fact too many to permit such a conclusion, it appears that the average shift is towards higher frequencies with increasing refractive indices, an effect exactly opposite to Kundt's law.

In Fig. 6 are compared the refractive indices and frequencies of the peak of the band in different solvents which are numbered as in Table I and II. In like manner the effect of the dielectric constant which is also considered a

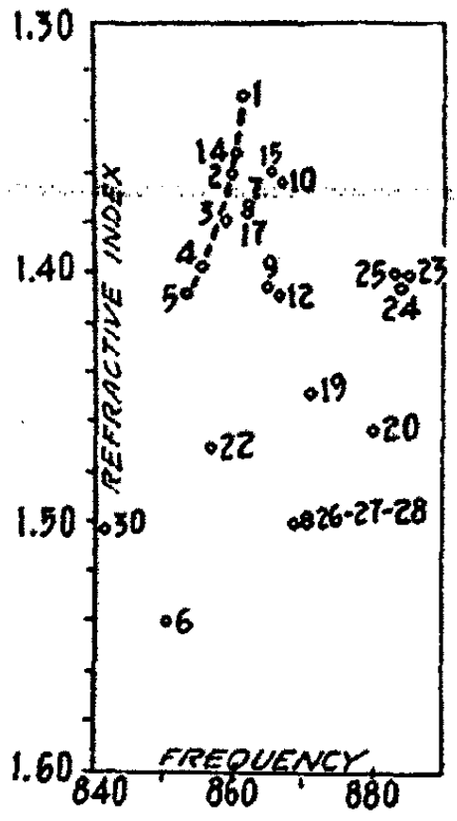



FIG. 6

Relation between the refractive index at 20° and the absorption frequencies. The numbers refer to the solvent numbers in Table II.

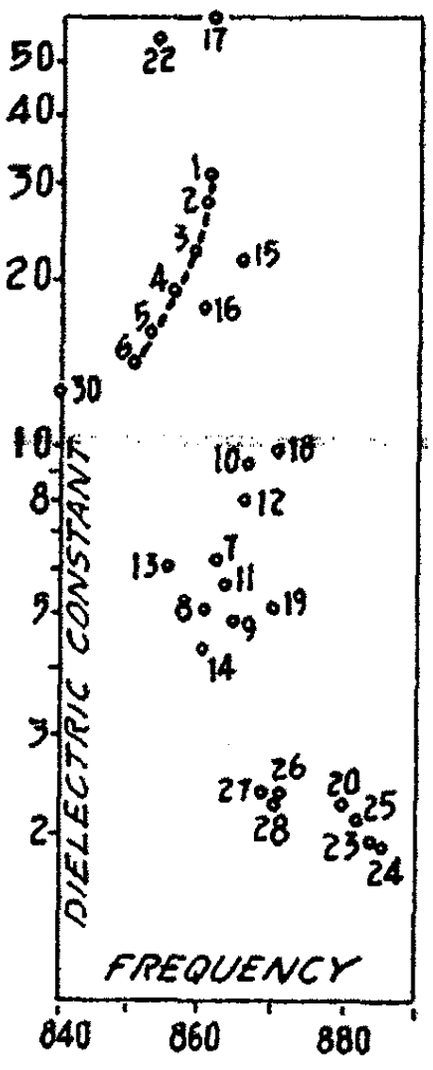



FIG. 7

Relation between dielectric constants at 20° and absorption frequencies.

molecular property of the solvent, appears to have very little effect, Fig. 7, but here again, it may be pointed out that in homologous series there may be some relation. This relation in regard to homologous series may and probably is due to some other effect than a change in the dielectric constant or refractive index, although this effect and the force which changes the dielectric constant and refractive index are probably fundamentally related. As would be expected, similar substances such as xylene and tetrahydronaphthalene (tetralin) give similar frequencies of vibration and also closely related dielectric constants and refractive indices.

By plotting the frequency values of the absorption band of the dye in some of the various solvents against their refractive indices or dielectric constants

figured over to the theoretical value at their critical temperatures a somewhat better agreement is obtained and some of the discrepancies which existed before, as in the case of the saturated hydrocarbons and the aromatic hydrocarbons are corrected. There are still too many exceptions and deviations to draw any conclusions, Figs. 8-9. The values have also been plotted for the dielectric constants at their boiling points with about the same agreement, or disagreement, depending upon the angle from which it is viewed, Fig. 10. The objection may be raised, and it is quite legitimate, that the observations

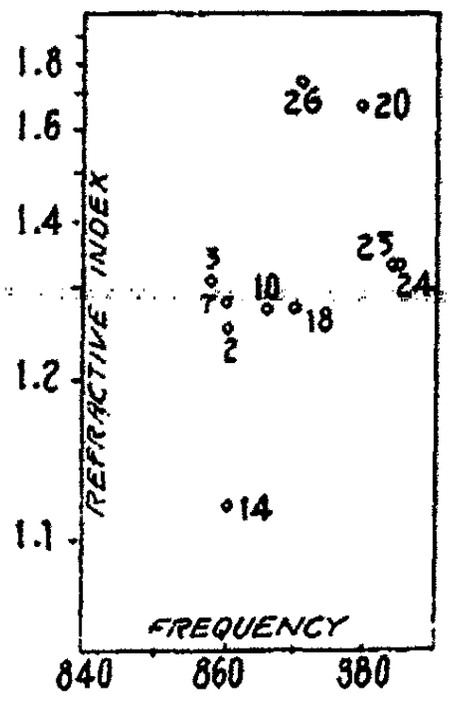



FIG. 8

Relation between refractive indices at the critical temperature and absorption frequencies of the solvent.

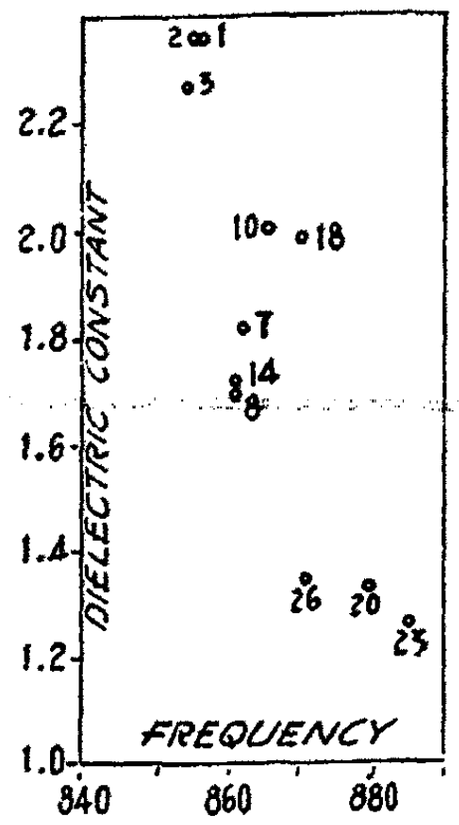



FIG. 9

Relation between the dielectric constants at the critical temperature and the absorption frequencies.

were not made at these temperatures and that comparison is being made between two unrelated sets of figures. It may be pointed out, however, that the shift of the absorption band with temperature is slight, especially with azo dyes[1] whereas the changes in the refractive indices and dielectric constants with change in temperature are large and the values widely varied, but that at the critical temperature or boiling point they fall into a more regular series with a more uniform change.

## Mixed Solvents

In determining the effect of a solvent on the absorption maximum of a dye it was quite essential to determine the effect of mixed solvents, or the effect of an impurity on the shift in the absorption band. In these experiments, solutions of benzene and alcohol, carbon tetrachloride and alcohol, ligroin and alcohol, water and alcohol, and ligroin and benzene were used. The first two

[1] Bureau of Standards Sci. Papers, No. 440; Kayser; "Handbuch der Spektroscopie", 3, 92.

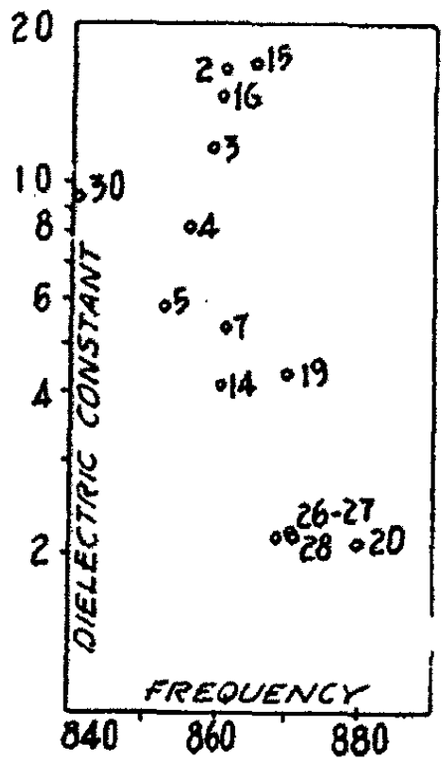



FIG. 10

Relation between dielectric constants at the boiling point and absorption frequencies.

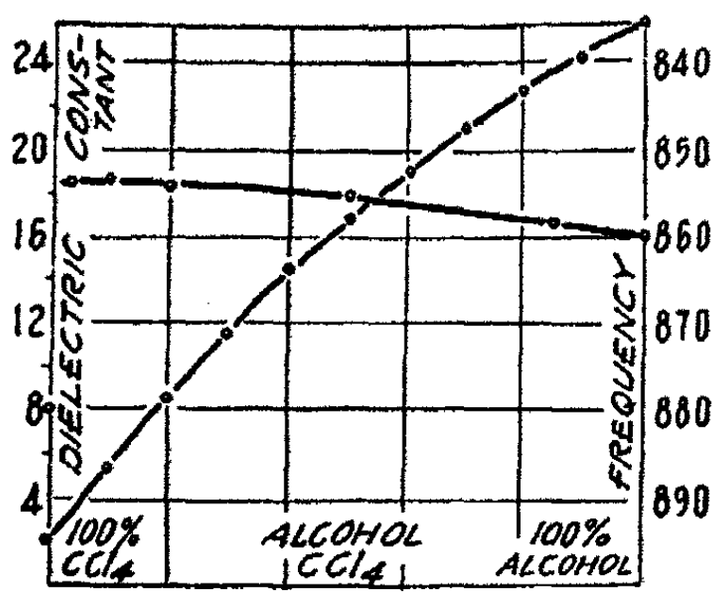



FIG. 11

Effect of mixtures of alcohol and carbon tetrachloride on the dielectric constant and absorption frequency.[1] Dotted line = frequency.

[1] Givan and Patrick: J. Am. Chem. Soc., 45, 2799 (1923).

of these were of special interest as data were available on the dielectric constants and refractive indices of these mixtures. From these data a careful check could be obtained on the relation between the absorption shift and the refractive indices and dielectric constants. The results are indicated in Figs. 11-13. The effect, although one which might be predicted, is far from being a function of either of these two physical properties. As small an amount of alcohol as 1% was sufficient to shift the band to the alcohol band in both benzene and carbon tetrachloride. The shift is quite apparent and would

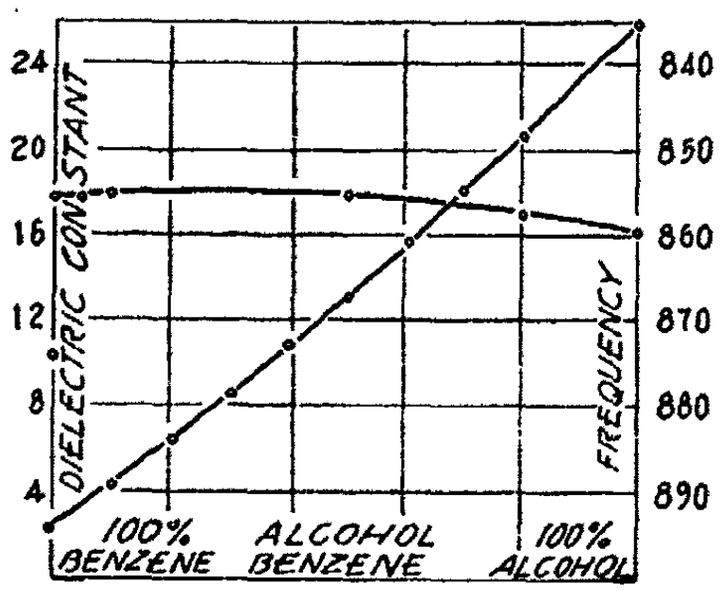



FIG. 12

Effect of mixtures of alcohol and benzene on the dielectric constant and absorption frequency.[2] Dotted line = frequency.

[2] King and Patrick: J. Am. Chem. Soc. 41, 1143 (1921).

undoubtedly have taken place for much smaller concentrations of alcohol, the 1% solution being the lowest percentage tried. It is apparent that the more polar the solvent the greater tendency it has to shift the band to its own vibratory frequency giving the effect of the dye being entirely dissolved in the solvent, and this solution being suspended in the other solvent. In the case of ligroin and benzene the effect appeared to be a gradual change as compared with the sharp change due to alcohol. In both the benzene and the carbon tetrachloride mixtures the band seemed to shift to a point somewhat beyond the ordinary frequency of alcohol (855) and then on increasing the percentage of alcohol it gradually returned to 860. The same effect was noticed on dilution of the alcohol solution with water. The band was gradually reduced in frequency with an increase in the water percentage to about the same values, indicating possibly that the effect is merely one of dilution. The dye being insoluble in water, there is no shifted band in this case, the main band being simply reduced in intensity. This reduction does not take place until the percentage of alcohol becomes very small. This effect accounts to some extent for some of the wide variations in the shifting of the band, as in the case of the chloroform which was known to contain a small amount of alcohol and in which the band was not shifted to anywhere near the extent to which it was shifted in carbon tetrachloride.

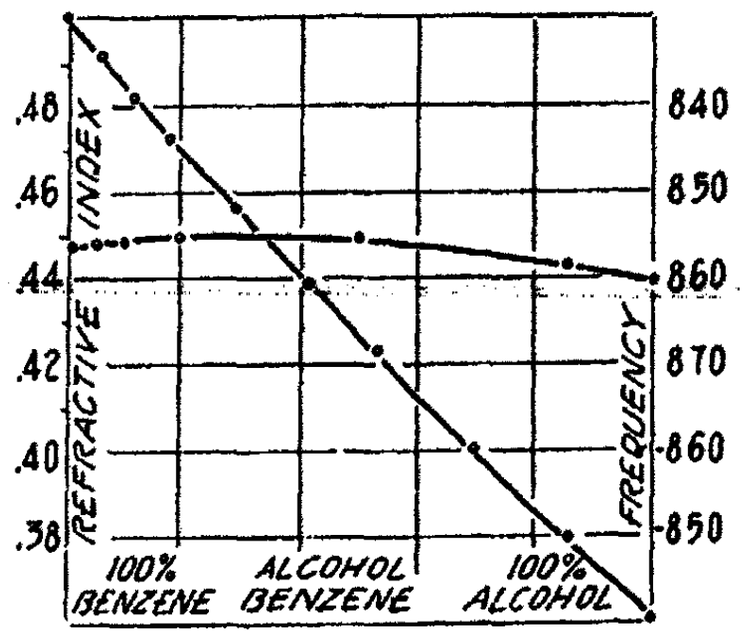



FIG. 13

Effect of mixtures of alcohol and benzene on the refractive index and absorption frequency. Dotted line = frequency.

## Summary

1. The absorption limits of some 30 organic solvents have been determined and their region of total absorption has been observed throughout the ultra-violet to a frequency of 1360 for a thickness of 1 cm.

2. The absorption spectrum of benzeneazophenol has been observed in these solvents.

a. From these data it appears that for this simple azo dye, and in all probability for other simple azo dyes, Kundt's law does not hold.

b. There appears to be no definite relation between the refractive indices or the dielectric constants of these solutions and the frequency of the absorption band of the dye dissolved in them.

3. In mixtures the dye appears to give the absorption frequency for the most polar solvent, even if this solvent is present in a very low percentage and there is a slight dilution effect in such cases.

4. The height of the band appears to be greater for polar solvents than for non-polar solvents.

# SOLUBILITY RELATIONS OF ISOMERIC ORGANIC COMPOUNDS
# VI. SOLUBILITY OF THE NITROANILINES IN VARIOUS LIQUIDS

BY ARMAND R. COLLETT AND JOHN JOHNSTON*

This investigation of the solubility of the three nitroanilines in a series of liquids was undertaken with two main objects in view. The first was to discover, if possible, whether some particular solvent would be specially advantageous in the separation of a mixture of such isomers, or in the purification by crystallization of any one of them. The second was to learn more as to the solubility relations of such closely related substances as the *ortho*, *meta* and *para* isomers $C_6H_4XY$. It was hoped moreover that any conclusions which could be drawn from the behavior of one series could be applied—at least as a first approximation—to other series which are not too dissimilar.

The substances chosen were the nitroanilines, which are readily obtainable in a pure state and are convenient to work with. Although these compounds are important dye intermediates, little reliable information on their solubility is available; for, with the exception of the work of Bogojavlenski et al.[1] on their solubility in benzene, nitrobenzene, and dibromoacetylene, and the more recent work of Sidgwick and Rubie[2] in benzene and in water, only questionable data at 20° and 25° are available. The solvents investigated were selected as typical substances in common use as solvents.

## Materials

In purifying the nitroanilines by recrystallization we found the process to be more effective with two solvents used separately than with a single solvent; it is questionable however, as we shall see, in how far the use of a second solvent is in general beneficial in the separation of one isomer from the other.

*Ortho-Nitroaniline* was crystallized from 95% alcohol and then repeatedly from hot water, from which it came out in fine orange-colored needles. The melting temperature as determined from the flat on the time-temperature curve[3] is 69.3°, although by the ordinary capillary tube method it appears to be 72°.

*Meta-Nitroaniline* was crystallized twice from alcohol and then from water; this yielded lemon-yellow blade-like crystals, the melting temperature of which is 111.8°.

*Para-Nitroaniline*, crystallized several times from water, yielded, on solution in hot alcohol, a reddish residue; so it was recrystallized from alcohol and subsequently from water. The final product consisted of light yellow needles the melting temperature of which is 147.5°.

---

*From the dissertation presented to the Graduate School of Yale University, in June, 1923, in candidacy for the degree of Doctor of Philosophy.

[1] Bogojavlenski, Bogoliubov and Vinogradov: through Chem. Abs. 1, 2875 (1907).

[2] Sidgwick and Rubie: J. Chem. Soc., 119, 1013 (1921).

[3] Cf. Kohman: J. Phys. Chem., 29, 1048 (1925).

*Water*: all the distilled water used was boiled to expel dissolved air.

*Alcohol*: 95% alcohol was refluxed with lime, distilled, dried with sodium, and redistilled twice; the major fraction boiled at 78.4° and 762 mm.

*Benzene*: Pre-war thiophene-free benzene was dried over sodium and distilled; redistillation yielded a major fraction boiling at 80.3-80.4° and 762 mm.[1]

*Chloroform* (C. P.) was dried for several days over calcium chloride and then distilled; it boiled at 61.2-61.4° and 768 mm.

*Carbon tetrachloride* (C. P.) was treated similarly; it boiled at 76.5-76.55° and 765 mm.

*Ether* (U. S. P.) was washed several times with sodium carbonate solution, subsequently with water until the aqueous layer proved to be neutral. After being dried for a week over calcium chloride, it was distilled twice; the product boiled at 34.5-34.8° and 760 mm.

*Ethyl acetate* (U. S. P.) was treated similarly; it boiled at 77.0-77.3° and 760 mm.

*Acetone* (C. P.) was dried over calcium chloride and twice distilled; the fraction used boiled at 56.1-56.2° and 756 mm.

Every effort was made to prevent moisture from reaching the solvents; the distillation apparatus was thoroughly dried, and the solvents were preserved in flasks stoppered with a calcium chloride tube.

## Method

Most of our determinations have been made by a slight modification of the synthetic method which has been used by a number of previous investigators[2]; a few were made by analysis of the solution saturated at a fixed temperature, as a check on the accuracy of the synthetic method. The essence of this method is to ascertain the temperature at which the last crystal just disappears, when a known mixture of solute and solvent is slowly heated. The chief objections to this procedure, as usually carried out, are that the observed saturation temperature may be in error because the rate of change of temperature is not slow enough to insure the attainment of equilibrium, of composition or of temperature, and that the composition of the solution may change owing to volatilization of the components. The procedure finally adopted, after a large number of preliminary experiments (not detailed here) is substantially free from these objections, and yields results which compare favorably with those obtained by analysis of a solution in contact with crystals of a definite temperature; it is as follows. Into a small bulb, of 2-4 cc. capacity, blown on a tube about 6 mm. diameter, was introduced a known weight of the substance; the tube was drawn down to capillary size at a distance of 3-4 cm. from the bulb, an appropriate quantity of solvent introduced, the tube sealed off and

[1] Richards and Barry give 80.2° at 760 mm: J. Am. Chem. Soc., 37, 996 (1915).

[2] Alexeiev: Ann. Physik, 28, 327 (1886); Schröder: Z. physik. Chem., 11, 449 (1893); Bogojavlenski, Bogoliubov and Vinogradov: through Chem. Abs. 1, 2874 (1907); Sidgwick et al: J. Chem. Soc., 107, 1202 (1915); 119, 979, 1001, 1013 (1921); 121, 1844, 1853, 2256, 2263, 2536 (1922); 123, 2813, 2819, (1923); Kendall et al: J. Am. Chem. Soc. 43, 979 (1921); 45, 958 (1923); Carrick: J. Phys. Chem., 25, 648 (1921).

weighed so as to secure the weight of the solvent. The tubes were not completely filled, a space, usually about 1 cc., being left to permit of stirring, which was accomplished by attaching the tube horizontally to a heavy wire which had been soldered to the (vertical) hammer of an ordinary electric bell; this proved to be an effective method of agitation, and was used throughout the series of observations. The tube was now surrounded by a three-liter beaker containing either water (up to 80°) or paraffin (beyond 80°) which was kept thoroughly stirred by a stream of air; and a calibrated thermometer, graduated in tenths, was immersed so that its bulb was close to the tube, a second thermometer being used to enable the proper stem correction to be made. The flame was adjusted so that the rate of heating of the bath was about 0.1° per minute, and the temperature noted at which the last crystal disappeared; the bath was now allowed to cool slowly until about half the solute had crystallized, whereupon it was again raised in temperature and maintained for half an hour at about 1° below that first recorded. Finally the bath temperature was raised at about 0.05° per minute, and the temperature at which the last crystal now disappeared was taken to correspond to saturation for the particular mixture weighed into the tube. Determinations made in this way check within about 0.2°; whereas, if one may judge from the data, the corresponding divergence in many of the previous results obtained by this general mode of experiment, has been 1° or even more. A correction (which in all cases was small) was made for the change in composition caused by the presence of some of the solvent in the vapor space; it was computed from the vapor pressure of the pure solvent, and its mol fraction in the solution on the basis that Raoult's law holds. A similar calculation showed that the corresponding correction for the nitroanilines is negligible.

In the analytical determinations, solvent with excess of solute was placed in glass-stoppered bottles with gum covers, or in sealed tubes, which were rotated in a thermostat. When equilibrium had been attained, the solid was allowed to sttle, and filtered samples of the solution were weighed and analyzed. A search of the literature for a method of analysis for nitroaniline revealed only one which appeared satisfactory[1] namely, that of Knecht and Hibbert[2], who titrate with titanous chloride in absence of oxygen. Their procedure however had to be modified somewhat to give the accuracy desired. The solution of titanous chloride, $TiCl_3$, used was approximately 0.2 normal; it was kept under an atmosphere of hydrogen, as described by Knecht and Hibbert. Methylene blue, prepared by adding 0.5 grams of methylene blue to 500 cc. of water, shaking and filtering, was used as indicator; it was reduced to the colorless condition with $TiCl_3$ and kept in an atmosphere of carbon dioxide. With

[1] As has been shown by Carnelley and Thomson, (J. Chem. Soc., 53, 782 (1887)) and from our observations, the amount of nitroaniline in a solution cannot be estimated by evaporating the solvent owing to the high volatility of the solute; even at 40° appreciable amounts of nitroaniline are volatilized. Yet as late as 1904 Farmer and Warth (J. Chem. Soc., 85, 1713 (1904)) used this inaccurate method. The colorimetric method used by Carnelley and Thomson was not adopted in this case because of the inaccuracy, as suggested by the authors themselves, resulting from the color change of the solutions on exposure to light.

[2] Knecht and Hibbert: Ber., 40, 3819 (1907); 36, 1549 (1903); q.v.

these solutions the experimental error in analysis was easily reduced to 0.5% when the samples titrated were from 0.05 to 0.5 grams. The presence of the solvents employed in this investigation was found to have no effect upon the results; Knecht and Hibbert give a correction for the effect of the alcohol, but this difference probably results from the fact that they did not boil the solution and consequently did not expel the dissolved air before they added the titanous chloride.

TABLE I

Mean Experimental Results on the Solubility of the Nitroanilines in Various Solvents, as determined analytically.

| Solvent | Temp. C. t | Solubility g. per 100 g. solvent | Solubility mols per 100 mols solution C |
|---|---|---|---|
| | *Ortho* | | |
| $H_2O$ | 25.0 | 0.1212 | 0.158 |
| | 40.1 | 0.2423 | 0.315 |
| $C_6H_6$ | 25.0 | 20.80 | 10.52 |
| $C_2H_5OH$ (abs.) | 25.0 | 27.87 | 8.47 |
| $CHCl_3$ | 0.0 | 11.17 | 8.81 |
| | *Meta* | | |
| $H_2O$ | 25.0 | 0.0910 | 0.119 |
| | 40.1 | 0.1785 | 0.232 |
| $C_6H_6$ | 25.0 | 2.718 | 1.53 |
| | 40.1 | 5.137 | 2.82 |
| $C_2H_5OH$ (abs.) | 0.0 | 4.035 | 1.33 |
| | 25.0 | 7.778 | 2.53 |
| $C_2H_5OH$ (95%) | 25.0 | 7.155 | —— |
| $CHCl_3$ | 0.0 | 1.358 | 1.16 |
| | 25.0 | 3.216 | 2.60 |
| | 40.1 | 6.102 | 5.01 |
| | *Para* | | |
| $H_2O$ | 25.0 | 0.0568 | 0.074 |
| | 40.1 | 0.1157 | 0.151 |
| $C_6H_6$ | 25.0 | 0.5794 | 0.325 |
| | 40.1 | 1.040 | 0.555 |
| $C_2H_5OH$ (abs.) | 0.0 | 3.382 | 1.110 |
| | 25.0 | 6.048 | 1.978 |
| | 40.1 | 8.234 | 2.674 |
| $C_2H_5OH$ (95%) | 25.0 | 5.674 | —— |
| $CHCl_3$ | 0.0 | 0.4331 | 0.373 |
| | 25.0 | 0.9290 | 0.797 |
| | 40.1 | 1.559 | 1.330 |

The results of the determinations by the analytical method are presented in Table I, each datum being the mean of from three to five concordant measurements made by approaching the equilibrium both from under- and from over-saturation.

The direct experimental saturation temperatures (t) secured by use of the synthetic method are presented in Table II, in terms of mol percentage[1] (C) of solute (corrected only for the amount of solvent in the vapor space). For convenience of reference, we have included the results of Sidgwick and Rubie, recalculated in terms of mol-percentage. Solutions of *meta*-nitroaniline and carbon tetrachloride, containing from 60-85 mol percent of the former, break up into two liquid layers, with some decomposition. The same thing happens with *para*-nitroaniline in carbon tetrachloride, even at concentrations as low as 45 mol per cent; consequently work on this system was abandoned. The results for the system *para*-nitroaniline-ether are less accurate than for the other solvents, by reason again of a partial decomposition, as evidenced by a charring of the solute.

TABLE II

Mean Experimental Results on the Solubility of the Nitroanilines in Various Solvents, as determined by the Synthetic Method.

*Ortho-Nitroaniline*

| mol percent C | temp. t | mol percent C | temp. t | mol percent C | temp. t |
|---|---|---|---|---|---|
| **Acetone** | | **Ethyl Acetate** | | **Chloroform** | |
| 46.75 | 32.3 | 40.43 | 32.3 | 26.30 | 28.2 |
| 50.21 | 35.8 | 52.74 | 44.0 | 33.29 | 34.0 |
| 62.67 | 47.8 | 70.41 | 55.6 | 43.82 | 41.2 |
| 75.24 | 57.4 | 84.18 | 63.6 | 57.17 | 48.6 |
| 80.37 | 60.8 | | | 78.07 | 60.4 |
| | | | | 88.81 | 65.8 |
| **Ethyl Alcohol (abs.)** | | **Ether** | | | |
| 16.14 | 37.7 | 21.11 | 29.5 | | |
| 31.56 | 47.1 | 25.30 | 35.1 | | |
| 47.49 | 51.7 | 42.84 | 47.1 | | |
| 64.30 | 56.7 | 57.98 | 52.9 | | |
| 66.61 | 57.6 | 78.86 | 62.3 | | |
| 79.27 | 62.0 | 80.60 | 62.8 | | |
| 88.70 | 65.9 | | | | |

[1] The following molar weights were used: nitroaniline 138.1; benzene 78.05; chloroform 119.4; carbon tetrachloride 153.8; ethyl alcohol 46.05; acetone 58.05; ether 74.1; ethyl-acetate 88.06.

TABLE II (continued)

| mol percent C | temp. t | mol percent C | temp. t | mol percent C | temp. t |
|---|---|---|---|---|---|
| Carbon Tetrachloride | | Benzene | | Benzene (S & R) | |
| 5.26 | 41.3 | 14.56 | 31.2 | 7.32 | 10.5 |
| 13.24 | 47.8 | 32.78 | 42.4 | 13.38 | 23.2 |
| 21.29 | 50.0 | 46.18 | 47.9 | 22.35 | 39.2 |
| 31.19 | 51.6 | 58.49 | 52.6 | 44.81 | 47.4 |
| 46.44 | 53.1 | 76.71 | 60.3 | 54.86 | 50.2 |
| 58.32 | 55.5 | | | 67.53 | 55.0 |
| 74.06 | 60.2 | | | 81.72 | 62.0 |
| 84.68 | 64.2 | | | 92.03 | 67.2 |
| | | | | 100.0 | 71.1 |

*Meta-Nitroaniline*

| Acetone | | Ethyl Acetate | | Chloroform | |
|---|---|---|---|---|---|
| 24.69 | 36.5 | 19.82 | 38.9 | 5.27 | 44.6 |
| 38.17 | 62.0 | 22.84 | 48.9 | 11.54 | 61.3 |
| 48.06 | 75.6 | 36.91 | 71.3 | 20.66 | 71.6 |
| 56.20 | 83.4 | 49.61 | 83.0 | 47.06 | 86.6 |
| 66.64 | 91.9 | 61.74 | 91.5 | 71.15 | 99.3 |
| 84.65 | 103.3 | 81.49 | 103.1 | 84.32 | 104.8 |

| Ethyl Alcohol (abs.) | | Ether | |
|---|---|---|---|
| 5.64 | 50.2 | 5.34 | 34.7 |
| 11.40 | 65.9 | 8.93 | 52.0 |
| 23.25 | 78.5 | 21.53 | 76.4 |
| 36.80 | 85.0 | 40.87 | 89.4 |
| 45.57 | 88.7 | 49.66 | 93.0 |
| 61.32 | 94.7 | 64.36 | 98.1 |
| 69.76 | 98.4 | 81.54 | 105.2 |
| 82.52 | 104.6 | | |

| Carbon Tetrachloride | | Benzene | | Benzene (S & R) | |
|---|---|---|---|---|---|
| 5.19 | 87.3 | 13.56 | 70.4 | 2.54 | 38.2 |
| 13.84 | 94.7 | 24.21 | 79.5 | 8.54 | 60.9 |
| 17.53 | 95.8 | 36.57 | 85.4 | 21.32 | 78.4 |
| 19.29 | 95.9 | 48.99 | 90.5 | 47.46 | 88.7 |
| 33.76 | 97.2 | 56.85 | 92.7 | 68.78 | 99.2 |
| 45.41 | 98.8 | 77.04 | 102.1 | 84.40 | 105.4 |
| 55.90 | 99.6 | | | 93.72 | 110.3 |
| 86.72 | 100.0 | | | 100.0 | 114.6 |

TABLE II (continued)

*Para-Nitroaniline*

| mol percent C | temp. t | mol percent C | temp. t | mol percent C | temp. t |
|---|---|---|---|---|---|
| **Acetone** | | **Ethyl Acetate** | | **Chloroform** | |
| 24.48 | 52.5 | 12.51 | 45.8 | 4.98 | 78.5 |
| 35.03 | 83.4 | 24.83 | 83.7 | 11.59 | 94.8 |
| 42.22 | 95.4 | 37.48 | 102.2 | 21.68 | 104.8 |
| 49.51 | 105.5 | 44.59 | 110.1 | 48.61 | 118.9 |
| 67.96 | 124.5 | 67.72 | 127.6 | 65.09 | 127.4 |
| 82.66 | 136.0 | 89.41 | 142.2 | 89.92 | 141.9 |
| **Ethyl Alcohol (abs.)** | | **Ether** | | | |
| 2.45 | 34.8 | 3.688 | 66.6 | | |
| 6.05 | 66.2 | 5.66 | 89.1 | | |
| 16.96 | 92.0 | 9.53 | 104.6 | | |
| 36.59 | 109.0 | 16.88 | 114.1 | | |
| 44.19 | 113.7 | 20.53 | 117.1 | | |
| 59.74 | 122.8 | 32.82 | 120.0 | | |
| 74.45 | 132.3 | 51.77 | 126.6 | | |
| 83.83 | 137.2 | 53.51 | 127.2 | | |
| | | 72.89 | 134.2 | | |
| | | 86.08 | 141.1 | | |
| | | **Benzene** | | **Benzene (S & R)** | |
| | | 4.61 | 90.9 | 1.84 | 70.0 |
| | | 9.44 | 101.7 | 6.79 | 95.0 |
| | | 22.49 | 113.3 | 16.04 | 108.6 |
| | | 31.72 | 116.1 | 40.02 | 119.5 |
| | | 40.62 | 119.8 | 60.16 | 122.5 |
| | | 56.92 | 127.0 | 71.62 | 132.3 |
| | | 83.61 | 139.5 | 94.42 | 143.7 |
| | | | | 100.0 | 147.0 |

All of the data were plotted on a large scale, in terms of C vs. t[1], and the best curve drawn through, or very nearly through, the points. To draw these curves satisfactorily is not always easy, since many of them are initially concave, and at lower temperatures convex, to the C axis; and many show a very rapid change of slope at values of C around 10%. The only adjustments made, all of which were slight, were on the basis that the several curves should all converge to the melting temperatures of the solute, and should not cross one another in that region. The general form of the curves is evident from Fig. I, in which a number of them are reproduced. The graphs show that the results

[1] Plots of log C vs. 1/T, and of the data in terms of other variables, were tried and serve as a check upon the interpolation; but apart from this none of them in this case possessed any apparent advantage.

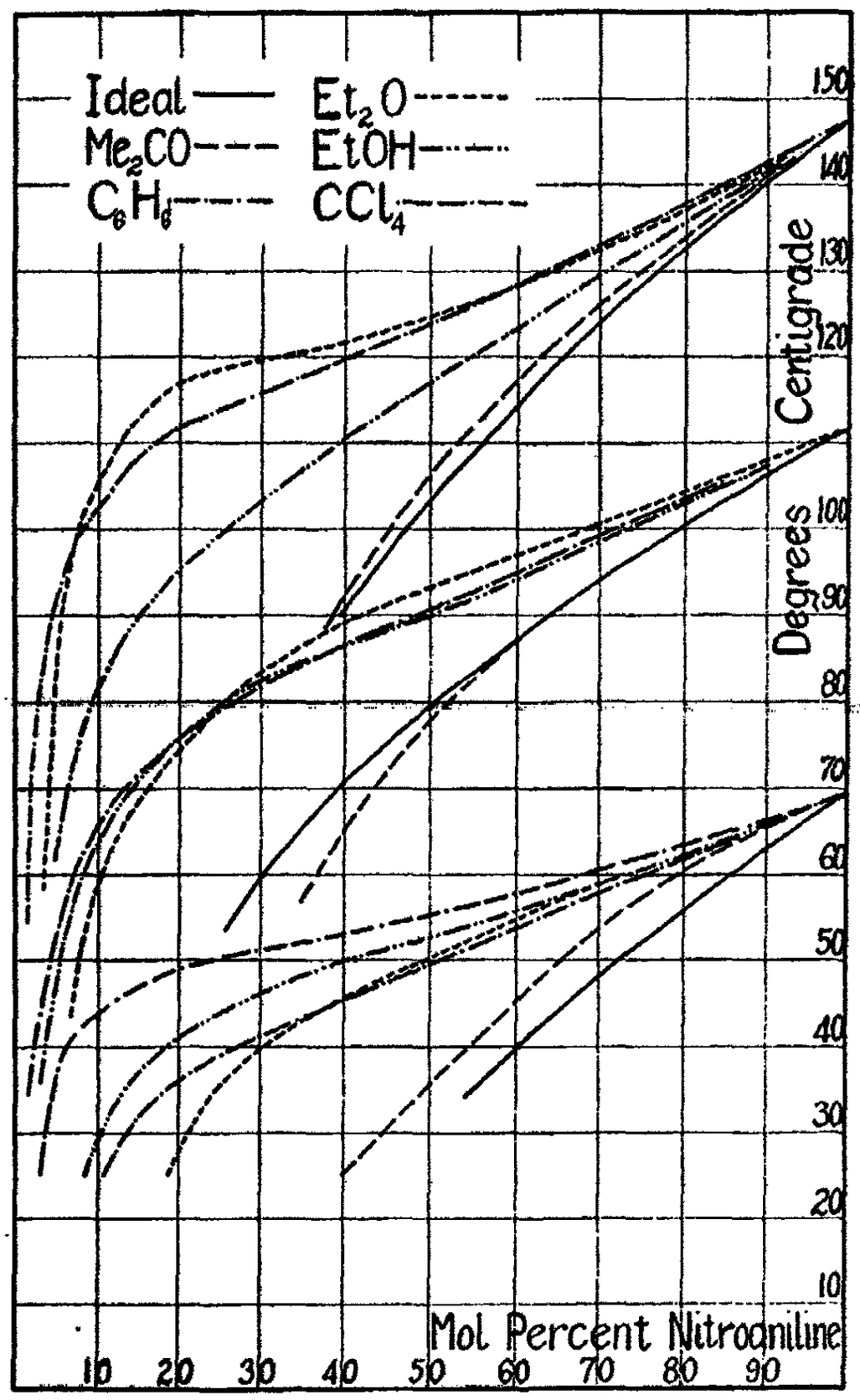



FIG. 1

secured by the two methods are in good accord. The only data with which ours may be compared are those on the solubility of each of the three isomers in benzene, as given by Bogojavlenski, Bogoliubov and Vinogradov[1] and by Sidgwick and Rubie[2]; both of these sets of data show small, and somewhat irregular, departures from our curve, the average difference however being less than 1°. For purposes of comparison, the data of the former authors on the solubilities in nitrobenzene and in dibromoacetylene were also plotted.

[1] Bogojavlenski, Bogoliubov and Vinogrsadov: through Chem. Abs. 1, 2874 (1907).
[2] Sidgwick and Rubie: J. Chem. Soc., 119, 1013 (1921).

Values of the solubility of each isomer in each solvent hitherto investigated, for a series of even values of $t$, obtained by interpolation on the large plots, are given in Table III[1]; it also includes the ideal values, as derived from thermal data, which are in fact found when the solvent is another of the nitroanilines[2].

## Discussion of Results

Inspection of the solubility curves obtained shows that the corresponding curves for the three isomers are in general very similar, though there are also significant differences between them, these differences being evidently correlated with the melting temperature (presumably, also, with the heat of melting) of the isomer. For instance, the double curvature is barely appreciable in the case of the *ortho* (which has the lowest melting temperature), is somewhat greater with the *meta*, and most evident with the *para*.

At temperatures in the neighborhood of the melting temperature of each isomer, the sequence of the "solvents", arranged in order of decreasing solubility—or of decreasing effect in lowering the melting temperature—of the nitroaniline, is: ideal, acetone, ethyl acetate, (nitrobenzene), chloroform, (dibromo-acetylene), benzene, alcohol, ether, carbon tetrachloride. At temperatures farther from the melting temperature, however,—which is the region of practical importance—the sequence is not invariable because some of the curves cross; for instance, the pair for ether and benzene, intersect at about 40 mol per cent *ortho*, at 30 per cent *meta*, and at 6 per cent *para*. Again, over the great part of the range, the solubility of *ortho* in benzene is greater than in

TABLE III

Solubility of the Nitroanilines in Various Solvents, as interpolated at a Series of Temperatures, expressed in Terms of Mol-percentage.

*Ortho* (m.p. 69.3°)

| Solvent | t | | | | |
|---|---|---|---|---|---|
| | 60 | 50 | 40 | 30 | 25 |
| Ideal | 85.9 | 72.5 | 60.6 | | |
| acetone | 79.2 | 65.6 | 54.5 | 44.6 | 40.0 |
| ethyl acetate | 77.6 | 61.6 | 48.2 | 38.3 | 34.1 |
| chloroform | 77.3 | 60.0 | 42.0 | 28.4 | 23.0 |
| benzene | 75.8 | 51.6 | 27.6 | 13.6 | 10.5 |
| ether | 74.0 | 50.1 | 30.6 | 21.5 | 18.7 |
| alcohol | 74.0 | 40.3 | 18.7 | 10.4 | 8.5 |
| $CCl_4$ | 73.9 | 21.1 | 4.6 | | |
| water | | | 0.31 | | 0.16 |
| $C_6H_5NO_2$ | 76.0 | 56.4 | 39.8 | 29.0 | 24.8 |
| $C_2Br_2$ | 76.0 | 56.4 | 39.8 | 29.0 | 24.8 |

[1] Some scattered data, mainly for 20°, may be found in Seidell: "Solubilities of Inorganic and Organic Compounds", 2nd Ed., p. 78-80.

[2] See Kohman: J. Phys. Chem., 29, 1048 (1925).

TABLE III (continued)

Solubility of the Nitroanilines in Various Solvents, as interpolated at a Series of Temperatures, expressed in Terms of Mol-percentage.

| Solvent | t 140 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 25 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Meta* (m.p. 111.8°) | | | | | | | | | | | | |
| Ideal | | | | 79.1 | 64.0 | 50.8 | 39.7 | 30.5 | 23.0 | | | |
| acetone | | | 96.8 | 78.9 | 64.1 | 52.4 | 43.7 | 36.9 | 31.2 | 26.3 | 21.7 | 19.5 |
| ethyl acetate | | | 96.1 | 76.0 | 59.2 | 46.0 | 35.6 | 28.2 | 23.4 | 20.0 | 17.3 | 16.1 |
| chloroform | | | 95.5 | 73.3 | 54.0 | 33.1 | 19.0 | 10.8 | 6.6 | 4.4 | 3.1 | 2.6 |
| benzene | | | 95.6 | 72.7 | 48.7 | 25.2 | 13.3 | 7.2 | 4.1 | 2.8 | 1.8 | 1.5 |
| alcohol | | | 94.9 | 73.0 | 49.5 | 25.8 | 14.1 | 8.5 | 5.6 | 4.1 | 2.9 | 2.4 |
| ether | | | 94.6 | 68.6 | 42.1 | 25.6 | 16.4 | 11.3 | 8.4 | 6.3 | 4.5 | 3.6 |
| $CCl_4$ | | | | 86.7 | 7.0 | | | | | | | |
| water | | | | | | | | | | 0.23 | | 0.12 |
| $C_6H_5NO_2$ | | | 96.1 | 76.0 | 59.2 | 46.0 | 35.6 | 27.0 | 21.3 | 16.7 | 13.0 | 11.3 |
| $C_2Br_2$ | | | 95.6 | 72.7 | 50.8 | 33.0 | 20.0 | 12.5 | 7.8 | | | |
| *Para* (m.p. 147.5°) | | | | | | | | | | | | |
| Ideal | 89.5 | 65.8 | 56.1 | 47.3 | 39.8 | 33.3 | 27.6 | 22.8 | 18.6 | | | |
| acetone | 88.8 | 63.0 | 53.2 | 45.1 | 38.6 | 33.5 | 29.7 | 26.5 | 23.8 | | | |
| ethyl acetate | 87.1 | 56.5 | 44.6 | 35.8 | 28.6 | 22.9 | 18.8 | 15.8 | 13.4 | 11.4 | | |
| chloroform | 86.5 | 51.0 | 29.8 | 16.1 | 8.8 | 5.3 | 3.6 | 2.5 | 1.8 | 1.3 | 1.0 | 0.8 |
| benzene | 84.8 | 40.9 | 16.8 | 8.4 | 4.3 | 2.6 | 1.7 | 1.2 | 0.8 | 0.6 | 0.4 | 0.3 |
| alcohol | 87.5 | 54.7 | 39.2 | 25.9 | 15.3 | 9.4 | 6.6 | 5.1 | 3.9 | 2.9 | 2.2 | 2.0 |
| ether | 85.6 | 32.4 | 12.7 | 7.9 | 5.7 | 4.7 | 3.8 | 3.4 | | | | |
| water | | | | | | | | | | 0.15 | | 0.074 |
| $C_6H_5NO_2$ | 87.1 | 59.0 | 48.6 | 39.2 | 31.2 | 24.6 | 19.3 | 14.9 | 11.7 | 9.3 | 7.5 | 6.7 |
| $C_2Br_2$ | 84.8 | 46.2 | 30.9 | 18.8 | 11.0 | 6.5 | | | | | | |

alcohol, whereas that of *para* in benzene is less than in alcohol, and the two solubility curves of the *meta* are practically coincident. It is thus evident that one can not set up an invariable sequence of liquids, arranged in order of solvent power over a group of crystalline substances, even for these three isomers which might well be supposed to resemble one another very closely in this regard.

This lack of definite sequence implies differences of behavior of the three isomers with respect to any particular solvent; and these differences were made evident in the course of our attempts to find a method of plotting such that the three curves for any one solvent could be superposed. In these attempts many pairs of variables were tried[1], but we were unable to discover any method, or any factor[2], which would enable us to derive the solubility of one isomer from that of another, except as a rough approximation. Nevertheless the curves so derived show comparatively little curvature and so such plots have some practical value; for if the curve for one isomer is known, the relation can be used to check, and to minimize the number of, the individual measurements of the solubility of the other two isomers.

The fact that these curves are apparently not superposable is evidence of a difference, from one isomer to another, in the mode of variation with temperature of the (differential) heat of solution in a given solvent[3]; and this can be shown directly by a plot of the relative slope of the log C vs. $1/T$ curve, for this slope is at any point proportional to the heat of solution. It may be possible to be more definite on this matter when work on other similar systems, now under way, is completed.

It appears however that, in any given solvent at a specified temperature, the isomer with the lowest melting temperature is most soluble, the highest melting the least soluble, when the equilibrium is between crystals and solution. On the other hand, Sidgwick and his collaborators have measured the solubility of similar groups of isomers as liquids in water and benzene, and find[4] that the vapor pressure and solubility relations in the liquid state are "in the majority of benzene derivatives very little influenced by the orientation of the substituents", but that "the solubility of the solids is largely determined by the crystalline forces, which themselves are greatly affected by the orientation". It appears therefore that the differences in solubility of the solid isomers are to be ascribed to the same factors which cause differences in their melting temperatures and heats of melting.

With respect to the question of the separation of the isomers from one another by a process of recrystallization, the general similarity of the groups

[1] For instance, by plotting, for equal values of mol fraction in solution, $t_o$ against $t_m$ or $t_p$, or similarly $\Delta t_o$ against $\Delta t_m$ or $\Delta t_p$; or the corresponding values for each isomer, at a series of values of C, of the expression $\Delta H_A(1/T - 1/T_A)$, where $\Delta H_A$ is the heat of melting at the melting temperature $T_A$, a method which brings the ideal curves into substantial coincidence.

[2] Such as that proposed by Mortimer: J. Am. Chem. Soc., 45, 633 (1923).

[3] This has been used by Sidgwick and his collaborators as a criterion of the nearness of the temperature at which the solution will separate into two liquid layers.

[4] Sidgwick and Callow: J. Chem. Soc. **125**, 529 (1924); q.v.

of curves makes evident that the several solvents—with one exception, carbon tetrachloride—would be about equally effective. In any specific case, the solubility data readily enable one to make an estimate of the number of recrystallizations required to ensure purity, on the basis that the solubility of one isomer is not appreciably affected by the presence of another—an assumption which in such cases is in all probability not far from the truth. For instance, if we start with 100 mols benzene saturated at 60° with all three, we would have in solution 313.2 mols *ortho*, 7.8 mols *meta* and 1.2 mols *para*, corresponding to an initial mixture containing 97.2% *ortho*, 2.4% *meta*, 0.4% *para*; from the solution cooled to 25°, there would separate 301.5 mols *ortho*, 6.3 mols *meta* and 0.9 mols *para*, and the composition of the crystals would be about 97.7% *ortho*, 2.0% *meta* and 0.3% *para*. From this it is evident that this process (the amount of benzene used in each case being just sufficient to dissolve all of the ortho at 60°) would have to be repeated at least four or five times to insure pure crystals of *ortho*, the theoretical yield of which would be about three-fourths of the present initially. Moreover the number of recrystallizations required would change little with variation of the temperature limits, and within the group of solvents studied, carbon tetrachloride excepted; this material difference is brought out by Table IV.

TABLE IV

Solubility of the Nitroanilines in Benzene and in Carbon Tetrachloride expressed as mols per 100 mols solvent.

| | Benzene | | | $CCl_4$ | |
|---|---|---|---|---|---|
| Temp. | *o* | *m* | *p* | *o* | *m* |
| 25 | 11.7 | 1.5 | 0.3 | 2.0* | 1.0* |
| 40 | 44.2 | 2.9 | 0.6 | 4.8 | 1.4* |
| 50 | 106.6 | 4.3 | 0.8 | 26.7 | 1.7* |
| 60 | 313.2 | 7.8 | 1.2 | 283.1 | 2.0* |

*Extrapolated and so less certain.

If 100 mols carbon tetrachloride are saturated with both *ortho* and *meta* at 60°, the resulting solution will contain 283.1 mols *ortho* and 2.0 mols *meta*; when this solution is cooled to 25°, 281.1 mols *ortho* and 1.0 mol *meta* will separate. Hence it is obvious that a second similar crystallization process would yield pure *ortho*, and in quantity almost equal to that originally present. There does not appear to be any way of predicting the fact that carbon tetrachloride is so much more effective than the other solvents in purifying *o*-nitroaniline from its isomers by recrystallization; but we may, with some assurance, infer that it would be similarly effective in some other similar cases, and recommend that carbon tetrachloride—which moreover is non-inflammable and cheap—be tried out for this purpose in place of some of the solvents more commonly used.

It appears therefore that in general a number of recrystallizations would be necessary for the separation of, say, the *ortho* isomer from the other two,

there being in this type of case no likelihood of appreciable solid solution. In many cases however there may be some admixture of a second *ortho* compound, and the two would form mix-crystals; under such circumstances the number of recrystallization processes necessary would clearly be much larger.

## Summary

Solubility data, determined by a synthetic method, for the three isomeric nitroanilines in acetone, ethyl acetate, chloroform, benzene, alcohol, ether, carbon tetrachloride over a range of temperatures extending up to the respective melting temperatures, are presented and discussed. The respective solubilities in water and 95% alcohol at 25° and 40° have also been measured, Though the solubility curves are in general very similar, yet there are significant differences as between the three isomers.

# REVERSIBLE PERMEABILITY OF MEMBRANES AND ITS RELATION TO CELL METABOLISM

BY CHARLES GURCHOT

## Introductory

It is well-known that a living cell removed from its parent organism can be kept alive in the proper liquid medium. If, instead of a single cell, a community of cells or a piece of tissue is kept in a nutritive liquid, the tissue not only will be preserved but it will grow and proliferate. In other words, in its own small way, it behaves more or less as a complete organism as long as the medium remains constant and as long as the tissue remains the same as it was at the start. But the isolated cell behaves differently. Its isolation is tantamount to a physiological divorce in addition to an anatomical one for the cell appears to be permanently at rest and in this condition it is impermeable for almost everything which it ordinarily uses for food and to the products of its metabolism which are formed in the interior of the cell[1] "from the undissolved carbohydrate reserves, and also for inorganic salts and salts of organic acids". Naturally the cell cannot behave in this way when still a part of the original organism. Another significant phenomenon takes place after death. Then the cell behaves as an ordinary membrane which retains colloids only.

It seems fairly well established, now, that the cell is surrounded by a pellicle which functions as a semi-permeable membrane. Deductions from the second law of thermodynamics embodied in Willard Gibbs' principle show that all substances present in the cell and which lower its surface tension must concentrate at the periphery, that is at the interface between the cell contents and the surrounding medium[2]. It has been shown that the concentration of some bile salts may exceed the solubility[3]. Such substances will be deposited then as solid films enclosing the cell. One is forced to ask whether something does not take place in the mass of tissue which alters the permeability of the cell through something which is either stored or produced in cells en masse. Unfortunately it is impossible at the present time to exact an equivocal answer to this question from the cell directly, for the simple reason that the composition of cell membranes is not known. Yet previous considerations suggest that we ought to find in the membrane substances which lower the surface tension of water considerably. Such are the fatty compounds. Nor is it known what makes the membrane semi-permeable, let alone how the permeability is altered.

It is necessary to work backward, so to speak, and to proceed by analogy. It seems advisable therefore to consider the whole question of semi-permeable membranes and perhaps of membranes in general. Experiments must be

---

[1] Beehhold: "Colloids in Biology and Medicine", 244 (1919).
[2] Bayliss: "Principles of General Physiology" (1918).
[3] Ramsden: Proc. Roy. Soc., 72, 156 (1904).

made first on easily reproducible membranes of definite composition and for which the technique has been worked out already. Copper ferrocyanide offers a membrane of definite composition which in many ways behaves not unlike living semi-permeable membranes. Copper ferrocyanide has been the subject of painstaking investigations of which those of Walden[1] are among the most important. Walden investigated the action of many inorganic and organic salts and acids on several membranes without, however, observing to see whether any of the substances which passed through had a permanent effect. It is true that his method of procedure made such observation impossible. Walden always had the reagents with which he formed his membranes on each side of them. In this way the membranes were constantly regenerated and the observation of permanent injury was out of the question. This same mode of manipulation enabled Collander,[2] recently, to reach unwarranted conclusions regarding the behavior of living membranes.

We are confident that, in order to pursue its metabolic functions, the cell must, in some way, change its permeability; and, in fact, we know that it does. The larval cells of Arenicola when in a state of contraction lose the pigment ordinarily present in the cells[3]. Pilocarpine makes certain cells more permeable, atropine makes them less permeable, to certain dyes[4]. The egg cell on fertilization and the muscle cell on contraction increase their electrical conductivity[5]. More than this we have evidence that permeability changes are reversible. One example will suffice. The seaweed Laminaria increases its electrical conductivity when immersed in a ca. 2.5% solution of pure sodium chloride. On adding a little calcium chloride to the solution Laminaria returns to normal conductivity without showing signs of permanent damage[6]. Clowes[7] offers an explanation which, although insufficient, is nevertheless an advance over previous ones. He compares the cell membrane to an oil-water emulsion in which soaps concentrate at the interface between oil and water and lower the surface tension of one or the other liquid depending on whether or not there is present an oil or a water-soluble soap. Clowes goes on to summarize Bancroft's explanation for emulsions as follows:—"soaps of monovalent cations being readily dispersed in water but not in oil form a film or diaphragm which is wetted more readily by water than by oil, consequently the surface tension is lower on the water than on the oil side. Since the area of the inside surface of a film surrounding a sphere is smaller than that of the outside surface, the film tends to curve so that it encloses globules of oil in water, in this manner reducing the area of the side of greater surface tension to a minimum as compared with that of lower surface tension. On the other hand a film composed of soaps of divalent or trivalent cations being freely dis-

[1] Z. physik. Chem. 10, 699 (1892).
[2] Kolloidchem. Beihefte, 20, 273 (1925).
[3] Lillie: Am. J. Physiol. 37, 764 (1913).
[4] Garmus: Z. Biol. 58, 185 (1912).
[5] McClendon: Am. J. Physiol., 27, 240 (1910); 29, 302 (1912).
[6] Science, (2) 34, 187 (1911).
[7] J. Phys. Chem., 20, 407 (1916).

persed in oil but not in water is wetted more readily by the oil than by the water, the surface tension is lower on the oil than on the water side, and the film tends to curve in such a manner as to enclose the globules of water in an outer or continuous oil phase". The process[1] "is dependent on the presence of a film of soap between the phases and it is interesting to note the powerful effect of sodium oleate in destroying red blood corpuscles". On the addition of calcium chloride the resulting water in oil emulsion "would be impermeable to water but permeable to substances soluble in oil. A change of the latter kind if complete would not give us the properties which the normal cell-membrane possesses". It would be permeable to water and its solutes only on reversal to the oil in water emulsion. Such a membrane would be entirely too labile to enable the cell to manifest the osmotic pressure which it has actually. It is perhaps better to conceive of the cell membrane as a more or less rigid colloidal suspension, irreversible as we understand an emulsion to be reversible, but, as we shall see later, possessing a reversibility of its own. We shall see also that the degree of permeability can be altered in such a membrane.

Another interesting feature of the work of Clowes is the analogy which is drawn between the elongated drop stage, in the course of the reversal of the emulsion, when the dispersing liquid flows as through narrow channels, and the porous sieve-like character of the copper ferrocyanide membrane as conceived by Traube[2]. A great deal has been done to prove that water flows through a copper ferrocyanide membrane as it would through a series of capillary tubes.[3] Poiseuille's equation[4] has been called upon to prove this:

$$Q = \frac{KD^4PT}{L}$$

where Q is the amount of liquid, K a constant for a definite temperature, D the diameter of the pores, P the pressure applied, and L the length of the capillaries. From this equation values have been calculated for the diameter of the pores. It is unfortunate that Poiseuille's equation should have been misused in this way. The equation expresses exactly the results of motion of a viscous fluid through pipes of circular cross-section. It is assumed that the velocity is everywhere perpendicular to the cross-section of the pipe and it has been pointed out by Lamb that if any appreciable amount of slipping at the boundary of the pipes, used by Poiseuille, took place a deviation from the law of the fourth power of the diameter would become apparent. It becomes perfectly clear, therefore, that the difference in pressure between the inlet and the outlet of the pipe or tube is not an accurate measure of the pressure gradient because some of this pressure difference is required to give kinetic energy of motion to the water in the eddy currents which will be formed whenever the diameter of the pipe or tube is not uniform throughout. It is more than probable that this state of affairs obtains in the case of semi-permeable membranes.

[1] Bayliss: "Third Report on Colloid Chemistry", 4 (1921).
[2] Archiv für Anatomie, **1867**, 67.
[3] Bartell: J. Phys. Chem. **15**, 659 (1911); **16**, 318 (1912).
[4] Poiseuille: Compt. rend. **11**, (1840); **12**, (1841).

In other words if the equation for Bartell's membranes contained the term D raised to some other power than the fourth his results would have been the same. But as semi-permeable membranes generally operate at approximately atmospheric pressure and especially in the presence of electrolytes it might have been better to employ Fick's diffusion equation:

$\frac{dS}{dt} = k\,q\frac{dC}{dX}$ where dS/dt is the rate of flow, $k$ the temperature coefficient, $q$ the cross-section of the pores, dC/dX the rate of change in concentration of the diffusing solution. But after all has been said there is no reason to suppose that a semi-permeable membrane does not behave as if it were porous. After all, inter-molecular spaces are only a special type of pores. But we know that other factors, such as selective adsorption, affect the permeability of a membrane. It follows from this that both Poiseuille's and Fick's equations are useless to express the true diameter of pores even if it is granted that we have to deal with uniform capillaries. This we know is not true. Consequently all we can say is that copper ferrocyanide is porous. We know that this is vague to say the least. We also know that the statement does not mean anything for, strictly speaking, the water membrane between chloroform and ether is porous also. Attempts have been made to prove the copper ferrocyanide membrane to be an atomic sieve from the fact that progressively larger molecules diffused with increasing difficulty. Such a simple view is entirely inadequate at the present time. There is evidence to show that a copper ferrocyanide membrane does not work as a static system but rather as a dynamic one.

When Czapek[1] exposed cells of Echeveria to the action of various alcohols he noticed that an exosmosis took place of the tannin present in the cells. For methyl alcohol the critical concentration at 15-19°C. was about 15% by volume, for ethyl 10-11%, propyl 4-5%, butyl 1-2%, amyl 0.5%. Because the above solutions possessed a surface tension of about 68% that for pure water Czapek concluded that the surface tension lowering was responsible for the exosmosis, 68% of the value for water being the critical tension. This was as far as Czapek ventured. Had he known that tannin exists in colloidal solution he might have guessed that the exosmosis was due to coagulation of the cell membrane. Czapek found also that his plant cells gave the exosmose reaction with various organic and inorganic acids for concentrations exceeding N/6400. This was undoubtedly another case of coagulation owing to the adsorption of hydrogen ions by the cell membrane.

In 1906 Barlow[2], in the course of a series of osmotic pressure measurements through copper ferrocyanide, observed that the addition of alcohol to the outside solution caused a lowering of the osmotic pressure. Fearing that with alcohol in great excess the sign of the osmotic current might change, Barlow looked upon this phenomenon as an unfortunate incident—the alcohol having spoiled his membrane.

[1] Ber. deutsch. botan. Gaz. 28, 159 (1910).
[2] Phil. Mag. (6) 10, 1; 11, 595 (1906).

The whole question of membrane action seems to involve selective adsorption and coagulation; and the natural corollary is that the coagulation is reversible. There is no question that an investigation in this direction will throw some light at least on the behavior of cell membranes. In fact it seems very probable that our views on membrane action in general must undergo considerable revision.

The experiments described in the following pages will show that a copper ferrocyanide membrane behaves as a colloidal film analogous to a colloidal sol. It can be coagulated and it can also be peptized. On the other hand the peculiar spatial relations of a film in contrast to a sol make the consequences arising from the analogous behavior of the former very significant when we consider the reactions of living membranes. Such a film possesses, for example, a certain amount of rigidity and inertia which, to be sure, are essential if in the cell the film is to play the part of metabolic censor, so to speak. But as we shall see later, such properties make it very difficult to prove the analogy by experiment. If a continuous film—it is better to say a film with very fine interstices—can be converted at will into a sieve whose meshes can be closed when necessary we have here an answer to the question why a substance which ordinarily does not pass through a membrane will do so, nevertheless, at certain times. The antagonistic action of a peptizing agent toward a coagulating agent will enable us to explain the sodium-calcium antagonism in living cells. Of course it must not be expected that sodium and calcium will be antagonistic for copper ferrocyanide. There is every reason why they should not be. The antagonism will be of a different kind. After all, whatever may be the composition of cell membranes we are quite certain it is not copper ferrocyanide.

## Experimental

Copper ferrocyanide membranes were made by a modification of Collander's method. Glass tubes were used, 3cm. in diameter and 10cm. long. One end of each tube was ground and covered with a layer of cheese cloth to serve as a support for the membrane. This end was dipped into a warm ten per cent solution of gelatine freed from air bubbles by filtering through sand. The gelatine solution should not be heated higher than 40°C. Instead of a ten per cent a fifteen percent solution of gelatine may be used. It will give a firmer support and will be very much less liable to damage; but at the same time the membrane will take longer to be deposited in the denser gelatine layer where diffusion must take place more slowly. The gelatine was allowed to set to a stiff jelly on the cheese cloth, the tube being held downward after the excess of gelatine had been removed. It was found convenient to hasten the jellying by blowing compressed air on the tube for about a half minute. It is immaterial if a few air bubbles persist in the gelatine film at this stage. When the gelatine film was a firm jelly, 2cc of the same gelatine solution, freed from air bubbles, were introduced inside the tube on top of the first gelatine layer. It is important that there are no bubbles in this layer. The reason is, of course, that a bubble in the plane of the deposited membrane will destroy its continu-

ity. This upper layer was allowed to set to a stiff jelly also and it was hardened for twenty-four hours in a two percent solution of formaldehyde. The gelatine tubes were washed free of formaldehyde in several changes of distilled water, the tubes being allowed to remain about two hours in each change of water. They were suspended in tumblers or in beakers by means of two copper strips, about one centimeter wide, pinched at each end with paper clips. A small piece of Gooch rubber tubing at the top of each tube prevented the latter from slipping through the copper strips whose fastened ends rested on the edge of the tumbler or the beaker. A fresh solution containing 0.02 mols potassium ferrocranide was placed outside and a solution containing 0.02 mols copper sulphate was put inside the tube. In about a half hour copper ferrocyanide began to form near the inner gelatine surface as a uniform brown membrane. The reaction was allowed to go on for twenty-four hours if a ten percent gelatine solution was used. The reaction required forty-eight hours in case a fifteen percent gelatine solution was employed. After each membrane had been washed free of the reagents it was tested by putting a one percent solution of cane sugar inside the tube and distilled water outside. If there was no test for sugar in the outside water after sixteen hours, the membrane was considered satisfactory. The above procedure was carried out at room temperature, that is to say about 20°C. As a result never more than about two-thirds of the membranes made were found satisfactory. But as we shall see later certain considerations necessitated a change in method, and when the membranes were formed and kept at 8°C. the yield was one hundred percent and they lasted much longer. It is sometimes advised that thymol be added to the gelatine solution to prevent the membrane from being destroyed in the first process by bacteria which liquefy gelatine. This added inconvenience is unnecessary provided cleanliness is observed. There are bacteria which attack the copper ferrocyanide film and create holes in it. But by working at 8°C. this contingency is prevented also.

### Coagulation with Propyl Alcohol

The first thing to be investigated was the permanent action of alcohols on the copper ferrocyanide film. For this, twelve series of two tubes were used. In every test it must be assumed that three membranes were used unless it is stated otherwise. Propyl alcohol of varied strengths was put in each tube. Distilled water was put outside. At the end of sixteen hours, after the membranes had been washed thoroughly, a one percent solution of sugar was introduced inside each tube. The water outside was tested for the presence of sugar sixteen hours later. The semi-quantitative results are given in Table I.

It is interesting to note that greater strengths of alcohol were not followed with a more abundant Fehling precipitate. This is just what should be expected if the copper ferrocyanide film is conceived to be a close aggregation of colloidal particles each surrounded with a film of adsorbed water. On addition of alcohol the individual particles—or the small groups—unite to form larger aggregates. This is followed by an increase in porosity sufficient to let

TABLE I

| Membranes | Propyl alcohol % by volume | Precipitate with Fehling's solution |
|---|---|---|
| 1 | 1 | Faint trace |
| 2 | 1.5 | Large trace |
| 3 | 2.0 | Moderate |
| 4 | 2.5 | Moderate |
| 5 | 3.0 | Large trace |
| 6 | 3.5 | Large trace |
| 7 | 4.0 | Moderate |
| 8 | 4.5 | Moderate |
| 9 | 5.0 | Trace |
| 10 | 5.5 | Trace |
| 11 | 6.0 | Trace |

sugar through. But it must be much more difficult for these aggregates to unite and form still larger ones. To accomplish this it may be necessary to use much higher concentrations of alcohol. It is even possible that the resistance of the gelatine will prevent further coagulation even then.

If the coagulation of the membrane is an effect of the decrease in surface tension brought about by adding alcohol to water it is conceivable that coagulation might be reversed by bringing the membrane in contact with a liquid of higher surface tension, namely pure water. Accordingly the alcohol-treated membranes were exposed to water about forty-eight hours. At the end of that time no reversibility had taken place. The membranes were still permeable to sugar. A second treatment with water gave no better results. This, of course, does not prove that surface tension is not a factor in the coagulation of copper ferrocyanide.

### Coagulation with Methyl Alcohol

The experiments were repeated, this time methyl alcohol was used because it is available for smaller changes of surface tension than propyl alcohol. The alcohol and the sugar were put inside the tube at the same time. The results are given in Table II.

TABLE II

Alcohol inside tube; sugar solution 1%—exposure 16 hours; room temperature 20°C.

| Membrane | % Methyl alcohol | Fehling's precipitate |
|---|---|---|
| 1 | 0.1 | None |
| 2 | 0.2 | None |
| 3 | 0.3 | None |
| 4 | 0.4 | None |
| 5 | 0.6 | None |
| 6 | 0.8 | None |
| 7 | 1.0 | None |
| 8 | 1.5 | Faint trace |

The minimal concentration for methyl alcohol seems to be about 1.5%

The experiments were repeated with methyl alcohol outside the tube and the 1% sugar solution inside the tube. The results are given in Table III.

TABLE III

Alcohol outside tube; sugar solution 1% inside tube; exposure 16 hours; room temperature 20°C.

| Membrane | % Methyl alcohol | Fehling's precipitate |
|---|---|---|
| 1 | 0.1 | None |
| 2 | 0.5 | None |
| 3 | 1.0 | None |
| 4 | 1.5 | None |
| 5 | 2.0 | Trace |

The noteworthy difference is that more alcohol was necessary to coagulate the membrane here than when both sugar and alcohol were on the same side. This is not surprising. Since sugar is insoluble in pure alcohol the addition of the former to an aqueous alcoholic solution must raise the partial pressure of the alcohol. In other words when sugar and alcohol are on the same side of the tube alcohol behaves as if it were more concentrated.

Both series of membranes were also given the water treatments of forty-eight hours each, but no recovery took place. If, as was suggested, coagulation is a surface tension effect—which is doubtful as we shall see later—reversibility must nevertheless be difficult to obtain inside the gelatine support. Here something must be said about the question of minimal concentration. It is not devoid of ambiguity because just as soon as a membrane becomes ever so slightly permeable to sugar the permeability will not be apparent until the membrane has been exposed to sugar for a sufficient length of time. In addition to this a very long exposure to very dilute alcohol will show the same results as a correspondingly short exposure to more concentrated alcohol. The time must therefore be fixed arbitrarily, and the minimal concentration must be allowed to remain a function of the time, the temperature remaining constant. It is practically impossible, consequently, to know just exactly when a membrane becomes permeable to sugar. And in addition to this it is not at all surprising that reversibility, if it can be obtained at all, by increasing surface tension, is difficult to accomplish.

### Coagulation and Reversibility of Copper Ferrocyanide Sol

A corollary from the above experiments is that methyl alcohol must coagulate a copper ferrocyanide sol. But the precipitation of the sol proved to be much less sensitive than the test for the permeability of the membrane. In the case of the former the coagulated particles must gather in groups large enough to be seen with the naked eye. Under a microscope the precipitation would undoubtedly be more sensitive. The experiments were carried out in groups of three test tubes. The colloidal solution of copper ferrocyanide was made from very dilute reagents. One gram of potassium ferro-

cyanide and one gram of copper sulphate, each dissolved in 3000 cc of distilled water, were allowed to react. A very stable brown colloidal solution was obtained which showed no sign of having precipitated after standing for two weeks. The results are given in Table IV.

TABLE IV

| Group | Volume | % Methyl alcohol | Time | Degree of precipitation |
|---|---|---|---|---|
| 1 | 15cc | 0.10 | 2 days | — |
| 2 | 15cc | 0.22 | 2 days | — |
| 3 | 15cc | 0.30 | 2 days | — |
| 4 | 15cc | 0.40 | 2 days | — |
| 5 | 15cc | 0.45 | 2 days | — |
| 6 | 15cc | 0.50 | 2 days | — |
| 7 | 15cc | 0.55 | 2 days | — |
| 8 | 15cc | 0.60 | 2 days | — |
| 9 | 15cc | 0.65 | 2 days | — |
| 10 | 15cc | 0.70 | 2 days | — |
| 11 | 15cc | 0.75 | 2 days | — |
| 12 | 15cc | 0.80 | 2 days | — |
| 13 | 15cc | 0.85 | 2 days | — |
| 14 | 15cc | 0.90 | 2 days | — |
| 15 | 15cc | 0.95 | 2 days | — |
| 16 | 15cc | 1.00 | 2 days | — |
| 17 | 15cc | 1.05 | 2 days | — |
| 18 | 15cc | 1.10 | 2 days | — |
| 19 | 15cc | 1.18 | 2 days | — |
| 20 | 15cc | 1.28 | 2 days | — |
| 21 | 15cc | 1.32 | 2 days | — |
| 22 | 15cc | 1.36 | 2 days | — |
| 23 | 15cc | 1.41 | 2 days | — |
| 24 | 15cc | 1.46 | 2 days | — |
| 25 | 15cc | 1.50 | 2 days | — |
| 26 | 15cc | 1.55 | 2 days | — |
| 27 | 15cc | 1.59 | 2 days | — |
| 28 | 15cc | 1.64 | 2 days | — |
| 29 | 15cc | 1.68 | 2 days | — |
| 30 | 15cc | 1.73 | 2 days | — |
| 31 | 15cc | 1.77 | 2 days | — |
| 32 | 15cc | 1.82 | 2 days | — |
| 33 | 15cc | 1.86 | 2 days | — |
| 34 | 15cc | 1.91 | 2 days | — |
| 35 | 15cc | 1.96 | 2 days | — |
| 36 | 15cc | 1.96 | 2 days | — |
| 37 | 15cc | 2.44 | 2 days | — |
| 38 | 15cc | 2.91 | 2 days | — |

TABLE IV (continued)

| Group | Volume | % Methyl alcohol | Time | Degree of precipitation |
|---|---|---|---|---|
| 39 | 15cc | 3.40 | 2 days | — |
| 40 | 15cc | 3.85 | 2 days | — |
| 41 | 15cc | 4.30 | 2 days | — |
| 42 | 15cc | 4.75 | 2 days | ? |
| 43 | 15cc | 5.20 | 2 days | — |
| 44 | 15cc | 5.65 | 2 days | — |
| 45 | 15cc | 6.10 | 2 days | — |
| 46 | 15cc | 6.50 | 2 days | — |
| 47 | 15cc | 7.00 | 2 days | — |
| 48 | 15cc | 7.40 | 2 days | — |
| 49 | 15cc | 7.80 | 2 days | — |
| 50 | 15cc | 8.25 | 2 days | — |
| 51 | 15cc | 10.00 | 2 days | — |
| 52 | 15cc | 15.00 | 2 days | — |
| 53 | 15cc | 20.00 | 2 dyas | — |
| 54 | 51cc | 25.00 | 2 days | — |
| 55 | 15cc | 30.00 | 2 days | — |
| 56 | 15cc | 35.00 | 2 days | — |
| 57 | 15cc | 40.00 | 2 days | + |
| 58 | 15cc | 45.00 | 2 days | ++ |
| 59 | 15cc | 48.00 | 2 days | +++ |
| 60 | 15cc | 50.00 | 2 days | ++++ |

From the three tubes containing forty percent alcohol 14.5cc of the colorless supernatant liquid were pipetted off and substituted with the same amount of distilled water. The flocculated copper ferrocyanide was peptized immediately and had not visibly precipitated again after standing one week. This is clearly a case of reversibility without the encumbrance of a membrane. Here it may be argued that reversibility resulted from the increase in surface tension when water was substituted for aqueous alcohol. To say this is to argue *post hoc ergo propter hoc*. All we know from observation is that reversal was preceded by a surface tension increase. This is very different from saying that reversal was caused by the increase of surface tension.

It was pointed out above that the coagulation of copper ferrocyanide sol with about 40% alcohol is not a sensitive test. Yet a method was available whereby the sol could be made just as sensitive, if not more so, as its corresponding membrane to the action of dilute alcohol. But to make the phenomenon more general two other negative sols were used instead, namely sulphur and arsenious sulphide. Both sols were prepared by a method of condensation the details of which can be found in almost any book of laboratory methods in colloid chemistry.

The experimental procedure was to add just enough of some flocculating agent not to precipitate the sol and then to determine the quantity of alcohol—

ethyl alcohol was used—necessary to flocculate it. The experiments were carried out in test tubes disposed in series of four with several tubes kept as controls, Tables V-VI.

TABLE V

Arsenious Sulphide flocculated with M/8 Sodium Chloride
Volume of sol 5cc. Time 24 hours.

| M/8 NaCl | Reaction |
|---|---|
| 1cc | None |
| 1.5cc | None |
| 2.0cc | Marked turbidity |
| 2.5cc | Marked turbidity |
| 3.0cc | Marked turbidity |
| 3.5cc | Granular precipitate |

Three tubes to which 1.5cc M/8 NaCl had been added were treated with 0.03cc ethyl alcohol (about 0.5%). The fourth was kept as control. After 24 hours the three tubes treated were turbid. The fourth remained clear.

TABLE VI

Sulphur flocculated with N/400 Calcium Chloride
Volume of sol 5cc. Time 24 hours.

| N/400 $CaCl_2$ | Reaction |
|---|---|
| 0.1cc | None |
| 0.3cc | None |
| 0.5cc | None |
| 0.7cc | Slight turbidity |
| 0.9cc | Marked turbidity |

Three tubes to which 0.5cc N/400 calcium chloride had been added were treated with 0.02cc ethyl alcohol. The fourth tube was kept as control. After standing for 24 hours the three tubes were turbid while the fourth remained clear.

The results of these two series of experiments show that under the proper conditions sols can be precipitated by very dilute alcohols. Arsenious sulphide required about 0.5% and sulphur about 0.4% ethyl alcohol.

Some qualitative experiments were performed with glucose, sugar and ½% glycerin. A dilute sulphur sol was flocculated after 24 hours by glucose and sugar syrups and also by the glycerin solution.

### Coagulation with Acetic Acid

In order to confirm Walden's results with organic acids experiments were made also with copper ferrocyanide membranes and solutions of acetic acid. Sugar and acetic acid were placed inside the tubes and a solution of blue litmus was placed outside. The litmus turned red after two hours and the outside solution was tested for sugar. The results appear in Table VII.

TABLE VII

| % Acetic Acid | Fehling Precipitate |
|---|---|
| 0.2 | None |
| 0.5 | Faint trace |
| 1.0 | Trace |
| 1.5 | Moderate |

The critical concentration seems to be around 0.5% acid. Here again an attempt was made to effect a reversal by treating the membrane with water. No reversal was obtained. Then, since sodium hydroxide should peptize a negative sol, it was tried as a reversing agent. But here the membranes reversed entirely too much. A fifth-normal solution of NaOH entirely peptized the copper ferrocyanide membranes in six hours. The same result was accomplished when a N/50 NaOH solution was used. Then the membranes were exposed to a N/5 NaOH solution for twenty minutes. They turned purplish brown. They were then washed and put aside. Two hours later the gelatine support was detached from the glass and the membranes floated free. Some were then exposed to a N/500 NaOH for thirty-six hours. They showed no visible alteration but they remained permeable to sugar. In other words no recovery from coagulation took place.

### Further Attempts at Reversal

Several membranes which had been coagulated previously with methyl alcohol were treated for twenty-four hours with a saturated solution of sodium chloride. The solution was placed on both sides of the membranes so as to preclude dilution by osmosis if pure water was put on one side. Some of the membranes showed partial recovery. In other words the Fehling precipitate was much less abundant than before the salt treatment. But on standing for twelve hours they were again tested for sugar permeability. This time the cuprous oxide precipitate was as abundant as it had been before the salt treatment. If there was no large experimental error, the observation is an interesting one perhaps; but as far as indicating that reversibility took place it probably means nothing at all. At this stage it seemed almost a hopeless venture to attempt to reverse coagulated membranes although the thing must be, without a doubt, theoretically possible. On the other hand, looking at it from a different point of view, reversibility might not be so essential. In plant and animal cells the membrane-forming materials might be supplied continually. Recent work has thrown much doubt on this idea. Still if living membranes could reverse their increased permeability and if they availed themselves of the membrane-forming materials only in case of emergency if, at all, the procedure would be far more desirable in the economy of life. It seemed rather a pity that the latter situation should not prevail. It probably does in fact, as we shall see later.

### Effect of the Presence of Membrane-forming Reagents

Accordingly, some experiments were tried with copper sulphate on one side and potassium ferrocyanide on the other side of the membrane and of the

same concentration as the reagents used in making the membranes. Controls, without any of the reagents on either side, were used in every case. Although the contents on the inside of the tubes varied, the outside solution did not vary from one experiment to another. In every case potassium ferrocyanide and distilled water only were present outside the membranes. The presence of potassium ferrocyanide interfered, of course, with the detection of sugar. The hydrochloric acid which was added to hydrolyze the sucrose reacted with potassium ferrocyanide to form ferrocyanic acid. This came down as a white precipitate and in addition to using up the HCl obscured any other precipitate which might form. As a result the procedure summarized below was adopted. It was found to work perfectly well on known samples:

1. Precipitated $K_4Fe(CN)_6$ with slightly more than half its volume 0.04 molar copper sulphate.
2. Disregarded brown precipitate, added 2 drops conc. HCl and boiled.
3. Added 2cc of a saturated solution of $NaHCO_3$, boiled off $CO_2$ excess.
4. Allowed copper ferrocyanide precipitate to settle.
5. Pipetted clear supernatant liquid.
6. Boiled with Fehling's solution in the usual way.

The results of the experiments are given in Table VIII.

TABLE VIII

| Outside $K_4Fe(CN)_6$ | $CuSO_4$ | $CuCl_2$ | Inside $CH_3OH$ | NaCl | $CaCl_2$ | Sugar | Time Reaction | |
|---|---|---|---|---|---|---|---|---|
| 0.02M | 0.02M | | 3% | | | 1% | 48 hrs | — |
| 0.02M | 0.02M | | 5% | | | 2% | 72 hrs | — |
| 0.02M | 0.02M | | 10% | | | 2% | 24 hrs | — |
| 0.02M | 0.02M | | | 5% | | 1% | 48 hrs | — |
| 0.02M | 0.02M | | | 25% | | 2% | 24 hrs | — |
| 0.02M | | 0.02M | | 5% | .25% | 1% | 48 hrs | — |
| 0.02M | | 0.02M | | 25% | 1.25% | 2% | 48 hrs | — |
| 0.02M | | 0.02M | | | 5% | 1% | 48 hrs | — |
| 0.02M | | 0.02M | | | 12.5% | 2% | 48 hrs | — |
| 0.02M | | 0.02M | 2% | | 1% | 1% | 48 hrs | — |
| 0.02M | | 0.02M | 5% | | 5% | 2% | 48 hrs | — |
| | | | | 5% | | 2% | 10 hrs | + |

Only the last experiment, where no membrane-forming reagents were used, showed the membrane to have coagulated. All other tests showed negative results, even though in the case of sodium chloride the salt was found outside the membrane. Not so with calcium chloride. Cupric chloride was used instead of copper sulphate to prevent the formation of calcium sulphate.

## Critical Concentrations of Alcohols and Reversal of Coagulation

The next part of this investigation was carried out during cold weather when the temperature of the heated laboratory rose to 26°C. Indeed it reached 27°C. more than once. This circumstance was very unfortunate in one way, but it proved very fortunate in another way. First of all, the copper ferrocyanide membranes did not work properly. The yield was very small. Sometimes every new membrane was permeable to sugar before having been used at all. It was thought that the gelatine softened and impaired the membrane support. Various schemes were tried to find some twenty-seven degree-proof support for the membrane but none was found satisfactory. Among other things agar-agar was tried. Owing to the fact that agar is soluble in water only at about 85°C. it needs no tanning treatment and would make an ideal support if it were not that it shrinks on cooling and loosens itself from the glass tubes. This loosening did not take place however until the copper ferrocyanide membrane was deposited. This loosened membrane was, of course, useless for diffusion experiments, but its structure could be examined in detail. It was found that the membrane had formed about 1.5mm below the inside surface, and that the agar above the membrane was colored brown for a distance of about 1mm. This was clearly a case of peptization of copper ferrocyanide in agar and as far as the membrane itself was concerned it appeared intact. The peptizing agent could be only copper sulphate. On the potassium ferrocyanide side the membrane was not peptized visibly. There is nothing strange in this for the silver halides are peptized by silver nitrate and the corresponding potassium halide. Here was a suggestion for one more attempt at reversibility. But in the mean time stable membranes had to be made. This was finally done by using a 15% gelatine solution to begin with, forming the membranes, and keeping them at all times, in low temperature thermostats. Several were made, tap water being used as the cooling medium. All winter the temperature in the thermostats varied between 6 and 8 degrees centigrade. Once or twice it rose to ten degrees but never higher. Another possibility not to be overlooked was that copper ferrocyanide membranes might be coagulated by pure water at comparatively low temperatures. But before heat coagulation was investigated in addition to a possible reversal with copper sulphate it was necessary to determine the critical concentration for several of the alcohols used by Czapek and see what relation they bore to the critical concentrations which he obtained as a result of his experiments on exosmosis. The four alcohols chosen were methyl, ethyl, propyl and amyl. In addition to this, since it was found that sodium chloride coagulated copper ferrocyanide its critical concentration should also be determined and compared with that of potassium chloride and calcium chloride; three salts which play a very important part in the metabolism of living cells,Table IX.

TABLE IX

| Concentration | Sugar test | Estimate of critical concentration from appearances of ppts. |
|---|---|---|
| | **Methyl Alcohol** | |
| 0.1% | negative | |
| 1.5% | positive | Below 1.5% |
| | **Ethyl Alcohol** | |
| 0.4% | negative | |
| 0.6% | positive | Between .5—.6% |
| | **Propyl Alcohol** | |
| .13% | negative | |
| .20% | positive | About .2% |
| | **Amyl Alcohol** | |
| .08% | negative | |
| .10% | negative | |
| .17% | negative | |
| .20% | positive | Below .2% |
| | **Sodium Chloride** | |
| 0.1% | negative | |
| 1.5% | negative | |
| 2.0% | positive | About 2% |
| | **Potassium Chloride** | |
| 0.1% | negative | |
| 1.5% | negative | |
| 2.0% | positive | About 2% |
| | **Calcium Chloride** | |
| 0.5% | negative | |
| 0.1% | positive | |
| 1.5% | positive | Below 1% |

It is interesting to note that no calcium was found in the outside water for the 0.5% tube. A trace of calcium chloride was found for the 1% tube; and the 1.5% tube gave a very decided test for both calcium and chloride in the outside water.

The reversibility experiments with copper sulphate were much more successful than the previous attempts. The results were decisive except perhaps in the case of ethyl alcohol where a more concentrated copper sulphate solution had to be used in order to effect a reversal. Three tubes were used in every case for each alcohol. The sugar tests were negative, Table X.

There are, of course, many experiments which might have been tried on the basis of the results given above. Time did not permit it, however. The peptizing action of copper sulphate on precipitated copper ferrocyanide sols

TABLE X

| Coagulating agent | Concentration of copper sulphate | Number of tubes which recovered |
|---|---|---|
| Methyl alcohol | 0.02M | 3 |
| Ethyl alcohol | 0.02M | 0 |
| Ethyl alcohol | 0.20M | 2 |
| Propyl alcohol | 0.02M | 3 |
| Amyl alcohol | 0.02M | 3 |

might have been tried as an analogy to the peptization of silver halide precipitates. Also, the addition of copper sulphate to sodium chloride solution should raise the latter's coagulating concentration. The same should be true of copper sulphate and alcohols.

Another interesting suggestion was furnished from work done with colloidal solutions of ferric oxide (Briggs and Vannoy 1925). It was found that concentrated solutions of calcium chloride (above 30%) peptized ferric oxide formed from ferric chloride and ammonium hydroxide, producing a negative sol. But when coagulated copper ferrocyanide membranes were treated with syrupy calcium chloride solution (70%) not only did they not recover, but after the treatment they allowed far more sugar to go through than before.

### Coagulation by Heat

For these experiments a small oven was used jacketed with running water and heated with a bunsen flame. The temperature varied within one degree. The net result obtained was that copper ferrocyanide membranes were coagulated by pure water between 23 and 24°C.—more probably 24°C. The futility of working with such membranes at room temperature of 26°C. becomes apparent at once. There is no doubt, of course, that when the temperature of the water is raised its surface tension is lowered; and coagulation of copper ferrocyanide at 23 or 24 degrees may have been brought about by the surface tension lowering. But it is also true that adsorption decreases with rise of temperature, that consequently the film of adsorbed water around the membrane particles is not as thick as it was before which is the same as saying that effectual pores may be formed allowing such things as sugar to go through which would otherwise be retained by virtue of the negative adsorption exhibited by copper ferrocyanide towards sugar. This is all the more convincing when we consider the lack of agreement between the surface tensions of several alcohols and water at 23.5°C, Table XI.

TABLE XI

| Reagent | Concentration | Surface tension | % Lowering of surface tension against HOH at 8°C |
|---|---|---|---|
| Methyl alc. | 1.5% | 66.5 dynes | 11% |
| Ethyl alc. | 5-6% | 67 dynes | 10% |
| Amyl alc. | .2% | 68.5 dynes | 8% |
| Water 23.5° | | 71.8 dynes | 4% |
| Water 8° | | 74.5 dynes | 0% |

BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS
ORSAY



## Conclusions

Before discussing the relation between the experimental results and the behavior of cell membranes we must take up the question of coagulation from the point of view of semi-permeable membranes in general of the type represented by copper ferrocyanide. There is no question about the external appearance of copper ferrocyanide membranes deposited in gelatin. Microscopic examination undertaken by means of objectives of high resolving power (N. A. 1.4, Zeiss Apochromat) showed beyond a doubt that the membrane is granular in character. Separate grains or groups of them are present and make up the entire area. Their size could not be measured, of course, owing to the presence of overlapping diffraction halos; and it is difficult to see how Tinker[1] in 1916 calculated the size of copper ferrocyanide particles by means of the wretched photographs which he published. Since copper ferrocyanide forms a hydrosol each particle or group must possess a layer of adsorbed water. When alcohol is added there are three possibilities: First, coagulation is brought about by a decrease in surface tension. This explanation is tenable only if we consider the copper ferrocyanide film to be a continuous membrane like rubber. We know that this is not the case. But if we consider the membrane to be granular it is not clear how surface tension decrease can be a factor in coagulation. The particles should tend to break up into still smaller ones and in the end a finer grained membrane would result which if anything should be less permeable than before. Second, if coagulation is due to selective adsorption it may involve the entire alcohol molecule or the positive radical. But when a sol coagulates it does so because the charge on each particle which keeps all particles apart is reduced or neutralized and the particles agglomerate. In other words the adsorption of alcohol by a negatively charged sol like copper ferrocyanide must entail a reduction or neutralization of its negative charge.

The electrically neutral aggregates can unite to form larger units and finally one large coagulum will result. The difference between such a final aggregation and the original one is that its area is smaller, it is more compact and water, both adsorbed and not, will be present around it. At no time then *is coagulation reversed as in the case of decreased surface tension.* The last possibility is the removal of water of hydration from the supposedly continuous hydrated copper ferrocyanide membrane with consequent shrinkage and the formation of cracks which would render the membrane permeable to things to which it is ordinarily impermeable. It was this consideration which prompted Walden and others to retain the membrane-forming reagents on both sides of the copper ferrocyanide. But if coagulation were indeed a question of the removal of water of hydration—the fact that copper ferrocyanide is granular alone throws a damper over the hydration theory—the cracks formed in its substance could not be obliterated by peptizing with copper sulphate. It may be argued that copper sulphate did not peptize the membrane but that instead it reacted with adsorbed potassium ferrocyanide which could not be washed out and the cracks were healed by the reprecipitation of

[1] Proc. Roy. Soc., 92A, 357 (1916).

copper ferrocyanide. The microscopic examination of the membrane in agar which showed the presence of peptized membrane material militates against the strength of this argument in addition to the fact that we know such things as silver halides to be peptized by their own reagents. Unless something has been left out of consideration we can be fairly certain so far that coagulation is a question of selective adsorption, washing out the alcohol with water will not necessarily peptize the membrane and thereby make it impermeable to sugar once more. The coagulated particles merely take collectively their film of adsorbed water and the spaces remain through which sugar can pass. The rigidity of the gelatine support is alone responsible for this because we have seen that in test tubes a coagulated copper ferrocyanide sol could be repeptized by the addition of water. In the latter case the addition of water was tantamount to a mechanical disintegration for the flocculated copper ferrocyanide was still in a very fine state of subdivision. The amount of alcohol remaining after peptization of the sol was 1.3% which is the amount just necessary to make a membrane permeable to sugar. But, as it was suggested before, the degree of coagulation could not be appreciated possibly since 40% alcohol was necessary to make the phenomenon visible in a test tube to the naked eye. Then there is the question of coagulation by heat. If the membrane were a continuous one it is difficult to see how a decrease in the surface tension of about one dyne produced by an increase of a few degrees—it must be remembered that at 20°C. successful experiments were performed—should make it permeable to sugar, although we must admit that the thing would not be impossible. But if the phenomenon is connected with surface tension then there must be a critical tension when a continuous membrane becomes discontinuous—forms drops in other words. The evidence given above shows that there is not. Alcohols acted at about 90% the original tension, water at 96%. If we must postulate a toxic action certainly we cannot blame it on the water. The alcohols cannot be blamed either because the discrepancy between methyl, ethyl, normal propyl, iso-propyl, butyl, iso-butyl, amyl and allyl and tertiary butyl is attributed to a toxic action on the part of the latter two. But, after all, the microscopic evidence is unequivocal enough.

We cannot say that the copper ferrocyanide membrane operates like a sieve because such a statement is only a small part of the story. It may act as a sieve for sodium and potassium chloride only under certain conditions because if the salts are present in dilute enough solution they will go through the membrane without coagulating it. This can be easily explained. If the adsorption isotherm for chloride ion in the presence of sodium ion, for example, reaches a constant value much before the isotherm for sodium ion in the presence of chloride, there must be a concentration for which both ions will be adsorbed equally. Since sodium chloride is soluble in water it will dissolve in the adsorbed water layer, under such conditions, and pass through the membrane without coagulating it. At higher concentrations the sodium ion will be adsorbed more and more whereas the chloride ion will not. As a result there

must come a point when the membrane will no longer be negative and coagulation will ensue. From this point on sugar will pass through the membrane, provided the membrane-forming reagents are absent. Sugar molecules which are adsorbed negatively will not go through therefore, until effective pores have been formed. This will not happen as long as both the membrane-forming reagents are present.

The case of calcium chloride is interesting. Walden[1] found that sometimes it did go through and at other times it did not. This happened when he used copper acetate one on side and potassium ferrocyanide on the other. Here Walden must have been using calcium chloride solutions of somewhere near the critical concentration below which it would not go through copper ferrocyanide when the membrane-forming reagents were present. In fact earlier in his paper Walden says that his diffusing solutions were *about* normal. But finally he succeeded in preventing his calcium chloride solutions from going through when, instead of copper acetate, he used copper nitrate on one side of the membrane. When this is correlated with the results obtained from experiments on reversibility with copper sulphate, described earlier in the present paper the explanation is easy. Copper ferrocyanide probably adsorbs the nitrate ion more readily than it does the acetate ion. Consequently the membrane is kept negative, and for the same concentration of calcium chloride in both cases the latter will not go through in the presence of copper nitrate.

With calcium chloride the adsorption isotherm reaches its constant value probably at such a low concentration that calcium chloride will pass through the membrane in negligible amounts only without coagulating it. In other words calcium chloride will not pass through the membrane until it coagulates it. And so we find that as soon as we can obtain a test for calcium chloride in the outside water sugar is present there also.

Finally we can say that a substance in solution will go through a membrane by osmosis when like sodium chloride it will go through without producing coagulation. When a membrane allows any true solution to go through including those solutions whose solutes are adsorbed negatively, then it is acting as a dialyzing membrane. It is understood, of course, that a solution which passes through by osmosis may under proper conditions—namely, after the membrane has coagulated—go through by diffusion or capillarity as through a dialyzing membrane. Calcium chloride does not necessarily fall out of the first class because even though both its ions are adsorbed equally, only at extremely low concentrations very dilute solutions will go through appreciably after a long enough time has elapsed without the membrane having been coagulated. And so sugar will go through copper ferrocyanide not because the latter is an ultrafilter, but because it has been converted into one through selective adsorption of cations and consequent coagulation. When a substance is brought in contact with a membrane in this condition and for which it possesses greater adsorption for the anion than for the cation the situation is reversed, the pores are closed because the copper ferrocyanide is

[1] Z. physik. Chem. **10**, 699 (1892).

peptized and it is no longer permeable to sugar. Such a membrane represents therefore a dynamic system. Its structure and its behavior must depend on the character of the substance which is trying to pass through. All this is very suggestive when we consider what takes place in the case of living cells.

When Collander[1] contends that protoplasm probably acts as an ultra-filter toward substances which are not soluble in lipoids he does not apparently take into consideration the fact that cells are both permeable and impermeable for the same substance. In addition to this he assumes a sort of continuous lipoid film with holes in it. This is going beyond the facts known at present. Collander also takes it for granted that cells have present at all times on either side the membrane-forming reagents. No such simple assumption is adequate. It is not known how the membrane is formed. It may be kept intact by the constant accumulation on one side and dissipation on the other of substances which lower the surface tension of a liquid as they concentrate at the interface between the cell and the external medium; or by secretion or by a slow process of precipitation[2].

"A feature of the protoplasm of many cells is the existence of a more or less differentiated cortex. When the cortex is well differentiated, it is an appreciable zone of protoplasm which is more solid than the interior. This is specially well developed in many Protozoa. Paramoecium, for example, possesses a firm cortex, the ectoplasm, of a uniform thickness over the body of theorganism. It is a structural modification which cannot be easily, if at all, repaired by the more fluid endoplasm. In Paramoecium it is an elastic jelly-like wall which is under a certain tension due to internal turgor. This can be shown by tearing the ectoplasm with a micro needle. The fluid interior then pours out, while the torn edges of the ectoplasm curl in, and the entire animal shrinks in size. If the edges of the tear meet they unite and further outflow of the endoplasm ceases, otherwise all the endoplasm flows out and the ectoplasm soon disintegrates. The endoplasm as it pours out into the surrounding water occasionally forms a delicate surface film which maintains the integrity of the extruded mass. Usually, however, the endoplasm becomes entirely dissipated and disintegrates. In some species, e.g. Paramoecium bursaria, the torn surface very readily forms a surface film which frequently persists. The integrity of the cell is thereby maintained. In the few experiments that have been made on this form, the endoplasmic surface film is apparently unable to regenerate a differentiated ectoplasmic layer. Complete recovery occurs by a gradual contraction of the animal until the ectoplasmic edges bordering the ectoplasmic surface film, meet and unite". Again "The surface film of blood cells and of tissue cells isolated in blood plasma or serum is extremely susceptible to mechanical injury unless special precautions are taken to maintain conditions as normal as possible. The human red blood corpuscle furnishes an interesting example of a rapid breakdown of the surface film. When the surface film is punctured with a very fine glass micro needle the

[1] Kolloidchem. Beihefte, **20**, 273 (1925).
[2] Chambers: "General Cytology", 254, 255, 257 (1924).

hemoglobin immediately diffuses out all over the cell and leaves behind a transparent glutinous mass which can be torn into strands".

From what has just been said it is evident that living membranes are left pretty much to their own resources, as it were, to manifest their phenomena of semi-permeability. And, therefore, if the copper ferrocyanide membrane is to exhibit analogous properties it must be used so as to imitate most nearly the conditions imposed upon living membranes. The first of these conditions requires the absence of the membrane-forming reagents. This condition Collander did not fulfill in his experiments. In addition to this the statement that the living membrane is probably an ultra-filter needs further correction. Collander has not taken the trouble, apparently, to differentiate between a semi-permeable membrane and an ultra-filter. To be sure he is not the only one. An ultra-filter is something which has been taken more or less for granted, and as a result no really definite idea has been in vogue. Accordingly Bancroft[1] has formulated the definition that "an ultra-filter is essentially a porous membrane which will, by hypothesis, never become a semi-permeable membrane unless there is a strong negative adsorption—preferential adsorption of the solvent." "The conclusion that a substance which can be filtered out through an ultra-filter is in colloidal solution and not in true solution rests on the explicit assumption that any gas or vapor will go through any pore through which any other gas or vapor will go". According to this idea—with which, after all, Collander cannot be confronted—everything in the cell which is in solution will ooze out and everything which is in solution will go in. The composition of the inside of the cell, as far as solutes go, will be identical with that outside. This, of course, is impossible. The simple ultra-filter idea must be revised.

On the other hand coagulation of the membrane and a reversal of the same explain a great many things, even though the structural character of the membrane is still a puzzle. The objection to Overton's lipoid theory[2] was that water-soluble substances like sugar could not penetrate a lipoid membrane. If however we assume the presence of a granular lipoid membrane analogous to copper ferrocyanide, in other words with each solid fat particle, or group of particles, surrounded with an adsorbed film of water supported in a separate pellicle, which is known to be present, we have essentially the same sort of thing as the copper ferrocyanide membrane and there seems to be no reason why, should such a membrane exist actually, it should not exhibit coagulation changes when necessary and allow e.g. sugar to enter the cell at one time and not at another. We have still to account however for the entrance of lipoid solvents through such a membrane. This is not at all a hopeless endeavor. Mention was made above of a film of adsorbed water surrounding the lipoid particles. It need not be that necessarily. The film could be a solution possessing properties analogous to a pyridine solution. In other words it might dissolve substances other than and in addition to lipoid solvents. In this way

[1] J. Phys. Chem. **29**, 966 (1925).
[2] Jahrbuch wiss. Botanik, **34**, 669 (1899).

the lipoid particles would be available as carriers for substances like ether and chloroform. Such a membrane would have the advantage of manifesting osmotic pressure, unlike an emulsion, and also to exhibit permeability changes in localized areas of the cell surface. It must be understood that only a very generalized picture of cell membrane is attempted. Undoubtedly membranes must differ with the functions of the particular organs of which they form a part. It may be objected that a substance like pyridine which may dissolve lipoid solvents may also dissolve the lipoid portion of the membrane and so destroy it. This need not follow at all. Pyridine itself is soluble in rubber, but it has been used with rubber membranes successfully by Kahlenberg without the rubber being damaged even in boiling pyridine. On the other hand if the idea of a discontinuous membrane—that is a fine grained one—with adsorbed water around the particles is not an attractive one we can postulate the existence of a continuous lipoid film of some sort which acts ordinarily as a semi-permeable membrane allowing only such things to go through which dissolve in it. A change in the surface tension of the surrounding medium might coagulate such a membrane into solid or semi-solid drops and allow water-soluble substances to pass through. Such a membrane could be reversed by changing the surface tension of the surrounding medium perhaps in addition to the extraction of the coagulating agent from between the particles by the presence of a suitable solvent or reagent. The coagulating agent might be a water soluble soap resulting from the reaction between sodium chloride and some fatty compound. This soap would reduce the surface tension of the solid film and pores would be formed between the solid drops in the membrane. The presence of calcium chloride would form a water-insoluble inert calcium soap which would dissolve in the membrane and subsequently would be decomposed by the cell after an increase in the surface tension of the external medium reversed the membrane and made it once more continuous. Clowes was not far away from such an explanation but he insisted that the cell must be an emulsion.

For the membrane suggested at first, antagonism can exist between the substances which will tend to coagulate the membrane and those which will peptize it. In the case of copper ferrocyanide the antagonism established was between alcohol or an inorganic salt on the one hand and copper sulphate on the other. There are undoubtedly other substances besides copper sulphate which will accomplish the same thing. The object of the investigation was not so much to find what would peptize the coagulated membrane as to make sure that the re-peptization could be accomplished at all. The exact character of such antagonism as sodium-calcium must be left for future investigation when a membrane more nearly akin to a living one will be made.

We know that after death the cell membrane behaves as ordinary dialyzer. The phenomenon is probably a question of permanent and irreversible coagulation. Experiments with acetic acid suggest the cause to be increased acidity of living cells after death owing to the accumulation of lactic acid.

There is no doubt that coagulation and reversibility of cell membranes suggest an interesting line of attack for many a problem in physiology and pathology. Whether the analogy, which has been drawn, in this series of investigations, between an artificial membrane and ectoplasm is warranted time alone will tell.

## Summary

1. Copper ferrocyanide membranes are coagulated by low concentrations of methyl alcohol, acetic acid, sodium chloride, potassium chloride and calcium chloride, thereby becoming permeable to sugar.

2. A copper ferrocyanide sol is flocculated by aqueous alcohol, whereas alkalies and water peptize a copper ferrocyanide gel.

3. The coagulation of copper ferrocyanide is caused by selective adsorption rather than by decrease in surface tension.

4. Copper ferrocyanide forms a granular membrane between those particles adsorbed water is present which fills the spaces more or less completely.

5. Copper ferrocyanide membranes are coagulated by water at a temperature of about 24°C.

6. The coagulation of copper ferrocyanide is reversible.

7. Bartlow's experiments with alcohol, Walden's experiments with acids, and Czapek's experiments with alcohols and acids involved nothing more mysterious than a coagulation of the membrane.

8. Intermittent permeability in living membranes is probably also a question of reversible coagulation.

This problem was suggested by Professor W. D. Bancroft to whom the writer is greatly indebted for invaluable criticism and suggestions.

*Cornell University.*

# CATALYTIC ACTIVATION OF TITANIA

BY W. A. RUDISILL AND CARL J. ENGELDER

It is a well known fact that the activity of a catalyst is to a large extent dependent on its manner of preparation. The nature of the starting material and its subsequent chemical and physical treatment are factors in the preparation of a catalyst which have received scant attention by investigators. Adkins[1] and his co-workers have done some excellent work on selective activation. A recent article by Adkins and Bischoff[2] on the selective activation of titania catalysts points out how the activity of titania may vary with different titanium compounds as the starting material.

In the present investigation, a study has been made of some of the factors which influence the activity of titania catalysts in decomposing ethyl alcohol. As shown in the experimental results, the treatment given the catalysts during their preparation affects to a large degree the extent of the decomposition as well as the composition of the gaseous products. The decomposition of ethyl alcohol by various catalysts has been rather thoroughly investigated by Grigoreff[3], Ipatief[4], Sabatier and his colleagues[5], Engelder[6], Adkins and others. Oxide catalysts like $TiO_2$, $SiO_2$, and $ZrO_2$ possess the ability to decompose $C_2H_5OH$ according to the two main reactions:

$$(1)\quad C_2H_5OH \longrightarrow H_2 + C_2H_4O$$
$$(2)\quad C_2H_5OH \longrightarrow C_2H_4 + H_2O$$

the one a dehydrogenation and the other a dehydration, both proceeding simultaneously to an extent dependent upon the specific nature of the catalyst. Titania catalysts in particular differ widely in their specificity towards these two reactions. That this specificity is dependent, to a considerable extent, on the physical factors involved in the catalyst's preparation has been the object of this research.

The factors which have been studied here are as follows:—

1. Variation of the Temperature of Ignition of the Catalyst.
2. Variation of the Time of Ignition of the Catalyst.
3. Variation of Anion.
4. Variation of Degree of Fineness of Catalyst.

## Experimental

*Apparatus and General Plan.*—The general mode of procedure was to pass the vapors of ethyl alcohol at a uniform rate over the catalyst mass contained in the decomposition apparatus and to collect and measure the gas volume

[1] J. Am. Chem. Soc. **44**, 2175 (1922).
[2] J. Am. Chem. Soc. **47**, 807 (1925).
[3] J. Russ. Phys. Chem. Soc. **33**, 173 (1901).
[4] Ber. **34**, 596 (1901); **35**, 1047, (1902); **36**, 1990 (1903).
[5] "Catalysis in Organic Chemistry."
[6] J. Phys. Chem. **21**, 679 (1917).

evolved and determine its composition. The apparatus was similar to that used by Engelder with certain modifications suggested by Adkins and Nissen[1]. The alcohol was accurately measured and controlled by allowing mercury to fall into a burette from which the alcohol was displaced. It passed first through a preheater and then into the reaction tube of Pyrex glass. The catalyst was placed in a porcelain boat in the center of the tube. This reaction tube was maintained at a constant temperature of 350° by being surrounded by an electrically heated furnace, the temperature of which was controlled by a Leeds and Northrup thermo-regulator. The reaction products passed through a spiral condenser and then into an ice-cooled receiver, to collect the liquid products, the gases passing on into a large collecting bottle containing saturated salt solution, which served as a gasometer. Provision was made for sampling the gases from the gasometer, as well as from a sampling cock on the line leading to the collecting bottle.

*Gas Analysis.*—The gas mixture was analyzed according to the usual methods of gas analysis. In some cases hydrogen was determined by the fractional method over spongy palladium as well as the regular slow combustion method over mercury. Ethylene was adsorbed in bromine water, $CO_2$ in KOH solution and CO in acid $Cu_2Cl_2$ solution. All gas volumes were recalculated to N.T.P. and reported as such.

*Uniform Procedure.*—After considerable preliminary work in which the apparatus was perfected, the technique standardized, and a score or so of weakly active catalysts were made and tested, the following uniform procedure for catalyst testing was adopted:—

All catalyst samples were ground to pass a 100-mesh sieve (except those whose degree of fineness was being studied). In each run 2.5 grams of the heated catalyst was used. The temperature for all runs with alcohol was 350°C. Absolute ethyl alcohol was used. The preheater was maintained at about 170°C. and the alcohol admitted at a uniform rate of 6 cc. per hour. Readings of burette, temperature of preheater and reaction tube, and volume of gas were recorded at intervals of 3 to 5 minutes and slight adjustments made in the rate of flow whenever necessary. Alcohol was passed through the apparatus under the above conditions for one hour to free the train from air. At the end of the first hour the collected gas was discarded, and the run continued for another hour. The volumes of gas recorded and their composition are for the second hour.

### 1. Variation of Temperature of Ignition of Catalyst

*Preparation of Catalysts.*—Preliminary work indicated that the temperature to which the catalyst is subjected during its preparation is an important factor in determining its specificity. Accordingly two series of titania catalysts were prepared, starting with titanium potassium oxalate, kindly furnished us through the courtesy of the Lindsay Light Co., Chicago, Ill.

[1] J. Am. Chem. Soc. **46**, 140 (1924).

*Catalysts designated by G.*—The "G" series was made as follows: Titanium potassium oxalate was dissolved in water and precipitated with ammonium hydroxide. The precipitate was washed four times by decantation, filtered, and then washed on the filter. The precipitate was dissolved in dilute HCl and reprecipitated with $NH_4OH$. It was then washed again as described above. The precipitate was dried at 150°C. and then heated at the same temperature for three hours. It was then ground to pass a 100-mesh sieve. Separate portions of this were heated for periods of two hours each at temperatures of 300°, 350°, 450°, 550°, 650°, and 750°C., giving respectively catalysts $G^1$, $G^2$, $G^3$, $G^4$, $G^5$, and $G^6$. A portion of the 100-mesh, dried batch was reserved for later work.

*Catalysts designated by H.*—The "H" series was prepared in the same way, with the exception that the first precipitate of $Ti(OH)_4$ was redissolved in dilute $H_2SO_4$ instead of dilute HCl. Separate portions of the dried, 100-mesh batch were heated for two hours each at temperatures of 250°, 300°, 350°, 450°, 550°, and 650°C, giving respectively the catalysts $H^0$, $H^1$, $H^2$, $H^3$, $H^4$, and $H^5$. Other portions of this preparation were reserved for later work.

The activity of these "G" and "H" samples was then determined in the uniform manner adopted. The results are tabulated below in Table I.

The results clearly show the importance of proper temperature of drying the catalyst. With increasing temperature of ignition, for both series, beyond 350°C the total gas evolution falls off rapidly, and there is a corresponding decrease in the volume of $C_2H_4$ per cc. of alcohol, particularly with the "H" series. In general the "H" series of titanias is more active, especially in regard to dehydration (ethylene production). The best catalyst is that precipitated from the sulfate solution and ignited at 300°C. Quite apparently, changes have been brought about by the higher temperatures of ignition modifying the surface conditions, especially as regards the dehydration ability of the catalyst.

Small amounts of carbon dioxide and carbon monoxide were always found, doubtless arising from secondary decomposition.

Considerable amounts of ethane were always present, amounting to 23.8% in the case of the "H" catalyst ignited to 650°. The particular mechanism by which this is formed has not been definitely determined. Adkins[1] believes that the ethane is produced probably according to the reaction:

$$2CH_3CH_2OH \longrightarrow CH_3CH_3 + CH_3CHO + H_2O$$

one molecule of the alcohol being reduced to the saturated hydrocarbon, the other oxidized to acetaldehyde. It is possible, on the other hand, to assume hydrogenation of the ethylene, yet no evidence here or in previous work is available to substantiate this.

### 2. Variation in Time of Ignition of Catalyst

To determine whether the length of time of igniting the catalyst is an important factor, two series of runs were made with portions of the "G" and "H" lots reserved for this purpose. Separate portions of the reserve supply

[1] J. Am. Chem. Soc. **47**, 817 (1925).

TABLE I

All runs made at 350°C at the constant rate of 6 cc. alcohol per hour, with 2.5 grams of catalyst. Time of ignition, two hours.

| Catalyst | Pptd from | Temp. of Ignition | Gas Envolved per cc. Alcohol 2d hr. | Composition of Gas Mixture. | | | | | cc. $H_2$ per cc. alcohol | cc. $C_2H_4$ per cc. alcohol |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | % $C_2H_4$ | % $H_2$ | % $C_2H_6$ | % CO | % $CO_2$ | | |
| $G^1$ | Chloride Solution | 300° | 85 | 46.4 | 38.7 | 14.6 | 0.9 | 0.5 | 31.9 | 39.4 |
| $G^2$ | " " | 350° | 92 | 48.9 | 29.8 | 18.3 | 0.7 | 1.1 | 27.4 | 45.0 |
| $G^3$ | " " | 450° | 78 | 47.7 | 35.2 | 16.0 | 0.8 | 1.2 | 27.4 | 37.2 |
| $G^4$ | " " | 550° | 60 | 41.8 | 41.8 | 15.6 | 0.7 | 1.0 | 25.1 | 25.1 |
| $G^5$ | " " | 650° | 34 | 24.8 | 62.7 | 11.1 | 0.5 | 0.7 | 21.1 | 8.4 |
| $G^6$ | " " | 750° | 16 | 7.5 | 82.7 | 7.5 | 0.7 | 0.7 | 13.2 | 12.0 |
| $H^0$ | Sulfate Solution | 250° | 113 | 71.4 | 7.2 | 20.4 | 0.8 | 0.8 | 15.8 | 80.8 |
| $H^1$ | " " | 300° | 140 | 67.8 | 7.7 | 22.8 | 1.2 | 1.4 | 10.7 | 94.9 |
| $H^2$ | " " | 350° | 93 | 73.3 | 8.5 | 17.1 | 0.8 | 0.7 | 8.4 | 72.5 |
| $H^3$ | " " | 450° | 95 | 71.4 | 9.2 | 18.1 | 0.9 | 1.2 | 8.7 | 67.8 |
| $H^4$ | " " | 550° | 74 | 63.4 | 15.8 | 20.1 | 0.8 | 1.0 | 11.7 | 46.9 |
| $H^5$ | " " | 650° | 35 | 51.1 | 24.2 | 23.8 | 0.6 | 0.3 | 8.4 | 17.8 |

were heated, at 350°C. for 1, 4, and 6 hours giving respectively the samples designated as $H^6$, $H^7$, $H^8$, and runs made under identical conditions as with $H^2$. A similar series was made with the "G" lot precipitated from chloride solution. The results for one set are here reported.

TABLE II

All runs made at 350°C. at the constant rate of 6 cc. alcohol per hour with 2.5 grams of catalyst, precipitated from sulfate solution.

| Catalyst | Time of Ignition | Gas evolved per cc. alcohol 1st hr. | Gas evolved per cc. alcohol 2d hr. | % $H_2$ | % $C_2H_4$ | % $C_2H_6$ | % CO | % $CO_2$ |
|---|---|---|---|---|---|---|---|---|
| $H^6$ | 1 hr | 105 | 98 | 7.9 | 74.9 | 16.1 | 0.9 | 0.8 |
| $H^2$ | 2 " | 112 | 99 | 8.5 | 73.3 | 17.1 | 0.8 | 0.7 |
| $H^7$ | 4 " | 95 | 90 | 8.4 | 74.8 | 15.3 | 0.7 | 0.8 |
| $H^8$ | 6 " | 150 | 91 | 6.9 | 68.3 | 21.8 | 1.0 | 1.3 |

The results show that the time factor of ignition is of little importance, the yield of gas being almost the same after the first hour and its composition practically the same for the several catalysts. Somewhat lower yields were obtained with the corresponding "G" catalysts, but they were practically constant both as regards total volume and percentage composition.

### 3. Influence of Anion

The series of experiments recorded in Table I indicated that the catalysts made by reprecipitation from a sulfate solution gave in general a more active catalyst than that series prepared by reprecipitation from a chloride solution. Both series otherwise received the identical treatment, such as uniformity in concentration, quantity of wash water, etc. The observed differences in behavior might be ascribed to the influence of the anion in the solution from which precipitation was made, or to adsorbed anions. To obtain further data on this point, some additional catalysts were prepared and two series of runs on alcohol made.

The catalysts designated as "J" were prepared in the same way as the "H" series except that the final precipitate was purposely not washed free from sulfate. One portion, $J^1$, was heated to 300°C and the second portion, $J^2$, to 350°C. These unwashed samples were compared in their effect on alcohol at 350°C. with the thoroughly washed samples, $H^1$ and $H^2$.

Catalysts "K" were made by dissolving potassium titanium oxalate in water and precipitating by ammonium hydroxide. The precipitate was washed four times by decantation, filtered and then washed on the filter. Up to this point, the treatment was identical as that given to the lot from which the "G" and "H" series were derived. The mass was then dried at 150°C for three hours. One portion was heated for two hours at 300°C, giving $K^1$; another portion was heated to 350°C for two hours, giving $K^2$. Runs were made with alcohol at 350°C by the standard procedure.

Still another series of catalysts was made by precipitating the hydroxide, filtering, dissolving in hydrochloric acid and then largely diluting and pre-

cipitating the $Ti(OH)_4$ by boiling. The hydrolyzed precipitate was washed, dried, heated to 150°C for three hours and separate portions, passing a 100-mesh sieve, were heated to 300°C and 350°C, giving respectively the catalysts designated as $L^1$ and $L^2$.

The tabulated results are given in the table below.

TABLE III

All runs made at 350°C at the constant rate of 6 cc. alcohol per hour with 2.5 grams of catalyst. Time of ignition two hours.

| Catalyst | Method of Preparation | Temp. of Ignition | Gas evolved per cc. Alcohol 1st hr. | Gas evolved per cc. Alcohol 2d hr. | Composition of Gas Mixture % $C_2H_4$ | % $H_2$ | % $C_2H_6$ | % CO | % $CO_2$ |
|---|---|---|---|---|---|---|---|---|---|
| $H^1$ | Sulfate-Washed | 300° | 150 | 140 | 67.8 | 7.7 | 22.8 | 1.2 | 1.4 |
| $J^1$ | Sulfate not washed | 300° | 155 | 84 | 69.7 | 4.8 | 23.8 | 0.9 | 1.1 |
| $K^1$ | Oxalate | 300° | 84 | 27 | 40.9 | 20.6 | 35.7 | 1.4 | 1.1 |
| $G^1$ | Chloride | 300° | 104 | 85 | 46.4 | 38.7 | 14.6 | 0.9 | 0.5 |
| $L^1$ | Hydrolysis of Chloride | 300° | 117 | 103 | 76.0 | 4.6 | 18.0 | 0.4 | 1.5 |
| $H^2$ | Sulfate Washed | 350° | 112 | 99 | 73.3 | 8.5 | 17.1 | 0.8 | 0.7 |
| $J^2$ | Sulfate not washed | 350° | 150 | 81 | 66.0 | 3.1 | 29.1 | 0.9 | 1.0 |
| $K^2$ | Oxalate | 350° | 89 | 25 | 31.0 | 27.9 | 36.9 | 0.9 | 3.0 |
| $G^2$ | Chloride | 350° | 111 | 92 | 48.9 | 29.8 | 18.3 | 0.7 | 1.1 |
| $L^2$ | Hydrolysis of Chloride | 350° | 139 | 128 | 70.8 | 4.7 | 22.9 | 1.0 | 1.1 |

That thorough washing is necessary to give an active catalyst and one that does not depreciate with prolonged use is shown by a comparison of $H^1$ with $J^1$ and $H^2$ with $J^2$. The unwashed samples rapidly lost their activity.

Reprecipitation is very important, as shown by the runs with the samples prepared from the oxalate without reprecipitation. A rather inactive catalyst, particularly in its dehydrating ability results from only one precipitation.

The unusually high values of ethane are significant.

Preparation of samples by hydrolysis yields a very active catalyst. This bears out the results of other investigators who have found that in general hydrolytically prepared catalysts are very efficient.

### 4. Variation in Degree of Fineness

It is to be expected that for the same weight of catalyst, the finer particle size and hence the more surface exposed, the greater will be the activity, other conditions being the same. Since titania influences both decomposition reactions of ethyl alcohol, it was thought interesting to study the variation of

particle size with the extent to which these simultaneous reactions are effected. Accordingly, a series of samples was prepared as follows:—The method of preparation of the "G" catalysts was followed closely. The lot dried at 150° for three hours was divided. One portion was ground to pass a 20-mesh sieve, but withheld by a 40-mesh sieve; this is designated as $M^1$. Another portion was ground to pass a 100-mesh sieve; this is called $M^2$. A third portion passed a 200-mesh sieve; this is $M^3$. Each portion was then heated for two hours at 350°C.

Runs by the uniform procedure were then made with alcohol, using as always, 2.5 grams of the catalyst. The data are given in Table IV.

TABLE IV

All runs made at 350° at the constant rate of 6 cc. alcohol per hour with 2.5 grams of catalyst.

| Catalyst | Temp. of Ignition | Time of Ignition | Gas per cc. alcohol 1st hr. | Gas per cc. alcohol 2d hr. | Composition of Gas Mixture % $C_2H_4$ | % $H_2$ | % $C_2H_6$ | % CO | % $CO_2$ | cc. $C_2H_4$ per cc. alcohol. | cc. $H_2$ per cc. alcohol. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 20-40 mesh ($M^1$) | 350° | 2 hrs. | 106 | 91 | 49.2 | 34.0 | 15.1 | 0.8 | 1.0 | 44.6 | 30.9 |
| 100-mesh ($M^2$) | 350° | 2 " | 120 | 95 | 50.0 | 29.5 | 18.4 | 1.5 | 1.3 | 47.5 | 28.0 |
| 200-mesh ($M^3$) | 350° | 2 " | 130 | 115 | 51.5 | 25.2 | 20.9 | 1.3 | 1.3 | 59.2 | 28.9 |

An increase in activity is shown for an increase in the degree of subdivision. More interesting, however, is the increase in dehydration with the finer sized contact masses, as indicated in the increased amounts of ethylene obtained. An increase in the amounts of ethane is also observed. Degree of fineness is thus another factor influencing the specificity of catalysts.

### 5. Stability of Catalyst

The relative stability of the different catalysts used is indicated by a comparison of the volume of gas during the first and second hours. Of the many catalysts prepared and studied in this investigation the ones designated as $H^1$ and $L^2$ were the most active. In order to determine the life of the catalyst, i.e., its activity with prolonged use, a catalyst was made according to the H series with a preliminary ignition of two hours at 300°C., giving catalyst $H^9$, and subjected to a ten-hour run. The results of this run are given in Table V.

Samples of the gas were analyzed at the end of the second, fourth, seventh and tenth hours. Catalyst $H^9$ depreciated very slowly with continued use and the composition of the gas after the first three hours changed very little. There was a slight increase in ethylene and in ethane between the second and fourth hours. The percentage of hydrogen was low and showed very little change.

TABLE V

| Time | | Gas Envolved per cc. Alcohol | % $C_2H_4$ | % $H_2$ | % $C_2H_6$ | % CO | % $CO_2$ |
|---|---|---|---|---|---|---|---|
| 1st | Hr. | 154 | —— | — | —— | — | — |
| 2d | " | 139 | 69.2 | 6.9 | 22.3 | 0.9 | 1.3 |
| 3d | " | 132 | —— | — | —— | — | — |
| 4th | " | 136 | 66.2 | 3.9 | 25.9 | 1.1 | 1.4 |
| 5th | " | 135 | —— | — | —— | — | — |
| 6th | " | 126 | —— | — | —— | — | — |
| 7th | " | 128 | 66.2 | 4.6 | 26.5 | 1.2 | 1.4 |
| 8th | " | 120 | —— | — | —— | — | — |
| 9th | " | 122 | —— | — | —— | — | — |
| 10th | " | 118 | 66.9 | 5.4 | 26.8 | 1.4 | 1.5 |


## Summary

1. Some of the factors which influence the activity of a catalyst have been studied in detail by preparing a large number of titania catalysts, passing the vapors of ethyl alcohol over them at a temperature of 350°C., and noting the volume of gas produced as well as its composition.

2. It was found in the first place, that the temperature of ignition of the catalyst greatly influenced both the yield of gas and its composition. In general, it was found that with increase in temperature of ignition there was a decrease in activity, and further, a decided decrease in ethylene production. In order to produce a good dehydrating catalyst the temperature must be low.

3. The preliminary ignition period of two hours is sufficient for the preparation of an efficient catalyst. Heating beyond one hour has little effect.

4. It was found that the character of the anion present during precipitation is important. Those catalysts made by precipitating from sulfate and chloride solutions and by hydrolysis were the most efficient. Those prepared from the sulfate and by hydrolysis gave the highest percentage of ethylene and the lowest percentage of hydrogen. Catalysts prepared by precipitation from the oxalate gave the lowest activity, the lowest percentage of ethylene, and the highest percentage of ethane. Catalysts prepared from thoroughly washed precipitates were the more active.

5. The degree of fineness of a catalyst influenced to some extent its activity. As the degree of fineness was increased, the activity was increased. Grinding the catalyst to fine mass before final ignition gave a more active catalyst.

6. Some catalysts were prepared which depreciated very slowly with use. A catalyst prepared from the sulfate solution was very active after ten hours use.



*University of Pittsburgh,*
*Pittsburgh, Pa.*

*Oct. 1925.*

# FILMS OF ADHESIVES*

BY J. W. McBAIN AND D. G. HOPKINS

Our previous work[1] has divided joints into two classes, specific and mechanical. Joints between smooth surfaces are necessarily specific, that is, true adhesion must occur between the surfaces and the film of adhesive. We have noticed that the strength of such joints is parallel to the mechanical constants of the materials joined and the question immediately arises as to whether there should not be a similar definite relation between their strength and the mechanical properties of the film of adhesive itself.

The second class of joints has a purely mechanical explanation in that the adhesive is embedded in the pores and surface irregularities of the materials joined. Here the film of adhesive acts as a solidified casting holding the materials together. Glued wooden joints appear to be a conspicuous example of this class. It is evident that for any given material the strength of such a joint must depend upon the mechanical properties of the film of adhesive, its penetrating power in the liquified state, its rigidity and tensile strength and absence of brittleness in the solidified state. For both classes of joint the tensile strength of the film itself imposes an upper limit on the strength of joint obtainable, since the film in both cases must transmit the strain.

Thus an investigation of adhesive action necessarily involves a study of the properties of adhesive films. Even as a routine test the study of a film of the adhesive itself should give more direct information than could be obtained in any other way.

The difficulty in the way of most investigators has been to procure suitable test specimens of the dried adhesive, and has been overcome only in a very few instances by following an elaborate and troublesome procedure[2]. We find that it is possible to employ a very rapid and simple method by adopting

---

*This investigation was undertaken for the Adhesives Research Committee of the Department of Scientific and Industrial Research and the authors are indebted to the Department for permission to publish the results.

[1] Table III of the previous paper (J. Phys. Chem., 29, 195 (1925); see also Second Report of Adhesives Research Committee, 1925) should have been completed by the insertion of the following particulars with regard to the various grades of silicate of soda employed.

| Grade | $\rho$ = (density of solutions) | % $Na_2O$ | % $SiO_2$ |
|---|---|---|---|
| D | 1.70 | 18.5 | 36.0 |
| K | 1.56 | 13.8 | 32.9 |
| C | 1.50 | 11.65 | 32.85 |
| J | 1.375 | 9.06 | 26.44 |
| A | 1.39 | 9.14 | 29.36 |
| Experimental sample | 1.225 | 4.94 | 19.53 |

In footnote (***) of the same table the statement "three coatings instead of one raised the strength of joint with starch to 1600 lbs" should be amplified by pointing out that this special result was obtained with a double-cover plate type test piece, where the total load is given and not the strength in lbs per sq. in. The corresponding value for a high-grade glue is about 3000 lbs total load.

[2] Thus Hopp (J. Ind. Eng. Chem., 12, 365 (1920)) and Gill (17, 297 (1925)) both obtained values of 12,000 to 13,000 lbs. per sq. in. for a high grade glue.

the device of using very thin films, which can be tested with an accuracy far surpassing that of any known wooden join.

Furthermore, the strength of such films is far greater than that of any wooden join and is equaled only by the end grain strength of the strongest woods. Up to the present no really satisfactory type of wood joint has been evolved, either as regards of accuracy of measurement or absolute strength as compared with the glue itself. It appears that a glue may be appreciably deteriorated before there is any falling off observable in the strength of joins made there from, probably because the strength of the joins is such a small fraction of that of the glue itself. These thin films also allow a ready method of investigating not only the tensile strength but also such important mechanical properties as rigidity and brittleness and the limit of deformability.

The necessity for study of the film cannot be obviated by merely studying the properties of the liquid or dissolved adhesive such as jelly strength, viscosity etc., although this is commonly assumed in the case of glue. On the other hand, the writers are well aware that tensile strength, although an essential factor, is only one of the many mechanical properties of the film itself which have to be considered. Further, there are other important qualities which must be possessed by the solution (prior to the formation of the film) such as penetralibility, rate of setting etc.

## Paper Strip Method

Before describing our work with thin films some data may be given which show that the method of using strips of paper impregnated with glue[1] cannot be considered satisfactory, although it has recently been advocated by Bechhold.

This method is incapable of giving an absolute measure of the strength of adhesive films because the true cross-sectional area of the film cannot be determined even approximately, and further the effect of the presence of the paper cannot be gauged, nor the effect of the adhesive upon the paper itself. The method is limited to obtaining the order of magnitude of the tensile strength.

A slight modification of Millar's method was adopted in the following experiments carried out to investigate the possibilities of the method. Pure cellulose paper was cut into dumb-bell shaped strips 5″ long and 1″ wide in the narrow part. These test pieces were dipped into the adhesive solution and then hung up by the end to dry. When dry the process was repeated but this time they were allowed to dry in the reverse position so that a fairly uniform coating of adhesive was obtained. Tension tests were then carried out, the breaking loads being measured to the nearest pound and the mean of four determinations taken. The thickness of the strip at the point of fracture was determined in six places with a micrometer reading to 0.001″. Table I gives the order of magnitude of the tensile strengths of a number of adhesive films, made from aqueous solutions.

[1] Millar: J. Soc. Chem. Ind., 18, 16 (1899).

TABLE I

*Tensile strength of films of adhesive made from aqueous solutions.*

| Strip | Concn. % | Heated to (°C) | Thickness of strip ($10^{-3}$in) | Total breaking load (lbs) | Net* breaking load (lbs) | Tensile** strength (lbs/sq. in.) |
|---|---|---|---|---|---|---|
| Paper only | — | — | 3 | 7 | 0 | (2000) |
| Paper + adhesive H*** | 10 | 60 | 4 | 36 | 29 | 7000 |
| Paper + gelatine X*** | 10 | 60 | 5 | 41 | 34 | 7000 |
| Paper + starch | 2 | 60 | 4 | 14 | 7 | 2000 |
| Paper + gum arabic | 10 | 18 | 4 | 15 | 8 | 2000 |
| Paper + silicate† | | 18 | 7 | 16 | 9 | 1000 |

*Breaking load for impregnated strip less breaking load (7 lbs) for paper.
**Order of magnitude only = adhesive — paper.
***See p. 119 for information regarding these adhesives.
†Molar ratio 3.0, density 1.375

It is evident from these results that the paper strip method is not satisfactory for comparing the tensile strengths of different adhesives. Not only has the paper itself an unknown influence upon the structure and mode of fracture of the film but its own strength is too large a fraction of that of the film to allow the data to possess any quantitative significance. Some of these adhesives are many times stronger than would here be indicated.

*The preparation of test pieces of adhesive film.*

The most trustworthy method of testing the strength of films of adhesive is by measuring the strength of thin films which have been formed by allowing them to dry on a surface to which they will not adhere. The thinnest films obtainable should be used in order to minimise strains which may develop in drying. Such films also approach most nearly to the condition of the adhesive in a joint.

This simple method of procedure has been adopted by which thin films may be readily prepared and tested. The results are sufficiently concordant to warrant the assertion that this method will supplement and to some extent supersede those which are at present in use. It also affords a ready means of investigating the effect of addition of soluble substances, or powders (fillers) upon the strength of glue and gelatine films. This method has already supplied new and highly significant information.

Farrow and Swan[1], using a suggestion of J. H. Sturgess, prepared thin films of starch by pouring starch solutions on to very thinly greased ferrotype plates, where they were allowed to dry. The films were readily detachable from the plates. Neale[2] has thus found that such starch films possess considerable tensile strength ($2\frac{1}{2}$ to $4\frac{1}{2}$ tons per square inch).

Glue or gelatine was soaked in the requisite amount of water overnight and a solution prepared by heating at about 60°C. This solution was poured on to ferrotype plate coated with a trace of vaseline. On drying, which usually

[1] J. Textile Inst. 14, T465 (1923).
[2] J. Textile Inst. 15, No. 9.

takes a few days, the film very frequently separated spontaneously from the greased surface but if it had adhered it could be removed by upraising the edges with a knife. A few films (e.g. gelatine with added phenol, chloral hydrate, sodium fluoride or sodium iodide) adhered strongly to the greased plate and it was not possible to detach them in portions large enough for the making of test pieces. Celluloid was occasionally used in place of the ferrotype plate although it showed a tendency to warp.

Films of gum arabic are particularly interesting because as they dried they became so brittle that they spontaneously broke into small pieces from internal strain. They could be rendered soft and flexible by slightly humidifying them but were as brittle as ever when dried again. It is possibly for this reason that glycerine is frequently recommended as an addition to gum arabic adhesives and indeed small quantities of non-volatile solvents are added to most adhesive compositions.

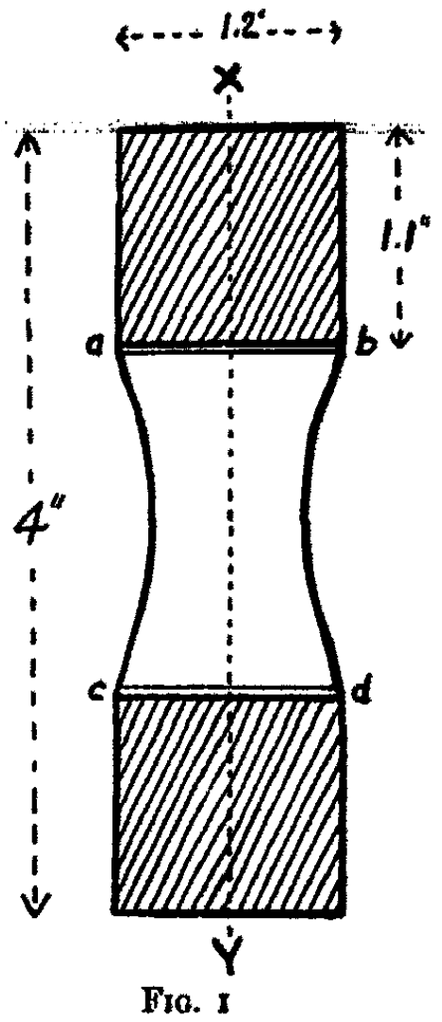


FIG. 1

Care has to be taken in order to obtain really good films. One of the principal difficulties to be overcome is the elimination of air bubbles, for fractures originate at such points. In order to get a perfectly homogeneous adhesive solution it is necessary to shake or stir very thoroughly. Each of these operations has a pronounced tendency to produce air bubbles which are extremely difficult to get rid of on account of their great stability. In practice it has been found most satisfactory to give a whirling motion to the solution. When solids are added to the adhesive solutions the difficulty is still further increased because the powdered materials themselves enclose considerable quantities of air. The powder also tends to separate out both in the vessel from which the suspension is poured and on the ferrotype plate. Particles of certain substances, such as barium sulphate, agglomerated in glue and gelatine solutions.

When studying the effect of the addition of soluble substances it is necessary to make the addition in such a way that the resulting solution is quite homogeneous. For instance, alum could not be satisfactorily dissolved in a 10% gelatine solution. It was found better to soak the gelatine in the alum solution. On the other hand, formalin could not be added to the water in contact with the gelatine as it rendered the latter insoluble; it was added to the warm gelatine solution.

When finally prepared the film was slightly rehumidified to prevent it from splitting and then cut with scissors into test pieces, two types of which have been employed. The first or earlier type is shown in Fig. 1. Parallel lines ab and cd are drawn lightly in black lead at right angles to the central axis XY so as to facilitate fixing in the testing grips in such a way that the

load is applied axially. The two wide end portions are reinforced with stiff paper so that a satisfactory grip can be secured in testing. This type of test piece may perhaps be criticised on the ground that it is easy to initiate a rupture when forming the curved edges by cutting with scissors. To obviate this the second and final type of test piece was designed (Fig. 2). It consisted of a straight strip the long sides of which could be cut out with one stroke of the scissors. The ends were reinforced with stiff paper as before, the paper being pressed on to the wetted adhesive strip. The results obtained with the

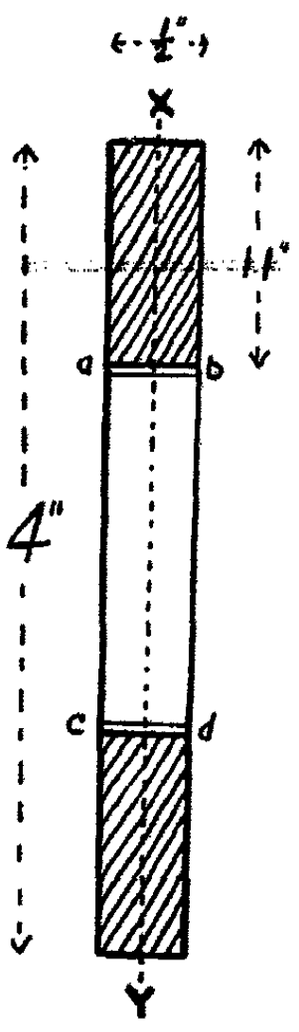



FIG. 2

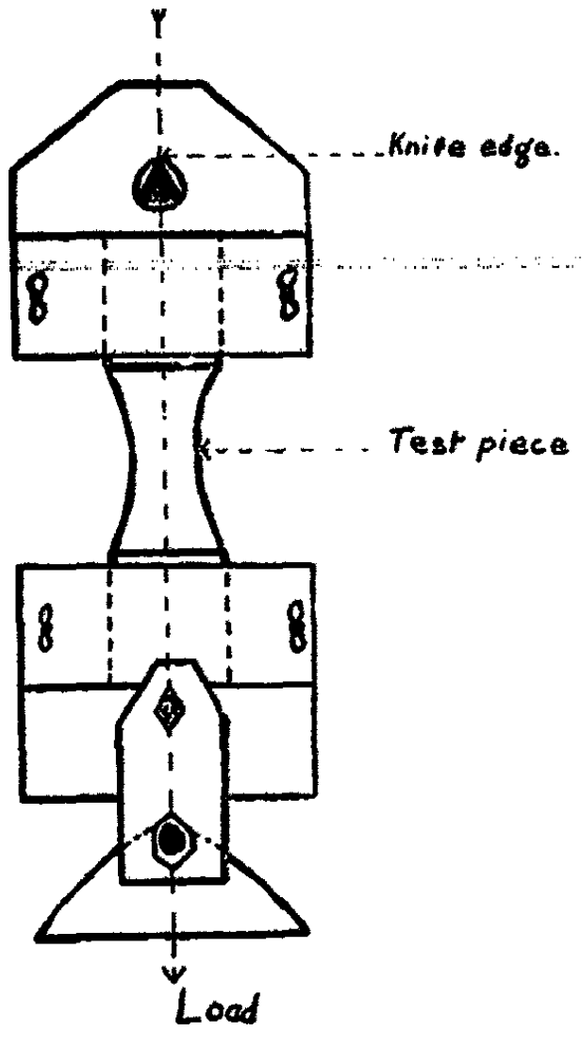



FIG. 3

two different forms of test piece were practically identical but the second type is to be prefered on account of its simplicity and from the point of view of economy of material.

The tensile strength of glue and gelatine films is greatly influenced by the hygrometric state of the atmosphere in which the tests are made. However, the variation of humidity in a room maintained at approximately the same temperature and otherwise under the same general conditions is often so small that it can be ignored in the case of most films. When certain soluble substances are added to the glue however, it becomes necessary to take the humidity factor into account and for accurate determinations, absolute or relative, it was necessary to carry out the experiments in an atmosphere of constant humidity. The humidity of the testing room was recorded in all later experiments being measured by means of a hair hygrometer.

The pattern of the grips employed is indicated in Fig. 3. The whole system was supported on a horizontal knife edge and the load applied by

placing weights and sand in a bucket suspended from the lower grip, the rate of loading being maintained constant as far as possible.

In the majority of films the mean thickness may be taken in calculating the cross sectional area but in those cases where the film was not of uniform thickness the mean of six readings, three on each side of the point of fracture has been used in calculating the tensile strength. All measurements were made with a micrometer gauge reading to a ten thousandth of an inch.

Particulars of the solutions from which the films have been prepared are given in Tables II-IV. A few notes are however necessary to indicate the nature of the adhesives employed which appear in the tables under arbitrary designations.

(*a*) *Gelatine and glue* (without additions)
Gelatine X—a high grade commercial gelatine.
Highly purified gelatine—supplied by Prof. Schryver.
Isinglass—refined.
Adhesive H—a high-grade commercial glue.
Glue size—a proprietary brand.

(*b*) *Glue with added solids* (powders).
Lead sulphate—ordinary quality.
Zinc oxide—Kahlbaum's heavy.
Aloxite—finely ground
Fine water ground flint (fired) } supplied by Sir Herbert Jackson.

(*c*) *Glue or gelatine with added soluble substances*
Potassium dichromate—the films were exposed to diffused sunlight for seven days.
Formalin
Potassium alum } —these substances increase the viscosity of glue and gelatine solutions.
Sodium benzoate—this salt lowers the jelly strength.
Sodium formate
Sodium salicylate } —these had been said to increase the adhesive power of the glue.
Glucose

*The effect of the prolonged heating of a glue solution on the tensile strength of the resulting films.*

The loss of adhesive power of a glue solution by continued heating at various temperatures has already been followed by determining the strength of wood joints set up with the heated glue solutions[1]. It was pointed out that the wood joint method could be fully satisfactory for this purpose only in the case of adhesives which are less tenacious than the wood. In the present series of experiments the cause of the degradation has been followed by measurement of the tensile strength of the glue films.

[1] McBain and Hopkins: J. Phys. Chem. 29, 203 (1925).

TABLE II

Glue and gelatine films (without additions)

| Adhesive | Grams Adhesive in 100 gms water. | No. of determinations | Humidity % | Tensile strength (lbs/sq. in.) Maximum | Minimum | Mean | Representative value. |
|---|---|---|---|---|---|---|---|
| Gelatine X | 10 | 12 | — | 13300 | 10700 | 11900 | 12800 |
| Highly purified gelatine | 10 | 5 | — | 9800 | 9200 | 9500 | 9500 |
| Isinglass (refined) | 10 | 3 | 63 | 9900 | 9100 | 9500 | 9500 |
| Adhesive H (1) | 15 | 6 | — | 13000 | 10200 | 12100 | 12400 |
| Adhesive H (2) | 30 | 5 | 44 | 13400 | 12100 | 12200 | 12200 |
| Glue size | 50 | 2 | 53 | 7800 | 6600 | 7200 | 7200 |

TABLE II

Powdered solid added to 15 grams of adhesive H in 100 grams of water

| Powder added | Wt. powder added (gms) | Added solid calculated on wt. of glue. | No. of determinations | Humidity % | Tensile strength (lbs/sq. in.) Maximum | Minimum | Mean | Representative value. |
|---|---|---|---|---|---|---|---|---|
| Lead sulphate (1) | 10 | 66⅔ | 5 | 61 | 8900 | 8200 | 8500 | 8500 |
| Lead sulphate (2) | 2.2 | 15 | 5 | 44 | 12400 | 11300 | 11900 | 11900 |
| Lead sulphate (3) | 1.5 | 10 | 5 | 44 | 12800 | 11200 | 11900 | 12300 |
| Zinc oxide | 10 | 66⅔ | 5 | — | 7800 | 5600 | 6700 | 7300 |
| Aloxite | 10 | 66⅔ | 3 | — | 6600 | 4900 | 5700 | 6100 |
| Fine water ground flint (fired) | 10 | 66⅔ | 5 | — | 6000 | 4300 | 5300 | 5700 |

TABLE IV

Glue (Adhesive H) and Gelatine X with added soluble substances

| Substance | Films prepared from (gms.) Adhesive | Water | Substance | No. of detns. | Humidity % | Tensile strength (lbs/sq. in.) Maximum | Minimum | Mean | Representative value. |
|---|---|---|---|---|---|---|---|---|---|
| **Films from glue (tensile strength without additions 12300 lbs/sq. in.)** | | | | | | | | | |
| Formalin | 15 | 100 | 5 (ccs) | 4 | 52 | 13200 | 11300 | 12000 | 12700 |
| Sodium benzoate (2) | 30 | 100 | 3.0 | 4 | 44 | 12600 | 11300 | 11900 | 12300 |
| Sodium formate (1) | 15 | 100 | 2.0 | 6 | 52 | 7600 | 6200 | 6800 | 7100 |
| Sodium formate (2) | 15 | 50 | 2.0 | 5 | 44 | 7900 | 6600 | 7400 | 7900 |
| Sodium formate (3) | 10 | 30 | 0.20* | 3 | 50 | 10500 | 9200 | 9800 | 9800 |
| Sodium salicylate (1) | 15 | 100 | 2.0 | 8 | 61 | 7300 | 4900 | 5900 | 5900 |
| Sodium salicylate (2) | 15 | 50 | 2.0 | 3 | 44 | 11000 | 9900 | 10500 | 10500 |
| Sodium salicylate (3) | 10 | 30 | 0.48* | 4 | 50 | 9100 | 8900 | 9000 | 9000 |
| Glucose (1) | 15 | 100 | 5.0 | 6 | 54 | 3000 | 2500 | 2800 | 2900 |
| Glucose (2) | 15 | 50 | 5.0 | 6 | 44 | 6100 | 5400 | 5800 | 6000 |
| Glucose (3) | 10 | 30 | 0.59* | 3 | 50 | 9000 | 8900 | 8900 | 8900 |
| Hydrochloric acid | 25 | 100 ccs N/10 soln.* | | 4 | 53 | 12900 | 11500 | 12200 | 12200 |
| Sodium hydroxide | 25 | 100 ccs N/10 soln.* | | 4 | 54 | 10000 | 9400 | 9700 | 9700 |
| **Films from gelatine X (tensile strength without addition 12800 lbs/sq. in.)** | | | | | | | | | |
| Potassium dichromate | 10 | 100 | 2.0 | 8 | — | 14100 | 11200 | 13200 | 13800 |
| Potassium alum (1) | 10 | 100 | 3.0 | 5 | 58 | 10800 | 8300 | 9400 | 9000 |
| Potassium alum (2) | 10 | 100 | 5.0 | 4 | — | 10800 | 8300 | 9400 | 10300 |
| Sodium benzoate (1) | 10 | 100 | 3.0 | 4 | 58 | 1500 | 1100 | 1300 | 1300 |

* = 0.1N solutions.

Ordinary aqueous as well as acid and alkaline solutions of glue have been experimented with, 25 grams of adhesive H being taken in 100 grams water or 100 grams of N/10 hydrochloric acid or N/10 sodium hydroxide. The solutions were prepared in the usual way and then transferred to sealed tubes or well-stoppered bottles and maintained at definite temperatures in thermostats. At intervals films were prepared and tested. An examination of the recorded humidities shows that it was possible to obtain satisfactory results without employing a constant humidity chamber by suitably choosing the times of testing.

No trouble was experienced in detaching films of acid glue from the greased ferrotype plate but those prepared from alkaline glue generally adhered quite firmly to the plate and in many instances it was impossible to detach them in a form suitable for testing. The results are given in Table VI.

TABLE VI

The effect of prolonged heating of a glue solution on the tensile strength of the films

| | Temp. °C | Tensile strength (lbs/sq. in.) after period of heating in days. 0 | 1 | 2 | 3 | 6 | 28 | 45 |
|---|---|---|---|---|---|---|---|---|
| Aqueous solution of adhesive H(25%) | 55-57.5[1] | 12200 | 12500 (53) | 11400 (53) | 11100 (53) | 12800 (44) | 11300 (50) | 7800* (51) |
| | 80[1] | 12200 | 11200 (50) | 11100 (50) | 9000* (50) | | | |
| | 90[1] | 12200 | 9700 (51) | 4300* (54) | | | | |
| | 100[2] | 12200 | ** | ** | ** | | | |
| | 57.5[2] | 12200 | 11200 (53) | 10300 (53) | 10400 (53) | 9300 (44) | *** | |
| | 55[3] | 9700 (54) | † | 8600 (54) | † | † | | |

[1] Aqueous solution of adhesive H (25%).
[2] 0.1 H Cl solution of adhesive H (25%).
[3] 0.1 NaOH solution of adhesive H (25%).
*Only one value obtained. Films very brittle and broken in fixing in machine.
**All films brittle and broken in fixing in machine.
***Films fractured spontaneously on drying. No test pieces could be prepared.
†Film adhered to greased plate.

Films prepared from 25% solutions of glue in water or in 0.1N hydrochlorid acid were equally tenacious. When, however, the solvent was 0.1N sodium hydroxide a scum appeared on the surface and the films were decidedly weaker.

Films from 25% aqueous glue solution that had been maintained at 55-57.5°C showed a slight reduction in strength after 28 days but after 45 days the loss was quite marked. At 80°C there was a decrease of about 9% after 2 days whilst after 3 days the strength had fallen to three quarters of the original value. At 90° the loss of strength was much more rapid, the value being reduced to one-third of the original in two days. Bogue[1] investigated

[1] Chem. Met. Eng. 23, 201 (1920).

the effect of the prolonged heating of glue solutions at 80° on their adhesive power by carrying out shear tests with the adhesive between maple surfaces and the loss of strength appeared to amount of more than 5% of the original strength per hour of heating, or to 67% loss in 12 hours. Continued heating of a glue solution is known to reduce its covering capacity and it is possible that thinning of the glue accounts for the discrepancy between Bogue's results with wood joints and the more direct ones obtained by the film strength method.

The rate of loss of tensile strength of films prepared from a 25% solution of glue in 0.1N hydrochlorid acid maintained at 57.5° is much greater than with the aqueous solution, presumably on account of increased hydrolysis. The effect of alkali on the strength of a glue film is appreciable even at a temperature of 55°, a reduction of 11% taking place after 48 hours of heating.

One of the most important observations arising from the present series of experiments is that hydrolytic deterioration of a glue is accompanied by increasing brittleness of the adhesive film, especially at higher temperatures. Many films of comparatively high tensile strength were found to be exceedingly brittle and this factor is of considerable importance in estimating the adhesive power of a glue.

## Discussion

The extreme variation between maximum and minimum values of tensile strength found in repeated experiments with a given adhesive was well within 10% whereas it is well known that results with wooden joints fluctuate by 20 or 30% even with the most careful control.

Gill[1] has determined the tensile strength, joint strength, viscosity and jelly strength of glues from six different sources (bone, hide and fleshings etc.) and found that the strengths of all the glues, except junk bone, were approximately the same (10000-12000 lbs/sq. in.). The strength of his wood joints with the same glues varied only from 3085 to 3940 lbs/sq. in. Gill concluded that the uniformity of tensile strength excluded the test as a means of discriminating between glues. This deduction is hardly justified by his own results since with junk bone where the tensile strength is as low as 4500-6500 lbs/sq. in. the joint strength is reduced to 2635 lbs/sq. in. Reference to Table II shows that the tensile strength of a film of a high grade glue (adhesive H) is nearly twice that of one prepared from a sample of glue size which had been selected as an example of a poor glue. Incidentally it may be remarked that the results of Gill's investigations demonstrate the absence of any parallelism between the joint strength and jelly strength or viscosity.

The tensile strengths of films of gelatine X and adhesive H indicate that at least for mechanical joints a high grade gelatine and a good glue are equally efficient. Refined isinglass and a highly purified gelatine were found to be of about the same tenacity but rather inferior to a first class commercial gelatine or glue.

[1] Ind. Eng. Chem. 17, 297 (1925).

The gelatine, glue and isinglass films, when loaded to near the point of fracture, developed permanent opaque markings which suggested the existence of slip planes or crystallisation of the adhesive. This persisted after the withdrawal of the load. However, examination of one of these fractured films by X-rays (transmission and reflection) gave no indication of crystalline structure.

The fact that gelatine and glue possess a tensile strength of more than five tons per square inch shows that wood joints do not measure the strength of a high grade glue. Wood is incapable of withstanding such a stress except in tension perpendicular to the end grain.

From the results obtained with addition of lead sulphate (Table III) it is evident that the effect of the addition of a powdered solid to a glue solution on the strength of the resulting films depends upon the quantity added. The addition of 10-15% of lead sulphate, calculated on the weight of glue, does not appreciably affect the tensile strength of the film, whilst if the addition was increased to 66⅔% the film was weakened by 31%. With such heavy loading of the glue, zinc oxide, aloxite, and fine water-ground flint (fired) caused even greater weakening. Even so, however, a weakening might escape detection in the use of wooden test pieces. Indeed, in some cases if surfaces to be united do not come into close contact, an added powdered solid may even increase the strength of the joint by enabling the film of adhesive to remain sufficiently voluminous to fill the space between the rough surfaces.

Only one of the soluble substances added to the glue definitely increased the tenacity of the film; namely, potassium dichromate. Formalin left it unimpaired. Potassium alum in two different concentrations reduced the film strength but alum separated in solid form when the adhesive solution dried on the ferrotype plate and this might have been of some account in bringing about the observed decrease.

A 10% solution of gelatine prepared in a 3% aqueous solution of sodium benzoate produced films which when tested in an atmosphere of 58% humidity were of very low tenacity and which elongated even under small loads. With a 30% glue solution prepared in a 3% solution of the same salt the films were of normal strength (12300 lbs/sq. in.) but the humidity in this case was only 44%, a factor which may largely explain the difference in the two values. Sodium formate, sodium salicylate and glucose weakened glue films considerably and the results obtained likewise show the influence of humidity.

## Summary

1. Determinations have been made of the tensile strengths of thin films of a high grade commercial glue and gelatine, highly purified gelatine, refined isinglass and glue size. The first two adhesives gave values of about 5½ tons per sq. in. or twice that obtained with glue size. Refined isinglass and the highly purified gelatine had approximately the same tenacity; namely, 9500 lbs/sq. in. The tensile strength depends upon the humidity of the atmosphere.

2. The addition of 10-15% of powdered lead sulphate did not affect the tensile strength of the film appreciably, although 66⅔% did. Similar results were obtained when the glue was loaded with zinc oxide, aloxite and fine water-ground flint.

3. The presence of potassium dichromate definitely increased the strength of the film whilst formalin had no effect. Potassium alum, sodium benzoate, sodium formate, sodium salicylate and glucose reduced the tensile strength. Films prepared from 25% solutions of glue in water or in n/10 hydrochloric acid were equally tenacious whereas films prepared from glue dissolved in N/10 sodium hydroxide were decidedly weaker.

4. The hydrolytic degradation of such aqueous, acid and alkaline solutions of glue continuously heated causes a relatively slight loss of tensile strength even after 28 days heating at 55-57.5°C but the effect is much greater at higher temperatures and the films even when of high tensile strength become extremely brittle.

5. The experimental error involved in determining the tensile strength of adhesive films by this method is generally much less than 10%. The results appear to warrant the assertion that the method will supplement and to some extent supersede the more indirect methods at present in use.

*Department of Physical Chemistry,*
*University of Bristol,*
*England.*
*October 2, 1925.*

6-69

# STUDIES ON THE CHEMISTRY OF GOLD

BY VICTOR LENHER AND C. H. KAO

It has been shown by one of us[1] that chloride of gold can be extracted from an acidified aqueous solution by certain aliphatic esters.

It has since been found that this property differs widely among individual members and is independent of the solubility of the organic compound in water and of water in the organic compound. Ethyl acetate, which is somewhat soluble in water, gives a better extraction of gold chloride than isobutyl propionate which is practically insoluble. On the other hand, diethyl malonate which is insoluble in water gives an excellent extraction.

In view of these facts, the whole subject has been studied by determining the partition coefficient of chloride of gold in water and esters under well defined conditions.

*Procedure.* Hydrochlorauric acid was prepared by solution of gold in aqua regia with excess of hydrochloric acid and evaporation over calcium chloride. The resulting product as shown by Lengfeld has approximately the formula $HAuCl_4 . 3H_2O$. Standard solutions of this salt were prepared, their gold content being determined by analysis. The esters used were all prepared by us.

20 cc portions of the chloride of gold solution and 20 cc of the ester were shaken in a thermostat at 20°. The system was allowed to stand only so long as was required to allow the two liquids to separate which was determined to be in most cases, five minutes. On long standing most of the esters hydrolyse and in some of them reduction takes place with the precipitation of metallic gold. The two liquids were then separated by a separatory funnel. The gold in the aqueous layer was determined by precipitation by sulfur dioxide, that in the ester by difference.

Attempts have been made to obtain the molecular weight in various esters, but have been unsuccessful, metallic gold being produced.

A study has been made of the distribution data of $HAuCl_4$ between water and a large number of esters, and a distribution of the second order has been shown to exist in all cases. The following were used; methyl acetate, methyl propionate, methyl butyrate, ethyl formate, ethyl acetate, ethyl propionate, ethyl butyrate, isopropyl formate, isopropyl acetate, isopropyl propionate, isopropyl butyrate, isobutyl formate, isobutyl acetate, isobutyl propionate, isoamyl formate, isoamyl acetate, isoamyl propionate, isoamyl butyrate. The acetates in general are better extracting agents than any other members while the ethyl esters are in general better than any other type. As the number of carbon atoms increases the extractive power decreases. Thus it has been found that ethyl acetate gives the best extractions.

[1] Lenher: J. Am. Chem. Soc., **35** 546 (1913).
[2] Lengfeld: J. Am. Chem. Soc. **26**, 324 (1901).

*Influence of various amounts of hydrochloric acid on the partition coefficients.* The effect of hydrochloric acid in varying amounts from 1% to 30% has been determined. The presence of hydrochloric acid is a very important factor on the partition coefficient. The separation of gold chloride into the ester layer successively increases until at approximately 10% concentration the maximum extraction is reached. Further addition of hydrochloric acid beyond this point of 10% has very little influence on the partition coefficient. At 30% concentration of HCl, the esters and water are miscible. Therefore considering all of the factors involved, it appears that ethyl acetate in 10% hydrochloric acid is the most efficient extraction agent for gold chloride.

To test the general applicability of the use of ethyl acetate as a means of purification of gold chloride, and separation from the chlorides of other metals, a number of experiments have been conducted to that end. The procedure is to treat a 10% hydrochloric acid solution of the particular chloride in a separatory funnel with an equal amount of ethyl acetate and shake vigorously. The two layers are allowed to settle after which they are separated. The ester layer is washed twice with small amounts of 10% hydrochloric acid. The combined aqueous solutions are again extracted with ethyl acetate until the ethyl acetate is colorless, which requires about four extractions.

The gold is then determined by evaporation of the ester and precipitation by sulfur dioxide.

*Gold Chloride alone*

| Number of Determinations | Au taken | Au found | Average Error |
|---|---|---|---|
| 2 | 0.0444 | 0.0443 | −.0001 |
| 2 | 0.3987 | 0.3986 | −.0001 |

*Separation from Sodium Chloride*

| Number of Determinations | NaCl taken | NaCl found | Error | Au taken | Au found | Error |
|---|---|---|---|---|---|---|
| 6 | .5849 gm | .5850 | ±.0004 | .1148 | .1149 | −.0005 |

*Separation from Potassium Chloride*

| | KCl taken | KCl found | Error | Au taken | Au found | Error |
|---|---|---|---|---|---|---|
| 5 | .5326 | .5323 | −.0004 | .1148 | .1147 | −.0001 |

*Separation from Magnesium Chloride*

| | $MgCl_2$ taken | $MgCl_2$ found | Error | Au taken | Au found | Error |
|---|---|---|---|---|---|---|
| 4 | .2992 | .2995 | +.0004 | .1378 | .1377 | −.0001 |

*Separation from Barium Chloride*

| | $BaCl_2$ taken | $BaCl_2$ found | Error | Au taken | Au found | Error |
|---|---|---|---|---|---|---|
| 4 | .4937 | .4935 | ±.0004 | .1378 | .1375 | .0003 |

*Separation from Ferric Chloride*

| Number of Determinations | $FeCl_3$ taken | $FeCl_3$ found | Error | Au taken | Au found | Error |
|---|---|---|---|---|---|---|
| 3 | .4218 | .4218 | ±.0003 | .1148 | .1146 | ±.0002 |
| 2 | .2109 | .2105 | −.0004 | .1148 | .1144 | −.0004 |

*Separation from Aluminum Chloride*

| $AlCl_3$ taken | $AlCl_3$ found | Error | Au taken | Au found | Error |
|---|---|---|---|---|---|
| .4332 | .4333 | ±.0006 | .1378 | .1375 | −.0003 |

*Separation from Strontium Chloride*

| | $SrCl_2$ taken | $SrCl_2$ found | Error | Au taken | Au found | Error |
|---|---|---|---|---|---|---|
| 4 | .3243 | .3240 | −.0003 | .0763 | .0759 | −.0004 |

*Separation from Calcium Chloride*

| | $CaCl_2$ taken | $CaCl_2$ found | Error | Au taken | Au found | Error |
|---|---|---|---|---|---|---|
| 5 | .5322 | .5328 | ±.0004 | .1258 | .1255 | −.0003 |

*Separation from Chromium Chloride*

| | $CrCl_3$ taken | $CrCl_3$ found | Error | Au taken | Au found | Error |
|---|---|---|---|---|---|---|
| 3 | .1609 | .1606 | −.0003 | .1761 | .1762 | +.0001 |

*Separation from Manganous Chloride*

| | $MnCl_2$ taken | $MnCl_2$ found | Error | Au taken | Au found | Error |
|---|---|---|---|---|---|---|
| 5 | .5085 | .5082 | −.0003 | .1378 | .1375 | −.0003 |

*Separation from Cobalt Chloride*

| | $CoCl_2$ taken | $CoCl_2$ found | Error | Au taken | Au found | Error |
|---|---|---|---|---|---|---|
| 4 | .5816 | .5812 | −.0004 | .1148 | .1146 | −.0002 |

*Separation from Nickel Chloride*

| | $NiCl_2$ taken | $NiCl_2$ found | Error | Au taken | Au found | Error |
|---|---|---|---|---|---|---|
| 4 | .5055 | .5055 | ±.0004 | .1148 | .1146 | −.0002 |

*Separation from Zinc Chloride*

| Number of Determinations | $ZnCl_2$ taken | $ZnCl_2$ found | Error | Au taken | Au found | Error |
|---|---|---|---|---|---|---|
| 4 | .4038 | .4035 | +.0005 | .1148 | .1147 | −.0001 |

*Separation from Mercuric Chloride*

| | $HgCl_2$ taken | $HgCl_2$ found | Error | Au taken | Au found | Error |
|---|---|---|---|---|---|---|
| 4 | .5020 | .5021 | ±.0002 | .1148 | .1146 | −.0002 |

*Separation from Copper Chloride*

| | $CuCl_2$ taken | $CuCl_2$ found | Error | Au taken | Au found | Error |
|---|---|---|---|---|---|---|
| 4 | .4712 | .4710 | ±.0002 | .1148 | .1147 | ±.0002 |

*Separation from Cadmium Chloride*

| | $CdCl_2$ taken | $CdCl_2$ found | Error | Au taken | Au found | Error |
|---|---|---|---|---|---|---|
| 4 | .4945 | .4942 | ±.0003 | .1148 | .1146 | ±.0002 |

*Separation from Lead Chloride*

| | $PbCl_2$ taken | $PbCl_2$ found | Error | Au taken | Au found | Error |
|---|---|---|---|---|---|---|
| 3 | .0406 | .0403 | ±.0003 | .1375 | .1373 | −.0002 |

*Separation from Bismuth Chloride*

| | $BiCl_3$ taken | $BiCl_3$ found | Error | Au taken | Au found | Error |
|---|---|---|---|---|---|---|
| 4 | .2763 | .2759 | ±.0004 | .1375 | .1373 | ±.0002 |

*Separation from Antimony Trichloride*

| | $SbCl_3$ taken | $SbCl_3$ found | Error | Au taken | Au found | Error |
|---|---|---|---|---|---|---|
| 4 | .2548 | .2545 | −.0003 | .1375 | .1374 | −.0001 |

*Separation from Arsenic Acid*

| | $H_3AsO_4$ taken | $H_3AsO_4$ found | Error | Au taken | Au found | Error |
|---|---|---|---|---|---|---|
| 3 | .3654 | .3652 | ±.0004 | .1378 | .1375 | ±.0003 |

*Separation from Stannic Chloride*

| Number of Determinations | $SnCl_4$ taken | $SnCl_4$ found | Error | Au taken | Au found | Error |
|---|---|---|---|---|---|---|
| 4 | .3894 | .3894 | ±.0005 | .1378 | .1377 | ±.0003 |

## Conclusions

It has been established that auric chloride can be separated completely from all of the more common chlorides in a solution containing 10% free hydrochloric acid by means of extraction with ethyl acetate.

Ethyl acetate is the most efficient of the esters for this separation.

The method is particularly useful in separating gold chloride from the alkaline earth metals, since the more commonly used sulfur dioxide will form with them insoluble sulfates.

# THE PHOTOCHEMICAL OXIDATION OF LEUCO-BASES*

BY B. H. CARROLL

Although the early division of the spectrum into actinic, visible, and heat radiation has been abandoned, cases of photochemical reactions which are primarily sensitive to the longer wave lengths, are rare enough to be of particular interest. These reactions are generally oxidations.

It has been known for some time that the oxidation of leuco-bases to the corresponding dyes is accelerated by light; this photo-oxidation from the colorless base to the intensely colored dye obviously making possible a photographic process in which the leuco-base is the sensitive material, and the image is composed of dye instead of silver. Studies of the reaction by Gros[1], Konig[2], and Eder[3] demonstrated at least qualitatively, that the maximum of absorption of the dye coincides with that of sensitivity of the leuco-base. The process accordingly appeared to offer a possibility for photography of the red and short infra-red.

A study of the literature, supplemented by experiment, makes it appear probable that only the dyes of the triphenylmethane and xanthene series form stable and photosensitive leuco-bases. Other series are excluded because of instability of the bases in the dark, as in the case of the indigoid dyes, or lack of photosensitivity, as in the case of the indamines.

The malachite green series (derivatives of diparaaminotriphenylmethane) were finally selected because of their selective absorption of the red. Synthesis of the leuco-bases being found more satisfactory than reduction of the commercial dyes, four were prepared by the former method; leuco malachite green, leuco brilliant green, and two bases not in commercial use, obtained respectively by the condensation of benzylethylaniline with benzaldehyde, and of dimethylaniline with furfural. These will be designated as light green and furfural green respectively.

König established that the incorporation of the bases in collodion films not only provides a practicable form for photographic use, but also accelerates the photooxidation. The absorption spectra were found to be only slightly displaced toward the longer wave lengths, the maxima being as follows: malachite green 624 mμ, brilliant green 628 mμ, light green 628 mμ, furfural green 634 and 480 mμ. As the sensitivity of the plates so prepared is about that of "printing-out" paper, the investigation resolved itself principally into search for a sensitizer. Solutions of the leuco-base and sensitizer were mixed with the collodion, and plates were coated so as to give approximately 0.6 mg. collodion and 0.3 mg. base per $cm^2$. In preliminary tests they were exposed as soon as

*Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.

[1] Gros: Z. physik. Chem. 37 157 (1901).

[2] Konig: Z. angew. Chem. 17 1633 (1904).

[3] Eder: Sitzungsber. Akad. Wiss. Wien, 128 IIa. April (1919).

dry to a 250-watt gas-filled tungsten light at a distance of 30 cm. for 30 minutes. The plates being too insensitive for spectrograph exposures, the relative color sensitivity was tested by exposing part of the plate under Corning ruby glass, absorbing completely below 600 mμ, and another part under a Wratten H filter, absorbing above 520 mμ. The plates were fixed in changes of benzene, which was found to be quicker and less destructive to the film than the 10% aqueous solution of monochloracetic acid recommended by König. The extent of the reaction was measured in terms of density at 620–640 mμ, using a Fabry-Buisson microphotometer and a monochromatic illuminator as source

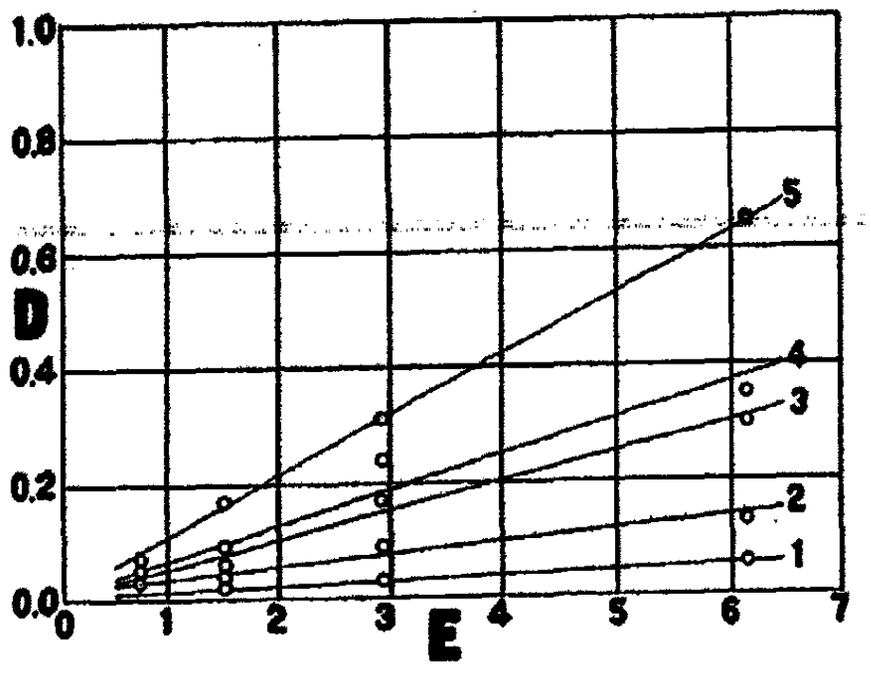



FIG. 1

Characteristic curves of leuco-base plates. Density at 620-40 mμ, plotted against exposure in candle-meter-seconds times $10^6$.

1. Unsensitized light green.
2. Light green sensitized by addition of quinoline.
3. Light green sensitized by addition of mannitol hexanitrate.
4. Light green sensitized by addition of quinoline and mannitol hexanitrate.
5. Unsensitized malachite green.

of light. (Density, in the photographic sense, being the negative logarithm of transmittancy, is proportional to the dye per unit area, assuming Beer's law).

Altogether some forty compounds were tried as sensitizers of one or more of the four leuco-bases. As might be expected, all four were similarly affected by a given compound. In general, the most photosensitive combinations oxidized the most rapidly in the dark, and while materials were found which accelerated the "light" reaction more than the "dark" reaction, nothing was discovered which gave promise of a stable plate of practicable speed. We therefore discontinued work on the process, although the reaction is worthy of further study for its scientific interest. The results may be briefly summarized:

1. Bases accelerate the oxidation and free acids retard it, both in light and dark. König's discovery of the sensitizing action of quinoline is a special case of this rule; the heterocylic and aliphatic amines are more efficient than the aromatic.

2. The nitric acid esters were the only oxidizing agents found to accelerate the light reaction relatively more then the "dark" reaction.

3. For the four bases tested, the greater the molecular weight of the group attached to the amino nitrogen, the better the stability.

The data in Table I indicate the relative spectral sensitivity and stability of three of the bases, sensitized with quinoline and mannitol hexanitrate; the leuco furfural green was too readily oxidized in the dark for quantitative measurements. Densities being additive, the density of the unexposed portion of the plate has been subtracted from the exposure values.

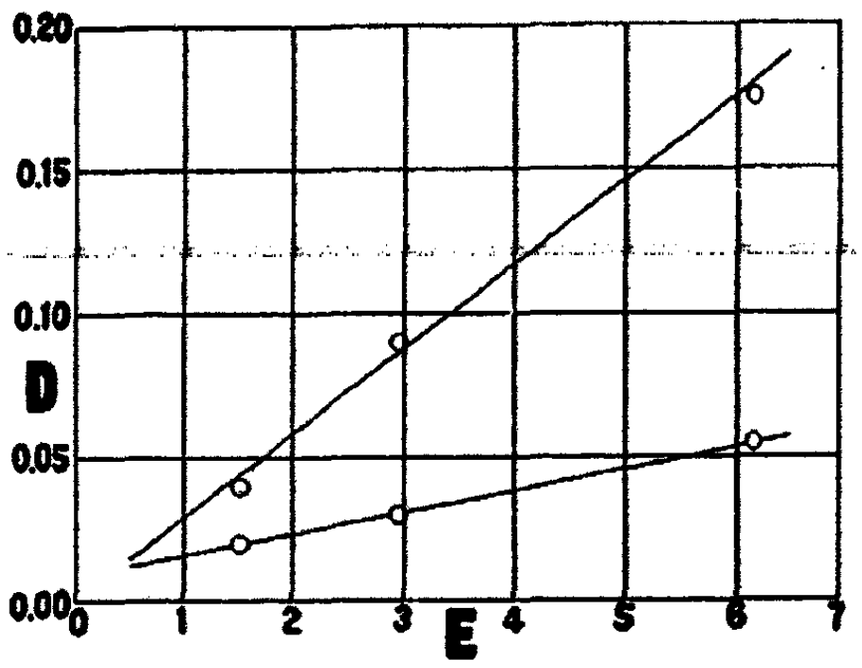



FIG. 2

Characteristic curves of leuco light green plates, unsensitized. Lower curve, exposure started forty minutes after pouring; upper curve, exposure started one hour forty minutes after pouring.

TABLE I

| Dye | On Complete oxidation | After 3 Days in dark | Density at 620-40mμ After Exposure Direct | Red glass | H filter |
|---|---|---|---|---|---|
| Malachite green | 3 | 3 | 1.05 | 0.63 | 0.13 |
| Brilliant " | 1.9 | 1.9 | 0.17 | 0.05 | 0.06 |
| Light " | 1.45 | 1.01 | 0.62 | 0.59 | 0.13 |

The relation between exposure and density was tested with an optical wedge (an Eder-Hecht "Kopier-Photometer"). This gives an intensity scale of exposure; the results with a time scale would be complicated by the rapid oxidation in the dark. The curves in Figs. 1 and 2 all show that within the limits of error, the dye formed in a given time is proportional to the intensity of light. The sensitivity of these materials is measureable in terms of the slope of the density-exposure curve, rather than as the reciprocal of inertia, as in the case of the silver bromide-gelatine emulsion; all curves appear to pass through the origin, without indication of an induction period. The sensitivity of the plates increased for a time after drying. This was particularly noticeable with leuco light green, the most stable of the bases; the magnitude of the effect is evident from Fig. 2.

## Discussion

The reaction is interesting not only because of unusual sensitivity to the longer wave-lengths, but also as an illustration of the different mechanisms by which added materials may influence a photochemical reaction. The amino bases do not affect the absorption of radiant energy, but increase the reactivity of the system. The nitric acid esters undoubtedly increase the reactivity of the system, yet their superiority over other oxidizing agents is probably due to their known sensitivity to light of short wave-lengths, so that at least part of the sensitivity of the plates to this region may be due to the leuco base acting as acceptor for the oxygen liberated in the photolysis of the collodion. The action of the dye formed by the oxidation of the base must, in the absence of a better understanding, be termed purely catalytic. Red light, absorbed by the dye but not by the base, is unquestionably effective in the oxidation of the latter. The experiments of Gros proved that the dye attains its maximum effect at very low concentrations; if this were not the case, the velocity of the oxidation would increase as it went on, and the observed proportionality between exposure and reaction (measured as density) would be impossible. We are therefore forced to ascribe the increase in sensitivity of the plates on standing to an unknown change in reactivity, rather than to the increase in dye resulting from the dark oxidation.

## Summary

The photochemical oxidation of leuco bases offers little hope of utility as a photographic process, but it may be followed quantitatively by optical methods of analysis, and is well adapted to study of photochemical catalysis.

# THE ADSORPTION OF IONS ON A MERCURY SURFACE*

BY W. A. PATRICK AND P. W. BACHMAN

It is the purpose of this paper to present a brief preliminary statement concerning the unequal adsorption of ions by mercury from dilute aqueous solution of mercury salts. The work has been done in this laboratory during the last year, and although not completed in all its details, it was thought best to give a brief description at this time, inasmuch as the essential points have been satisfactorily verified experimentally. Later on, a more comprehensive report, together with complete description of apparatus, etc., will be submitted.

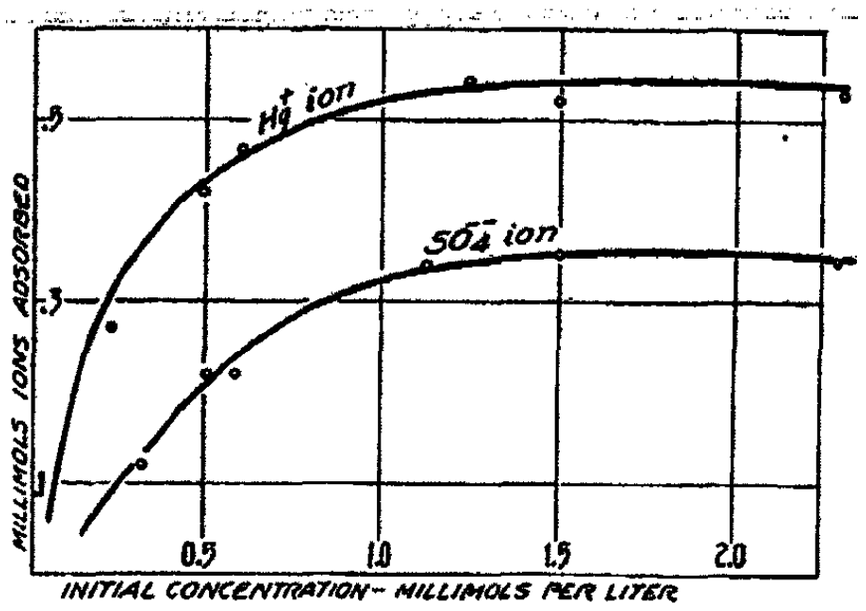



FIG. 1

Adsorption in $HgHSO_4$ solution

The experiments consisted in forcing pure mercury, by slight pressure, through chamois skin directly into a column of dilute aqueous mercurous sulphate or mercurous acetate. The glass tube which contained the solution was about four feet long and one inch in diameter. The mercury, issuing through the chamois in small drops, fell through the solution by gravity, and was collected at the bottom of the tube which was so arranged as to allow the mercury to drain off automatically. In passing through the column of mercury solution, the mercury drops adsorbed certain amounts of cations and anions. The amounts adsorbed were determined by analyzing the solutions both before and after a run. The analyses were made by electrolyzing the solutions with platinum electrodes under the proper conditions of current density, etc. The mercury depositing on the cathode was weighed directly, while the concentration of the sulfate ion or acetate ion was determined by titrating the remaining solution with standard sodium hydroxide. In this manner the amount of each ion removed by adsorption could be accurately de-

*Contribution from the Chemical Laboratory of Johns Hopkins University.

termined. By varying the initial concentration of the electrolyte, and keeping the time, during which the mercury was allowed to fall through, constant,—the amounts of ions adsorbed at different concentrations could be compared. In regard to this, it must be remembered that although the actual mercury surface exposed during a run could not be determined with great accuracy, the working conditions were such as to make all experimental results strictly comparable. (See later paper.) It is also necessary to mention that in the case of mercurous sulfate, it was shown by electrolytic analytical methods that the ratio of mercury to sulphate corresponds to the formula $HgHSO_4$.

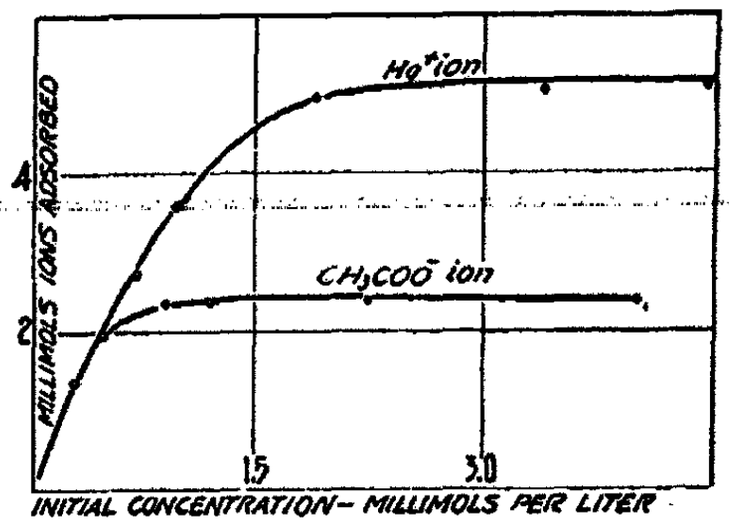



FIG. 2

Adsorption in $HgCH_3COO$ solution.

The results of the above experiments are best illustrated by the accompanying curves (Figs. 1 and 2) which show that, contrary to previous ideas concerning these systems, the mercurous ion is adsorbed to a much greater extent than either the sulfate or acetate ion. Of course, if the length of time of run is changed, different amounts of ions are adsorbed,—but the mercury ion always to the greater extent. The curves of Fig. 1 and 2 are obtained from runs all extending over the same period of time—approximately eight minutes.

In a later paper more complete results will be given, including the effect of acids and other electrolytes on the adsorption, the approximate thickness of the adsorbed layer of ions, and the corresponding effects attending the use of an adsorbent other than mercury. Furthermore an attempt is being made to correlate the experiments with absolute electrode potentials and the modern ideas concerning solutions of strong electrolytes.

## Summary

It has been shown that when mercury droplets are allowed to pass through dilute aqueous solutions of mercurous sulfate or mercurous acetate, the mercurous ions are adsorbed to a definitely greater extent than the sulfate or acetate ions.

## NEW BOOKS

**Radioactivity.** *By K. Fajans. Translated by T. S. Wheeler and W. G. King. 22 × 15 cm; pp. xii+138. New York: E. P. Dutton and Company, 1922. Price $3.50.* The chapters are entitled: the study of the chemical elements previous to the study of radioactivity; the radioactive transformations of the elements; the chemistry of the radio-elements; the displacement laws and their application; the end-products of the disintegration series and the isotopic varieties of lead; isotopy in ordinary elements; the atomic numbers of the elements; the artificial decomposition of atoms; the composition of atom-nuclei; the properties of isotopes; retrospect and prospect.

"Attention must be drawn to the fact that the half-life periods of the radio elements lie between such enormously wide limits as $10^{10}$ years for thorium and $10^{-11}$ seconds for thorium C." p. 26.

"According to one view, first put forward by Boltwood (1905), lead is the end-product of the uranium-radium-polonium series. This view is based mainly on the fact that lead is found in all uranium minerals, and in amounts which, in minerals of equal geological age, are in proportion to the uranium content, whilst in minerals of different ages, the proportion of lead varies directly with the age. This is to be expected if lead is actually formed by the slow disintegration of uranium, and so accumulates in the mineral; atomic weight considerations also seemed to support this view. Taking the earlier values for the atomic weight of uranium-I (238.5) and radium (226.4) the atomic weight of RaG was found by the usual calculation to be 206.5 or 206.4 respectively. Among the ordinary elements this agreed most closely with the atomic weight of lead (207.1); the discrepancy was thought to be due to small inaccuracies in the atomic weights. However, the revision of the atomic weights involved did not decrease the difference, but made it considerably larger. Calculated from the present values for the atomic weights of uranium-I (238.2) and radium (226.0), the atomic weight of RaG is 206.2 and 206.0 respectively, whilst that of lead, according to the latest determinations is 207.20.

"The arrangement of the radio-elements in the periodic system and the conception of isotopy indicated an explanation of this seeming anomaly, and simultaneously led to important revelations concerning the nature of the other "end-products." The application of the displacement laws to the transformations of the six radio-elements above shows that their end-products all belong to the lead-pleiad. As far as the qualitative chemical behaviour is concerned this result is, for RaG, in excellent agreement with Boltwood's hypothesis. Consequently the anomaly in the atomic weights is explained if it be assumed that RaG, that is the "lead" present in uranium minerals, has the same chemical properties as ordinary lead but not the same atomic weight; i.e. they are not identical, but isotopic," p. 47.

"From a thorianite from Ceylon, containing 68.9 percent thorium and 11.0 percent uranium Hönigschmid has isolated a lead which is obviously a mixture of thorium-lead and uranium-lead, and its combining weight (207.2) is identical with the atomic weight of ordinary lead. This thorianite-lead still shows its radioactive origin, as it possesses the activity of the lead isotope radium-D which was separated with it from the mineral. In about 200 years, however, when the radium-D (half-life period sixteen years) has practically compietely disintegrated, this lead will be indistinguishable from ordinary lead, provided always that the same qualitative and quantitative chemical methods are used. Hence it is not impossible that ordinary lead is such a mixture of thorium-lead and uranium-lead. Baxter and Grover investigated seven samples of ordinary lead obtained from very different mineral and geographical sources and, allowing for experimental errors, all had the same atomic weight; this proves that even if ordinary lead is a mixture its composition is everywhere the same. This is not so strange as might appear, for both uranium and thorium must have existed before the earth's crust solidified, and consequently uranium-lead and thorium-lead must have been present in the fused mass, hence it is only necessary to assume that they then mixed homogeneously in order to explain the constancy of the atomic weight of ordinary lead," p. 52.

"The above considerations give precision to the assumption, based on radioactive data, that helium is a constituent of other elements; they show that it is the helium nucleus which is contained in heavier nuclei and not the whole helium atom. This also applies to the hydrogen atom which, as will be shown in the following chapter, also enters into the structure of other elements. Since negative electrons are contained in the nuclei of some elements we conclude that even these minute nuclei are complex structures in which enormous electrical forces must be confined. This conclusion will be of great importance in the complete explanation of Prout's hypothesis. All large deviations from this hypothesis appear possible of explanation by assuming the elements in question to be isotopic mixtures; but certain smaller deviations cannot be accounted for in this way. Thus though it is highly probable that the helium nucleus (α-particle) which possesses the mass 4.00 and a double positive charge, is composed of four simple positively-charged hydrogen nuclei each of mass 1.008, together with two negative electrons; yet its mass is not exactly $4 \times 1.008$. According to the views set out above it should be possible to reduce the mass of atoms to the masses of their constituent positive and negative particles. Now the mass shown by moving negative electrons and positive hydrogen nuclei can be ascribed on the electromagnetic theory to the electrical and magnetic forces ("electro-magnetic mass") which originate from spherical particles carrying surface charges if it is assumed that the radius of the negative electron is of the order $10^{-13}$ cm. and that of the hydrogen nucleus is even smaller. Since the radius of the α-particle is also only of the order of $10^{-13}$ cm. (evidence for this will be given in the next chapter) the electromagnetic forces, regarded as mass, which are produced as a result of the common movements of the closely-packed constituents of the particle, will influence one another. From this it can be seen that the mass of the helium nucleus need not be equal exactly to four times the mass of the hydrogen nucleus (Harkins). A similar mutual electromagnetic action between the constituents of heavier nuclei can be assumed in order to explain those finer deviations from Prout's hypothesis, which may be expected to occur in other elements. The principle of relativity supplies another explanation; this will be discussed in the next chapter," p. 76.

"Darwin has calculated that the velocity imparted to a hydrogen nucleus which has been hit centrally—the most favourable case—will be 1.6 times greater than the velocity of the impinging α-particle which has four times the mass. Theoretical considerations show that such an H-particle possesses very nearly the same range as an α-particle of equal velocity and since the range of an α-particle is proportional to the cube of its velocity, the H-particle impelled by central impact should have about four times the range of the original α-particle.

"Indeed Marsden (1914) proved that this deduction was correct. Although the range of α-particles from radium emanation contained in a very thin-walled tube was 24 cm. in hydrogen at atmospheric pressure, yet scintillations could still be observed on a zinc sulphide screen at a distance of over 80 cm. from the tube. That these scintillations were caused by simple positively-charged particles of unit mass—H-nuclei—of very high velocity was proved by measuring the deflexion of these particles in electrical and magnetic fields," p. 80.

"There are those who still hold that chemically isotopes are to be regarded, not as very similar, but as absolutely identical. The theoretical and experimental results discussed in this chapter leave little doubt that this view is incorrect, for spectroscopic measurements of isotopes have shown differences both in the oscillations of the electrons situated in the outermost regions of the atoms and in those of the atoms within the molecules, and hence there must exist corresponding chemical differences; this has already been stated in Section 1. The vaporization experiments of Brönsted and v. Hevesy have proved that isotopes possess different molecular velocities; hence in a chemical reaction under favourable conditions between, for example, a gaseous mixture of isotopes and a solid substance, the rapid molecules will collide more frequently with the solid substance, so that isotopes should have different reaction-velocities and the separation of an isotopic mixture should be possible, even by 'chemical methods'.

"Strictly speaking, none of the properties of isotopes which can be determined experimentally are identical. This is true even for the electrostatic field of the nuclear charge—that fundamental property in the classification of the elements—which up till now had been assumed to be equal in isotopes. For the nuclear charge can be obtained either indirectly by the determination of other properties; for this purpose the characteristic X-rays are particularly suitable, and here the differences mentioned in Section 1 will probably be observed, or, the direct electrostatic action of the nuclei on α-particles coming into their immediate neighbourhood can be determined, as Rutherford and his co-workers have done. Assuming sufficient accuracy of measurement, the influence of the different compositions of the nuclei of isotopes should then be distinctly observed.

"Theoretically the isotopes are identical only in the equality of the algebraic sums of the positive and negative constituents of their nuclei; in all properties accessible to observation differences are to be expected. According to the view that isotopes are not different elements but merely varieties of the same element a chemical element cannot be definitely characterized by any property and certain variations in their properties have to be admitted. The fact, however, that these variations are exceptionally small for some properties but easily measurable for others, makes it possible and desirable for practicable purposes to differentiate between the two following groups of properties of isotopes. On the one hand we have, in addition to the nuclear charge, the qualitative behaviour, the general structure of the spectrum, the atomic volume, the molecular solubility of the salts, the boiling-point and melting-point and several other properties which, although not mentioned here, have already been investigated, e.g. the electro-chemical potential, the refractive index of solutions of the salts, the rate of diffusion in solution, the magnetic susceptibility, the specific electrical resistance in the metallic state and probably many other properties. Within a high degree of approximation all these properties are equal for all varieties of an element, i.e. for all members of a pleiad and their mixtures. Practically speaking they can be regarded as characteristic of the element, and can be called 'pleiad properties' or colligative properties of the isotopes. On the other hand we have the atomic weight and with it the general behaviour in quantitative analysis, the radioactive properties, the density in all states of aggregation, the solubility expressed in grams/litre, etc., which for every member of a pleiad and for every mixture of isotopes, for example, every variety of lead, have different values. These are the individual properties, and permit of a finer differentiation of matter than do the pleiad properties. It is obvious from the above that there exists no sharp limit between these two groups of properties," p. 104.

"The most important result of the investigations surveyed is the proof that the chemical elements, hitherto regarded as homogeneous are composite. Many of them are mixtures of isotopes, so that the atomic weight (combining weight) of these elements, hitherto so fundamental, is only a mean value of other numbers possessing a much deeper scientific significance. In their turn the single atoms have come to be regarded as being built up from the two simplest atoms, hydrogen and helium, in a way quite different. The latter is most probably formed from four atoms of hydrogen in particularly close combination; and Prout, over 100 years ago, similarly assumed that hydrogen could be regarded as the constituent of all other atoms. But even the hydrogen atom is composite, consisting as it does of one atom of positive, and one of negative, electricity; electricity then is the long-sought primordial matter, of which all elements and consequently the whole material world are constructed," p. 114.

*Wilder D. Bancroft*

**Die Methoden der Organischen Chemie.** *By J. Houben (and collaborators). 17 × 26 cm; pp. xxviii+1840. Leipzig: Georg Thieme, 1925. Price: paper 66 marks, cloth 75 marks.* With the exception of those whose long experience serves them better than any practical text-book, there can be few organic chemists who do not turn up "Houben-Weyl" as a matter of course as each fresh problem is encountered. The publication of a new and enlarged treatise on the practical methods of organic chemistry is therefore an event of interest.

The first volume, here under review, deals with the analysis and physical examination of organic compounds and with the physical processes used in their preparation and purification. It makes, perhaps, a special appeal to those whose problems often demand resort to physical methods. *Within its 1300 pages, copiously illustrated, are contained detailed* accounts of the standard methods for estimating elements and radicals in organic compounds, of the common operations of preparative work (including the handling of gases and colloids), and of the methods for determining such data as melting point, boiling point, solubility, density, molecular weight, optical rotation, refractive index, conductivity, hydrogen-ion concentration, intensity of fluorescence, heat of combustion, ignition-temperature, viscosity, etc.

In view of the recent introduction of Pregl and Dubsky's micro-analytical methods into many University and other laboratories the chapter on micro-analysis, written by Dubsky, will be widely read, and will doubtless do much to disseminate knowledge of these rapid and elegant processes, some skill in which will in future constitute a necessary part of the manipulative equipment of all research workers.

It is perhaps the inevitable consequence of an attempt at completeness that parts of the volume are of interest mainly to specialists, who, as a matter of fact, would probably turn for their information to special sources rather than to a general text-book of practical organic chemistry. Such, for example, are the sections on ultra-filtration, adsorption-analysis, interferometry, goniometry and the analysis of dyes. Yet, in spite of the wide scope of the work there are some surprising omissions. Thus it is curious that, in the chapter entitled "Erhitzen", one may read a detailed description of all the methods that have been devised for maintaining a constant level in a water-bath, but may look in vain for some simple directions for fixing up an electrically controlled thermostat. Considerable space is devoted to description of the old methods of plotting "absorption spectra", and, regardless of the fact, for years past generally recognised, that such determinations are meaningless from the quantitative standpoint, no account is given of the spectra-photometric apparatus whereby the variation with wave-length of the intensity of the light-source and sensitivity of the plate, and the variable absorption of the solvent if one is used, can be automatically eliminated and a quantitative absorption curve obtained. The section on magnetic rotation might well have been extended in view of the ease with which the ordinary polarimeter can be adapted for the determination of magnetic rotations. But these and other lacunae will probably not often be encountered when referring to the book in the course of ordinary laboratory practice, and it remains true that the new "Methoden" contains a wealth of useful information the collection of which under one cover is of great importance for all organic chemists. The succeeding volumes of this work will be awaited with interest.

*C. K. Ingold.*

**A Course of Metallurgy for Engineers.** *By F. C. Thompson. 15 × 22 cm; London: H. F. and G. Witherby, 1925. Price: 25 shillings.* Professor Thompson's book is the outcome of many discussions with Mr. W. E. W. Millington. It represents the cooperation of a metallurgist and an engineer and is designed as the title indicates, to instruct the engineer as to the nature of the metals used by his profession. As the author points out in his preface, although the Institution of Mechanical Engineers has by means of its Alloys Research Reports added materially to metallurgical knowledge over a long period, engineers were until recently, for the most part, deplorably ignorant of the structure and nature of the metals and alloys which they use.

The first chapter contains a brief account of the principal commercial ferrous alloys and their manufacture. Then follows one on the composition and structure of steel. The four succeeding chapters deal with ingots and ingot defects, the heat treatment of steels and the hot and cold working of steel. A special chapter is devoted to tool and case-hardening steels and another to cast iron. The latter section of the book is concerned with the principal non-ferrous industrial alloys, *e.g.* brass, bronze, alumnium alloys, and bearing metals.

Other books have been written purporting to instruct the engineer in metallurgical knowledge. None of them, however, have been quite of the right kind. For the most

part, they have not credited him with much intelligence. On the one hand, they have given him, at unnecessary length, elementary metallurgical knowledge of a kind that he does not particularly need, and, on the other hand, they have generally failed to tell him things which would be of the utmost importance to him. Although Professor Thompson is very modest about his book and writes that he "is woefully aware of its defects", we think that he has written by far the most useful book for engineers that has yet been published. He has assumed that the engineer possesses average intelligence in following a scientific argument. He has not overburdened his book with technical terms and for this the engineer will be grateful. The treatment throughout is scientific but the illustrations are always drawn from alloys well known and widely used. The engineer who is really interested in the structure and properties of the metals that he uses, will find this book of very real interest and value. He will probably need to supplement the knowledge obtainable in it with that contained in a good text-book of metallography written rather more from a metallurgical standpoint. Particularly will this be the case in reference to the interpretation of equilibrium diagrams which are only treated incidentally in the book under review. The equilibrium diagram is the sheet anchor of the metallurgy of alloys and we think the author might with advantage have given a rather fuller and more direct treatment of this branch of the subject. It is possible that Mr. Millington will not agree with this criticism, but it is perhaps worthy of being taken into consideration.

It is very unfortunate that the price of this book is so high. It ought to be very widely studied by engineers but unless its price is considerably reduced we fear that this is not likely to be the case. Could not the publishers, in a subsequent edition, reduce the price from 25/ to 15/? It will make all the difference to the sale of the book.

*H. C. H. Carpenter.*

**The Textile Fibers.** *By J. Merritt Matthews. Fourth edition, rewritten and enlarged. 23 × 16 cm; pp. xviii+1053. New York: John Wiley and Sons, 1924. Price: $10.00.* The third edition was reviewed nearly twelve years ago (**18**, 454). The present one is fifty percent larger than its predecessor, besides differing in other ways. The chapters are entitled: general classification; asbestos as a textile fiber; wool, its origin and classification; physical structure and properties of wool; the chemical nature and properties of wool and hair fibers; action of chemical agents on wool; reclaimed wool and shoddy; minor hair fibers; silk, its origin and cultivation; physical properties of silk; chemical nature and properties of silk; the vegetable fibers; cotton; the physical structure and properties of cotton; constituents of raw cotton; cellulose and its chemical properties; chemical properties of cotton; chemical treatment of fabrics for waterproofing and flame proofing; mercerised cotton; the minor seed hairs; artificial silks; linen; jute, ramie and hemp; analysis of fibers and yarns in fabrics.

Spun glass is made in a very simple way. "Solid glass rods, about 2 ft. 6 ins. long and of the thickness of a lead pencil, are made of pure soda glass that contains no adulteration of lead or other metal. The absence of lead and adulterations gives the quality of perfect flexibility to the fiber. On a simple desk is mounted a Bunsen burner or gas flame and blowpipe. By the side of the desk is mounted an ordinary bicycle wheel, minus the rubber tire, that revolves rapidly and regularly at rhythmic speed under power furnished by a small electric motor. A girl sits at the desk, melts the end of the glass rod in the flame of the gas burner, draws it to a thread and throws the thread around the wheel. If the thread breaks, she must repeat the process; if not, she slowly revolves the end of the rod in the constant flame, and it is automatically spun to a very thin filament. The hank of thread on the wheel, when it has assumed the dimensions of a bicycle tire, is taken off. Separated with the fingers, it curls and fluffs out like wool if the thread is sufficiently fine. It is packed in the hank as glass cotton, in the fluff as glass wool, and in the compressed form as glass wool or cotton according to the fineness of the fiber. The cheaper grades of spun glass formerly came from Germany; it is claimed that the Italian article is superior," p. 11.

"There can be little doubt that there is a definite relation between the softness of the asbestos fiber and the quantity of water of constitution it contains; 14.38 percent water has been found in very silky fiber, while a harsh, brittle sample gave only 11.7 percent.

This will explain the extreme brittleness of the amphibole fiber, some samples of which contain only 5.45 percent water. The effect of high temperatures on very soft fiber also demonstrates this fact. When part of the combined water has been driven off by excessive heat, the fiber loses its flexibility and becomes harsh and brittle; and the variations in strength and silkiness in various deposits of the mineral are best explained by assuming that the water content was originally nearly the same in all cases, and that the movement of associated rocks or the injection of molten rock has furnished sufficient heat to drive off part of the water," p. 31.

"The felting action of wool, however, must not be attributed solely to the interlocking of the scales on the surface of the fiber. This has been the general conception in the past, but the examination of felted fibers does not bear out this idea. If the felting were altogether due to the interlocking of the scales it would require that two fibers be brought together in opposite directions in order to have this interlocking take place. As a matter of fact, in a piece of felted cloth for example, the wool fibers are located in all manner of directions and only a small percentage of them would be juxtaposed in such a manner as to furnish the necessary conditions for felting by interlocking of the scales. The felting is largely due, in the first place, to the intermeshing of the fibers themselves by becoming twined round one another, and this condition is especially enhanced by the curl in the fiber. Again, in the felting operation of milling or fulling, the surface of the fiber no doubt is softened in such a manner that fibers coming in contact with one another and, under the influence of heat, pressure and the chemicals employed, become more or less glued together. As the substance of the scales of the fiber is in reality a form of glue or gelatine, it is easy to understand why this condition can readily be induced by the felting process. Microscopic examination of the intimate structure of felted fibers indicate a strong surface cohesion rather than a mere interlocking of the scales. This also explains why it is perfectly possible to felt wool fibers that do not exhibit well-defined free scales. Hair, though it has the surface scales, does not have these scales arranged so as to show very much free edge projecting from the surface of the fiber; also these scales are hard and not easily softened to the point where strong cohesion may take place between fibers in contact with one another. If, however, the surface scales are softened so that they become somewhat mucilaginous in character, then by heat and pressure hair fibers may also be felted much in the same manner as ordinary wool fibers," p. 91.

"When wool is treated with a four percent solution of formaldehyde it is made much more resistant to alkalies and also shows a decreased affinity toward dyestuffs. Kann has described this use of formaldehyde as a means of dyeing wool with vat dyes in which a strongly alkaline bath is employed. The formaldehyde may be added directly to the alkaline bath. It is also claimed that sulfur dyes may be applied to wool in the same manner. Wool treated with formaldehyde is said to be much more resistant to the action of steaming than untreated wool. There have been many attempts to devise a method of treatment whereby the wool fibers could be protected from the destructive action of the alkali which is required in dye baths employed for these colors. Kann has taken out a number of patents during the last few years describing the use of formaldehyde for this purpose. It was first recommended to employ a four percent solution of formaldehyde for the treatment of the wool, but it is now pointed out that the use of such a solution, although protecting the wool to a considerable degree against action of the alkali, decreases greatly its affinity for dyestuffs. In later patents formaldehyde was added to the alkaline dye bath, and it was eventually discovered that only small quantities of formaldehyde are necessary to produce the desired effect. When used in these proportions the formaldehyde does not decrease the affinity of the wool fiber for dyestuffs," p. 166.

"As regards the influence of tin weightings, whether simple or mixed, upon dyeing, they are all perfectly suitable for any color, and both for cuit and souple silks. The black-dyer is less dependent than others on the weighting, as he uses substances like tannin and iron salts, which themselves act as loaders. These bodies are barred to the color dyer for the most part as they darken the fiber, and he is confined to bleached tannin, alumina, and colorless salts. Tannin is dear, always darkens the fiber, and does not give enough weight

alone, although it gives far more than alumina or salts. In short, modern silk-dyeing is impossible without tin weighting. Tin can be applied at any stage of the preparation of the silk, or raw silk, to souple, or to boiled-off silk. Tinned raw silk can be scoured, without losing more tin than corresponds to the percentage of bast removed. It can be mordanted with iron, alumina, or chrome, and can be further weighted with Prussian Blue, and finally it can be dyed with natural coloring matters, or the coal-tar dyes.

"Silk-weighting is the basis of modern silk-dyeing. Any serious struggle against it is a hopeless fight against the natural development and progress, is based on mistaken ideas, and can only be useful against an exaggerated and irrational loading of the fiber," p. 312.

This argument is rather sophistical. The amount of tin that is added does not stand in any relation to the amount needed for dyeing. The weighting of silk must be judged on its merits and not with reference to dyeing.

Byssus "is also known as 'sea-silk' or 'pinna silk,' and is obtained from a marine mollusk, *Penna nobilis*, and related varieties. The shellfish possesses a long slender gland which secretes woolly fibers known as the *Byssus* or 'beard'. These fibers are of a brown color and are 4 to 6 cm. in length. The brown color is said to be due to an external covering which when removed leaves a colorless fiber. Sea-silk is somewhat used in southern Italy and in Normandy for the making of various ornamental braided articles. Though this fiber somewhat resembles silk in appearance, it is easily distinguished by the presence of natural rounded ends. The fibers vary considerably in diameter (10 to 100 microns) and are elliptical in cross-section, and are often twisted. Fine longitudinal striations are apparent, but as the fiber is solid no empty lumen or air canals are present. The finer fibers are smooth, but the coarser ones are rough and corroded. Frequently very delicate fibrils are to be observed branching from the larger fibers.

"The manufacture of materials from pinna silk was carried on at Taranto in Italy. The 'fish wool' (as it was called) was washed twice in water, once in soap and water, and again in tepid water, and finally spread out on a table to dry. While yet moist it was rubbed and separated with the hands and again spread on the table to dry. When quite dry it was drawn through a wide bone comb and then through a narrow one. It was then spun into a yarn with distaff and spindle. As it was not possible to procure much of the material of good quality the manufacture was limited to a few articles such as gloves and stockings, and these were quite expensive. The fabrics were very soft and warm and of a brown or glossy gold color," p. 316.

"It may be seen from these results of microscopic investigation that the behavior of the fibers on swelling in water is very remarkable and distinctive, and that in this particular very essential differences exist between vegetable and animal fibers.

"The investigation helps to explain the fact why ropes shorten when left in water. Fibers which are not stretched or are only slightly so, are arranged in ropes in permanently fixed spirals. Since the fibers can only be lengthened but slightly, or not at all, while they are thickened 20-25 percent by swelling, the rope as well as the single twisted fibers must become shortened. If the spiral fibers are very elastic, as is the case of the animal fibers which may be stretched 5 to 36 percent in the moist condition without breaking, then the cylinder composed of them will shorten but slightly on swelling (or even none at all), because the spirals are capable of being lengthened. Thus it has been observed that a hemp rope will shorten 8 to 10 percent, whereas a silk rope will shorten only 9.24 to 0.95 percent. Furthermore, a twisted single vegetable fiber will shorten only slightly, whereas it is easy to understand that a twisted animal fiber will perhaps become lengthened, while a silk cord is shortened," p. 346.

"Cellulose acetate is, for instance, unique in its dyeing properties, in that with ordinary methods it can be dyed only by means of basic dyes, which are among the most fugitive of coloring matters; direct cotton colors it refuses to take up, and the dyeing of fabric composed of cotton and artificial silk with direct colors, a very usual procedure, is not possible in the case of acetate silk. If this is attempted with acetate silk, the cotton takes up the color normally, but the acetate combines only with the basic impurities in the dye, with the result that the former may be the desired navy blue while the latter is perhaps a dirty yellow

shade, or while the former is black, the latter is brick-red. When dyeing is attempted with vat colors of the indanthrene type, which are coming into great demand on account of their remarkable fastness and consequent suitability for washable materials, cellulose acetate silk sometimes is partly decomposed, and loses its luster and silk-like properties. Considerable effort has been made to devise methods for the satisfactory dyeing of acetate silk with substantive dyes, and it has been found that a treatment of the fiber with a solution of caustic soda (saponification) previous to dyeing gives very good results without materially affecting the quality of the silk. It is understood that the manufacturers of this silk now place the treated material on the market ready for dyeing," p. 707.

"The differences experienced in the dyeing of different forms of artificial silk are of interest. The nitro or collodion silks have a strong affinity for basic dyes and unless care is used the colors will be uneven. The cuprate silks have less affinity for basic dyes, and for the production of full shades it is necessary to mordant with tannic acid. The direct cotton dyes give the best results; sulfur dyes and vat dyes may also be used but will generally injure somewhat the luster. Viscose silk is similar to mercerised cotton in its affinity for dye-stuffs. The acetate silk as at first produced could not be dyed satisfactorily as the cellulose acetate was impervious to water, but the acetate silk now produced is partially saponified and contains hydroxyl groups which give the silk a much greater affinity for dyestuffs. Cellulose acetate silk has but little affinity for the direct cotton dyes, and in order to dye with these colors special treatment must be resorted to, which consists of working the silk in a bath of caustic soda, or in some cases the caustic soda may be employed directly in the bath with the dyestuff. This treatment does not seem to have any effect on the material nor to effect the luster. The basic dyes have a direct affinity for acetate silk and no mordanting is necessary. Many of the acid dyes are also useful for acetate silk. The new series of dyestuffs discovered by Green and known as "Ionamines" have a remarkable affinity for acetate silk and may be dyed directly on that fiber," p. 710.

"Marine fiber is a recent product obtained by dredging in the shallow water of a gulf in South Australia. Chemically it is a hydrated lignocellulose, giving the typical reactions of lignin. Microscopically it is very similar to New Zealand flax. From this it is to be concluded that the fiber is not of marine origin, but has been produced by the natural retting of a land plant, which has become submerged by the sea. Owing to its lignified character it dyes directly with basic dyes and some acid dyes, but has little affinity for substantive dyes. The fiber is brittle and has but little strength.

"Marine fiber has its origin in the leaves and stem of *Posidonia australis*. It is a submerged marine flowering plant and the enormous beds of the fiber which have been discovered appear to be due to the covering of the dead bases of the leaves and stems by the shifting sand which serves to preserve the fiber from decay. In the mass it is pale brown and somewhat lighter in color than cocanut fiber. In is estimated that the workable areas of South Australia alone would furnish 4,500,000 tons of the material," p. 807.

"Solidonia fiber is a name given to a vegetable fiber brought out in Germany as a wool-substitute. It is supposed to be a fiber derived from an African plant similar to China grass, and it seems to be very similar to ramie. It is a very fine fiber and has a screw-shaped form which makes it somewhat resemble wool. The length of the fibers varies from 2.5 to 4 ins. in length in medium grades, while the finer grades reach a length of 6 ins. According to Valdenaire, the solidonia fiber when examined under the microscope shows filaments having branches and striations, and also has a large central canal or lumen of a yellow color. The Vetillard reagent colors the fibers a greenish red, inclined to a violet. The fibers obtained from the nettle, which are somewhat similar to solidonia, are stained blue by the same reagent. In the raw state solidonia is of a gray color, similar to flax, but is bleached very easily. It acts the same as cotton in the presence of dyestuffs and the dyeing operation is the same. The property possessed by solidonia of absorbing perspiration without creating a sensation of cold on the skin, enables it to be mixed with wool to advantage in the manufacture of knit goods.

"Solidonia is converted into yarn by either the carded woolen or worsted process and is spun by the worsted process not finer than 36's (cotton count). Up to the present time

the material has been used for knit goods, passementerie, in mixtures with short wool for dress goods and cheviots and in mixtures with long wool for imitation worsted.

"In Germany, solidonia gained a wide field of use on account of the shortage of wool during the War. As a substitute for linen, solidonia has been used in Germany for the manufacture of table linen of beauty and strength. It has been used for machine belting. German hosiery and underwear mills have produced from it socks and stockings which are difficult to tear, and unshrinkable underwear, and sporting jackets of fine quality and strength.

"The German woolen mills have manufactured an army cloth composed of 75 percent wool and 25 percent solidonia, which, it is asserted, surpasses in tensile strength any pure wool cloth. Similar results are claimed with respect to papermakers' felts, which, with a percentage of solidonia mixture, show a considerable increase in strength. Furthermore women's and men's clothing composed of half solidonia and half wool or shoddy, especially in piece-dyed goods, have found a ready market. In textile circles in Germany it is declared that there is an unlimited field for the use of this fiber. Previous to the War the price of solidonia in Germany was two-thirds the cost of good staple wool," p. 836.

While the author seems to have kept up pretty well so far as the technical developments are concerned, his knowledge of general theory has not gone much beyond the undergraduate stage. He speaks of alpha, beta, and gamma oxycelluloses, p. 538, as though they might exist. He believes in an alkali cellulose as a definite compound, pp. 505, 581, and ascribes mercerization to the intermediate formation of this substance. His views on dyeing, pp. 145, 550, are Botticellian in their primitiveness. One must differentiate sharply between the subjects on which the author is an authority and which constitute the greater part of the book, and the occasional ones on which he merely holds forth.

*Wilder D. Bancroft*

**An Introduction to Organic Chemistry.** *By Alexander Lowy and Benjamin Harrow 24 × 16 cm; pp. ix+389. New York: John Wiley and Sons, 1924. Price: $3.00.* The authors have tried to include "not only the well-recognized basic principles of organic chemistry, but also its more recent and more important applications; the entire story being woven together into a simple and readable narrative. The authors have also kept in mind the many connecting links that bind organic chemistry to a number of other sciences,—to medicine, dentistry, pharmacy; to agriculture; to the biological sciences; hence, the inclusion of such chapters as those dealing with lipoids; nucleoproteins and their decomposition products; the chemical changes which foodstuffs undergo in the body; plant and animal pigments; enzymes, vitamins and hormones; organic compounds of arsenic and other metals; dyes and strains, etc."

As a typical instance of what they are trying to do, let us take a paragraph, on p. 178. "In diabetes, the poisonous 'acetone bodies' or 'acid bodies,' which are so often produced, are derived from fats. These 'acetone' bodies include butyric acid, $\beta$-hydroxybutyric acid, acetoacetic acid, and acetone. The acetone is a by-product obtained probably from acetoacetic acid by the loss of $CO_2$. It would seem as if the diabetic has not only difficulty in oxidizing glucose, but also in completely oxidizing fats; the fats in his case are oxidized to the four-carbon stage and no farther. Working with the knowledge that the naturally-occurring fats all contain an even number of carbon atoms, and stimulated by Knoop's theory that fatty acids are oxidized in such a way as to lose two carbon atoms at each stage, Kahn has synthesized an odd-carbon fat—from margaric acid, $C_{16}H_{33}CO_2H$, a $C_{17}$ acid—which is said to produce 'acetone bodies' when given to the diabetic, because in the oxidation of this odd-carbon fat, the four-carbon acids are avoided; thus

$$C_{17} \longrightarrow C_{15} \longrightarrow C_{13} \longrightarrow C_{11} \longrightarrow C_9 \longrightarrow C_7 \longrightarrow C_5 \longrightarrow C_3 \longrightarrow C_1"$$

On p. 307 there is a table giving the chief known constituents of thirty-nine essential oils. What the authors planned to do was worth doing. If the performance is not up to the level of the dream, that does not make the dream any less beautiful. Portraits are given of Grignard, Pasteur, Emil Fischer, Kekulé, Gomberg, Backeland, Remsen, Perkin, and Baeyer.

*Wilder D. Bancroft*

# FOURTH REPORT OF THE COMMITTEE ON CONTACT CATALYSIS[1]

BY HUGH S. TAYLOR

It is the object of the present report to review the problems of contact catalysis as set forth in the First Report of the Committee, in order to estimate how far, as a result of research during the last four years, these problems have approached to a definite solution; an attempt will be made to set forth a point of view whereby the various phases of the problem of contact catalysis may find a unified theoretical treatment and to outline, as far as possible, the problems for future work which this suggests. No complete survey of the year's catalytic literature has been made, because it is felt that such a survey can profitably be made at less frequent intervals.

## The Mechanism of Catalytic Action

In the First Report of this Committee two distinct types of contact catalysis were apparently indicated; in the one case, catalysis was accompanied by the formation of a definite intermediate compound, while in the other case, catalysis was preceded by adsorption with activation. Examples were cited in support of both types. It was definitely pointed out, however, by Mr. Bray, that on the borderline between the two, cases might exist in which there might be indefinite intermediate compounds which could not be ascribed to either one or the other. Precision was given to this intermediate type by the example of cupric chloride as a catalyst for the Deacon chlorine process. Mr. Bray pointed out that it was not necessary to assume that a definite oxychloride of copper is produced in the conversion of hydrogen chloride and oxygen to chlorine and water. It was only necessary to assume that an exchange of oxide and chloride ions occurred at various points in the solid cupric chloride lattice[2]. The extent to which such an exchange will occur will obviously depend on experimental conditions such as oxygen and chlorine concentrations, temperature and the like. It would only be a fortuitous circumstance if these were such that on the average, half the chloride ions were replaced by oxide ions; nor, in rapid reactions, could the change be expected to extend much beyond the surface. From the subsequent discussion, it will emerge that the probable state of the surface at any moment during the change will be such that some of the lattice positions normally occupied by chloride

[1] Report of the Committee on Contact Catalysis of the Division of Chemistry and Chemical Technology of the National Research Council. Written by Hugh S. Taylor, assisted by the other Members of the Committee: Messrs. H. A. Adkins, E. F. Armstrong, W. C. Bray, D. W. Brown, R. F. Chambers, C. G. Fink, J. C. Frazer, E. E. Reid, and W. D. Bancroft, Chairman.

[2] The difficulty raised in the First Report as to anhydrous cupric sulphate as a catalyst for this reaction does not, in reality, exist. Dr. R. A. Beebe has shown that passage of hydrogen chloride gas alone or admixed with air over solid cupric sulphate at the temperature of the Deacon chlorine reaction results in the quantitative conversion of the sulphate to chloride. The experimental results bearing upon this will be published elsewhere. H.S.T.

ions in solid cupric chloride are momentarily occupied by oxide ions, the actual positions occupied by oxygen undergoing continuous change. The catalytic activity of copper chloride would then be attributable to the ease with which such exchange of ions proceeds. It is of interest to record this newer aspect of the matter since the choice of copper chloride as a catalyst was originally made from theoretical considerations, it being observed that in the case of the copper salt the energy involved in the change from oxide to chloride was a minimum. It is necessary to insist, as pointed out by Professor Bancroft that no stoichiometric relations hold for such cases—in contrast with other well-defined cases of intermediate compounds where stoichiometric relations hold rigidly. The non-stoichiometric cases are therefore best treated in the manner usual in the treatment of adsorption at surfaces.

*Adsorption and Activation.*—It was abundantly evident in the First Report that capillary condensation was not the origin of catalytic change. Catalysis could not be ascribed to the increased concentration consequent on adsorption processes, nor could alternative modes of reaction at different surfaces be explained by such concentration increases. Experimental measurements on adsorption by a variety of catalytic agents, metals, oxides and salts, the variation of the extent of adsorption with temperature, pressure, form of the catalyst and support material, as well as on the thermal magnitudes involved in such adsorption processes[1], have revealed that the adsorptions involved in catalytic change are not capillary condensation phenomena but are, on the contrary, specific in character, determined by the catalyst and by the gas, involving energy changes considerably greater than those demanded by liquefaction phenomena and approaching in magnitude those common to mild chemical reactions. The results obtained conform, in the main, though with important divergences in detail, to the concept, developed by Langmuir, that the adsorbed gas is held chemically by the unsaturated atoms at the surface of the solid. In broadest outline, Langmuir's point of view may be stated in his own words: "The surface of the metal is thus looked upon as a sort of checkerboard containing a definite number, $N_o$, of spaces per square centimeter. The number of elementary spaces, $N_o$, is probably usually equal to the number of metal atoms on the surface. But this is not essential, for, we can imagine cases in which each atom holds, for example, two adsorbed atoms or molecules, so that we should then have twice as many elementary spaces as metal atoms on the surface."

Langmuir detailed in his paper on the adsorption of gases by plane surfaces of mica, platinum and glass[2], the theoretical treatment of such adsorption processes, and demonstrated that his experimental results confirmed the theory in its simpler aspects. In its more complex aspects (e.g. Cases II and IV of his theoretical treatment), in which the surface may contain several kinds of elementary spaces and may adsorb several different numbers of adsorbed

[1] A résumé of such experimental data has already been given in the Third Report: J. Phys. Chem. **28**, 921-933 (1924).

[2] J. Am. Chem. Soc., **40**, 1361 (1918).

atoms or molecules, the theoretical equations are so complex that no satisfactory check on their accuracy can be expected from the form of the adsorption isotherms or isochores. The writer, has pointed out, however, that in the data accumulated on adsorptions of different gases by catalytic agents, their variation with temperature and pressure, the effect of catalyst poisons on adsorption and reaction velocity, a very definite proof of the composite nature of the catalytic reaction surface can be achieved. The arguments may be briefly summarized.

*Varying Saturation Capacity of a Surface for Adsorbed Gases at Varying Temperatures.*—The data of Gauger and Taylor[2] on adsorption of hydrogen by nickel at varying temperatures showed that, at each temperature, an upper limit to adsorption capacity was reached beyond which further increase of pressure brought about no further increase in adsorption. The upper limit of adsorption was, however, different at different temperatures. Thus, with a given sample of nickel, at 25°C., saturation was reached at 75 mm. pressure and a further ten-fold increase of pressure did not alter the adsorption (8.7 ccs.) by more than 1 per cent, the limit of experimental accuracy. At 305°C. saturation was reached at 250 mm., but, at this temperature, the adsorption was only 5.4 ccs.

Terwen[3] has sought an explanation of this varying maximum of adsorption at different temperatures, by assuming two modes of adsorption of hydrogen by the nickel atoms in the surface. At low temperatures the gas is assumed to be adsorbed as the molecule $\left(-\mathrm{Ni}\begin{matrix}\mathrm{H}\\ \mathrm{H},\end{matrix}\right)$ at high temperatures as atoms (−Ni−H). Terwen points out that the data of Gauger and Taylor indicate that the maximum adsorption at high temperatures does not fall below one half of the observed adsorption at low temperatures and seems to be approaching this half-value as a limit. It should be pointed out that other gases, for example, carbon monoxide on copper, show the same varying saturation adsorption with temperature. Since there can be no question of atomic linkages in this case it would be necessary to assume that at low temperatures one atom of copper adsorbs a molecule of carbon monoxide and that at high temperatures two atoms of copper are required. In this way the experimental facts could be visualised, but proof would be difficult. Terwen suggests that proof of his point of view might be obtained from determinations of the temperature coefficient of the heat of adsorption of hydrogen, since this should change markedly with change in the type of linkage. Experimental data on this point are now being sought in Princeton. Terwen also suggests that Gauger's data[4] on the critical potentials of hydrogen adsorbed on nickel indicate the existence of atoms and molecules on the catalyst surface. Gauger's measurements are being repeated in Princeton since his experimental method is not

[1] Proc. Roy. Soc., 108A, 105 (1925).
[2] J. Am. Chem. Soc., 45, 920 (1923).
[3] Chem. Weekblad, 21, 386 (1924).
[4] J. Am. Chem. Soc., 46, 2880 (1924).

entirely free from objection. At the same time the effect of temperature on the results will be studied.

While Terwen's conclusions are in agreement with the adsorption data, they are difficult to reconcile with the data on poisoning and reactivity. On his view of an equilibrium between adsorbed atoms and molecules, the effect of a poison would be to cut down the total surface, but without altering the ratio of adsorbed atoms and molecules. The effect ought, therefore, to be proportional to the poison present. We shall show that abundant experimental evidence now exists that this is not always the case, that poisons reveal a varied activity of surface atoms. Consequently, the varying saturation adsorption of the catalyst surface at varying temperatures constitutes, in our view, contributing evidence in support of the view that the various atoms in the surface have varying adsorptive capacity and consequently varying catalytic activity. This does not, however, exclude the possibility that there are varying modes of attachment of the adsorbate to the adsorbent, as postulated by Terwen.

*Varying Saturation Capacity of a Catalyst for Different Substances.*—Two examples will be cited, neither from the Princeton work, which contains many such examples. Hirst and Rideal[1] have found that copper shows saturation capacity for both hydrogen and carbon monoxide but, in their measurements, approximately 8.5 times as much carbon monoxide is adsorbed at saturation. Maxted has recently shown[2] that both lead and mercury ions are adsorbed by platinum sols and show maximum adsorptions not varying with increase of concentration. The lead ions are adsorbed, however, 3.5 times as much as the mercury ions, although there can be no great difference in the ion sizes. These cases are inconsistent with an assumption of unimolecular adsorbed films on surfaces the adsorptive capacity of whose constituent elements is invariable. Hirst and Rideal recognised this and suggested that multimolecular layers of the polar molecules of carbon monoxide might be formed. This represents a return to Bodenstein's original point of view. Such is not necessary. The experimental results are consistent with the assumption of a surface of variable adsorptive capacity, the fraction of which capable of retaining adsorbed molecules for measurable intervals of time varying with the gas. On such a view, a copper surface at saturation with hydrogen is relatively bare as compared with the same surface saturated with carbon monoxide.

*Varying Saturation Ratio for Adsorbed Gases on Different Preparations of the Same Catalyst.*—To illustrate this point the data of Hirst and Rideal may be compared with similar data obtained by Pease[3]. In both cases saturation of copper surfaces with hydrogen and carbon monoxide was observed. In Hirst and Rideal's case, the ratio $\alpha_{CO}/\alpha_{H_2}$ was 8.5. In Pease's case, the ratio was 2.86. Such a variable ratio with different preparations is quite inconsistent with an adsorbing surface of uniform adsorption capacity of the

[1] J. Chem. Soc., **125**, 685, 694 (1924).
[2] J. Chem. Soc., **127**, 73 (1925).
[3] J. Am. Chem. Soc., **45**, 2296 (1923).

constituent units. It demands the assumption of varying capacity of the constituent units, differing with variation in the mode of preparation.

*Varying Saturation Ratio on a Catalyst before and after Heat Treatment.*—Numerous examples in the Princeton work show that not only is the variable ratio secured by variation in the method of preparation but it may also be secured by heat treatment of a catalyst after the initial determination of the adsorption ratio. Thus, in the case of a copper catalyst adsorbing carbon monoxide and hydrogen, the effect of moderate heat treatment is to diminish the saturation capacity, the diminution being proportionately greater with the hydrogen, the less strongly adsorbed gas. It is evident therefore that the saturation ratio $\alpha_{CO}/\alpha_{H_2}$ will increase with heat treatment of the catalyst—a further index of varying adsorption capacity of constituent units of such a surface.

*Varying Saturation Ratio on a Catalyst before and after Poisoning.*—The same is true when the treatment involves poisoning. Thus, Pease[1] showed that poisoning a copper catalyst with mercury changed the saturation ratio $\alpha_{CO}/\alpha_{H_2}$ from 2.86 to 19 a change in the same direction as is produced by heat, and a further evidence of a composite as opposed to a uniform surface.

*Poisoning and Catalytic Reaction Velocity.*—Were the catalyst surface uniform, a poison would produce an effect on reaction velocity proportionate to the surface it covers. Pease and Stewart have shown[2] that this is not the case. Adsorption of 0.03 cc. of carbon monoxide on a copper catalyst capable of adsorbing 1.0 cc. of hydrogen at 1 mm. gas pressure reduced the rate of hydrogenation, not by 3 per cent, as the extent of adsorption would indicate, but by more than 90 per cent. The conclusion seems inevitable that the portions of the surface capable of adsorbing hydrogen are not all equally effective in promoting hydrogenation. Only a small fraction of the surface is relatively efficient in this reaction.

*Progressive Poisoning.*—Inequality in the catalytic efficiency of surface atoms at once suggests that control may be exercised on the catalyst whereby its activity may be suppressed in stages. This has actually been achieved in a research by Vavon and Husson[3] on progressive poisoning. They found that the hydrogenation of propyl ketone by colloidal platinum could be suppressed by the addition of a limited amount of carbon disulphide. The poisoned catalyst would, however, still effect the hydrogenation of both piperonal and nitrobenzene. A further addition of the poison in limited amount suppressed the activity of the catalyst in the hydrogenation of piperonal but not in that of nitrobenzene. Finally, with a large amount of poison, the remaining reaction with nitrobenzene can be stopped. One other combination of hydrogenation reactions was studied. Such evidence inevitably demands the assumption of a catalyst surface the catalytic activity of whose component

[1] loc. cit.
[2] J. Am. Chem. Soc., 47, 1235 (1925).
[3] Compt. rend., 175, 277 (1922).

parts is not uniform. The following theory of the catalytic surface may therefore be offered.

*A Theory of the Catalyst Surface of Variable Activity.*—The X-ray examination of metallic hydrogenation catalysts has shown that these catalysts, even when prepared at low temperatures, possess the definite lattice structure of the crystalline material. A granule of such a catalyst must, therefore, possess, in part, the ordered arrangement of the atoms found in crystalline material. The method of preparation of active materials suggests, nevertheless, that the ordered arrangement of the atoms has not been completely attained and that, here and there, on the surface of a partially crystalline material there are groups of atoms in which the process of crystallization is not yet complete.

The atoms in the plane surface of any face of the crystal, e.g., a face-centered cubic crystal of nickel, will be practically saturated by the neighbouring metal atoms in three dimensions, with the exception that there will be a certain degree of unsaturation towards the gas phase. In a sufficiently large plane surface of this type each atom will be identical in properties with the great majority of the others in the surface. There will be a certain variability in the surface fields of attraction with variation in the exposed face. The fields will be weakest in the closest packed faces, i.e., the 111 faces, stronger in the 100 faces and strongest in the 110 faces. Atoms in the edges of such a crystal will be one degree less saturated than the atoms in the surface, by reason of the fact that they are to a less degree surrounded by nickel atoms. For this reason they will possess stronger attractive forces for impinging atoms. Evidence for this is available in a study by Volmer and Estermann[1] of the growth of mercury crystals from the vapor. The crystals grow in the form of thin hexagonal leaflets the thickness of which is of the order of $1 \times 10^{-4}$ of the hexagonal face. From a quantitative analysis of the experimental observations Volmer concludes that molecules condensing on the face of the leaflets are held temporarily in the force field of the surface, retaining, however, their motion until they either (1) evaporate or (2) are attracted to, and held at, the edges of the surface or (3) through contact with other molecules form the nucleus of another lattice layer. This latter alternative only becomes important when the plates, by growth of the edges, have attained a length and breadth of 0.3 mm. This increased attractive force at an edge will be surpassed by that obtaining at a corner. In the incompletely ordered atoms the attractive force will progressively increase as the degree of saturation by neighbouring nickel atoms becomes less and less, until, finally, in atoms which are only held to the granule by one attachment e.g. Ni-Ni, the unsaturation of the metal atom and the attractive force for impinging molecules will become a maximum. The methods of preparation of active catalysts and the activation of inactive masses all tend to produce arrangements of atoms in which these varying characteristics are multiplied.

[1] Z. Physik, 5, 31, 188 (1921); 7, 1, 13 (1921); Z. physik. Chem., **102**, 267 (1922).

It is at once evident how this view of the composite nature of a catalyst surface is in harmony with the observations already made as to the adsorption characteristics of such catalysts. For, the ratio of faces to edges to corners and to extra-lattice atoms will vary with varying preparations and with heat treatment. The attractive force of a surface atom may be adequate to retain one gaseous molecule, whereas another gas would suffer a practically completely elastic collision. The less saturated atoms in the catalyst surface will be the preferred positions of attachment of catalyst poisons. Hence, the varying ratio of adsorption between poisoned and unpoisoned catalyst. Hence, also, a mechanism for progressive poisoning.

The present concept of the composite catalyst surface is more embracing than that stressed by Langmuir[1] in dealing with the problem of catalyst activation. Langmuir emphasises that the distribution of catalyst atoms more or less at random will vary the distances between adjacent adsorbed molecules over wide range and some of these distances will be exactly right for the reaction to occur at the highest possible speed'. Variation in the distances between catalyst atoms, otherwise identical, does not appear to be adequate to account for *all* the variations in adsorption characteristics of single gases recorded in preceding paragraphs. The present concept substitutes for varying atomic distances varying degrees of saturation of surface atoms, from those in a plane surface to those held to the surface by a single atom-atom linkage. With this varying degree of saturation in the lattice structure comes not only the varying attractions for impinging molecules but also a varying chemical reactivity. For, the outermost atoms of the catalyst granule, linked by a single bond to the solid mass, are the atoms of a solid body most closely resembling the gaseous molecule. Now, a gaseous nickel atom can attach to itself four molecules of carbon monoxide to form nickel carbonyl. It does not seem improbable, therefore, that the outermost singly-linked nickel atoms shall be able to take up three molecules of carbon monoxide, or three molecules the linkage of which to nickel is that obtaining between the metal and carbon monoxide. The possibility thus arises of both hydrogen and unsaturated body being attached to the same nickel atom in a single complex at a catalyst surface, thus ensuring a more intimate electronic association than could be secured by adsorption on adjacent catalyst atoms.

*Independent Evidence for the Theory.*—The theory of a catalytic surface which has been put forward is thus far an *ad hoc* hypothesis designed to fit more of the experimental facts now known than is possible with preceding theories. Experimental evidence that unsaturation of the surface such as has been postulated does exist would strengthen considerably its probability. Such evidence appears to be available from a recent research. Garner and Blench[2] have recently published data on the heat of adsorption of oxygen on charcoal. They have obtained values ranging from 50,000 calories at ordinary temperatures to the astonishing value of 224,000 calories at low pressures and

[1] Trans. Faraday Soc., 17, 618 (1922).
[2] J. Chem. Soc., 125, 1288 (1924).

450°C. The astonishing nature of this latter value is at once evident when it is remembered that the heat of combustion of solid carbon to gaseous carbon dioxide is only 94,000-97,000 calories. The heat of adsorption may therefore be more than twice as great as the heat of combustion of the solid body.

It is at once evident that on the basis of the theory put forward in the preceding section this high value is to be expected. The high value recorded would represent the heat effect produced by the interaction of oxygen with the atoms of carbon most detached from the main mass of the solid carbon. The process occurring will be intermediate between the interaction of gaseous carbon and oxygen in which no carbon linkages are broken and that of solid carbon and oxygen in which four carbon-carbon linkages are broken in the oxidation process. The combination of gaseous carbon and oxygen involves the abnormally high heat effect of 350,000 calories owing to the high heat of vaporisation of carbon or alternatively to the endothermic breaking of the carbon-carbon linkage[1]. The value obtained by Blench and Garner is intermediate between the values for the combustion of the solid and the gaseous forms, and constitutes experimental evidence for the existence of isolated extra-lattice atoms.

*Further Consequences of the Theory.*—From considerations similar to those just advanced it follows that the thermal data for materials having a high ratio of surface to mass should be of greater magnitude than those obtained with coarsely crystalline material. Bäckström in some unpublished calorimetric work has shown that finely ground Iceland spar has a higher heat of reaction with dilute acid than the coarsely crystalline material. Ray[2] found that the heat of solution in hydrofluoric acid of finely ground crystalline quartz was higher than that of the coarse crystals. Material smaller than 200-mesh evolved 32.46 kg. cals. as opposed to 30.3 kg. cals. for the coarse material. The greater solubility of finely divided materials such as barium sulphate indicates also a higher heat of solution of finely divided, as compared with coarsely crystalline, materials. It suggests that charcoal should have a higher heat of combustion than the more perfectly crystalline graphite. This is actually recorded in the literature, a value of 97000 calories as opposed to 94000 calories for graphite being obtained. Uncertainty has attached to the former figure owing to the difficulty of purification. But, on the basis of the present theory a definitely higher value should be obtained for charcoal and for all other materials in which the process of crystallization is not complete. Thus, the heat of oxidation of active catalytic copper or nickel in the incompletely crystalline condition here postulated should be definitely greater than that of coarsely crystalline metal. An attempt to establish this experimentally is being undertaken.

It is evident also that the initial rate of evaporation of such active catalytic metals should be greater than those of the bulk material, since the more

[1] Fajans: Verh. physik. Ges., 14, 324 (1912).
[2] Ray: Proc. Roy. Soc., 101A, 509 (1922).

unsaturated the atoms in the lattice, the greater should be their freedom in escaping into the vapor phase. This is in agreement with the high thermal sensitivity of active metal catalysts, their sintering at relatively low temperatures. It does not seem impossible that the vapor pressures of these materials may be actually determined. Furthermore, the theory leads to a semi-quantitative formulation of the sintering process which will be discussed in a later section.

The actual influence of the state of division on the properties of a material becomes much more pronounced when we come to deal with substances subject to dissociation. Thus, for example, taking the case of a dissociating oxide such as manganese dioxide, it seems fairly evident that the case with which the oxygen is given up by the oxide will depend to a large extent on the degree to which the material is in the ordered arrangement of the large crystal. With the various methods of preparation at low temperatures of extremely finely divided manganese dioxide it would be expected that a very considerable proportion of the oxide ions would be found in corners, edges, or filamentary projections of material. These oxide ions should show an abnormal tendency to split off from their neighbouring ions as they are in less constraint than the atoms in the surfaces or interior of a larger crystal. In other words such finely divided material should show an abnormally high dissociation pressure of the oxide, as compared with that of the coarser crystals. That this is experimentally realisable appears to be substantiated by the report of Whitsell and Frazer[1] on the properties of active manganese dioxide such as is used in Hopcalite preparations. Whitsell and Frazer note that "the loss of oxygen by such manganese dioxide is noticed even at room temperatures and in a wet sample, indicating a dissociation pressure of oxygen in the pure manganese dioxide *greater than the partial pressure of the oxygen in the atmosphere.*"[2] They record, also, that English[3] has found that "these oxides behave as solid solutions, the oxygen pressure varying with the composition of the mixture." This is exactly what would be expected of a manganese dioxide which is losing oxygen, first from exposed oxide ions and then less and less readily from the ions more and more saturated by ionic neighbours. The discrepancy between Whitsell and Frazer's observation of a manganese dioxide with a dissociation pressure, at room temperatures, greater than 150 mm. and that of Askenasy and Klonowsky[4], who found a dissociation pressure of 23 mm. at 382°C. is in entire agreement with the demands of this present theory of the nature of such active materials. It accounts for the exceptional oxidation activity of such oxides.

This concept of a dissociation pressure varying with particle size recalls immediately the results obtained by Kendall and Fuchs[5] on the dissociation of various mixtures of oxides. These authors established undoubtedly the

[1] J. Am. Chem. Soc., 38, 807 (1916).
[2] Italics are the present author's.
[3] Dissertation, John Hopkins University.
[4] Z. Elektrochem., 16, 104 (1910).
[5] J. Am. Chem. Soc., 43, 2017 (1921).

accelerated decomposition of silver oxide, mercuric oxide and barium peroxide in presence of other oxides. They claimed that the added oxide influences the dissociation pressure of the oxide. The present theory indicates in what manner the addition of oxides might promote increased dissociation pressure of the oxide. If the addition resulted, in effect, in a finer particle size by interspersing the added oxide more or less molecularly among the dissociating oxide an increased dissociation pressure should result. Their studies, therefore, merit further attention.

There is already a definite amount of evidence that the interspersal of one oxide in another very definitely alters the speed with which the latter can be reduced. Thus, as the Dewar-Liebmann patent[1] indicates, the presence of ten percent of copper oxide in nickel oxide very materially lowers the temperature at which reduction of the nickel oxide can occur. This patent claim was very thoroughly studied by Armstrong and Hilditch[2], who point out that "in order to obtain the reduction of the nickel at the relatively low temperature, the copper and nickel must, prior to reduction be intimately and chemically associated with each other. Simple grinding of nickel and copper compounds is of little use; to secure the effect the latter must be precipitated together before reduction." It is very evident that this latter conclusion is that which would be suggested by the present theory, in which smallness of particle size, brought about by intermixture of crystal lattices, would lead to higher reactivity.

A more striking example of this effect is to be noted in the recent patent literature. A patent to the Badische Anilin und Soda-Fabrik[3] indicates that, in the reduction of mixtures of copper oxide and zinc oxide, the reduction of copper oxide is always accompanied by simultaneous reduction of some of the zinc oxide, the more the greater the percentage of copper. The writer has made a brief test of this point and finds that in equimolar coprecipitated oxides of copper and zinc some reduction of the zinc oxide occurs when the reduction of the copper oxide is affected at 300°C. This is a striking increase in activity over that of zinc oxide alone.

It is easy to see how the present theory unifies the various points of view concerning catalysis, representing, on the one hand, the intermediate compound theory with definite compound formation, through the borderline cases where only a fraction of the catalyst lattice undergoes change of the definite compound type to the extremest cases where only a very few atoms, the extra-lattice atoms, by virtue of the fact that they are unsaturated by neighbours, are capable of combining with impinging atoms or molecules, the catalyst atom or molecule complex then further reacting with the second reactant, the extra-lattice catalyst atom being thereby regenerated. The extent of the surface which is active will be determined by the reaction which is under study and will vary from case to case. Langmuir's evidence is unequivocal that

[1] British Patent, 12981 (1913) and 15668 (1914).
[2] Proc. Roy. Soc., **102A**, 27 (1922).
[3] French Patent, 580905.

practically every atom in the surface of platinum is active in certain circumstances in promoting the catalytic oxidation of carbon monoxide. The monoxide strikes oxygen held on the surface of the platinum. The same is not true, however, of the oxidation of hydrogen-oxygen mixtures on platinum where there is distinct evidence of activation of the metal accompanied by a roughening of the surface, that is, the production of extra-lattice atoms in the sense of the preceding theory. It is probably from the quantitative data of the poisoning of such activated catalysts that the surest evidence of such varied activity of surface atoms will be obtained. We shall consider this aspect in more detail in a later section.

Armstrong and Hilditch[1] have suggested as a constructive extension of the preceding theory that the active atoms may be regarded as detached entirely from their association with the neighbouring metal atoms during the moment in which catalytic interchange is effected. The approximation of such extra-lattice atoms to the gaseous state suggests to Armstrong and Hilditch that the heat energy produced in the association of the reactants and catalyst atoms may suffice to effect this atom detachment. They thereby attain to a more definite conception of the "intermediate complex" of nickel, unsaturated body and hydrogen than they have previously been able to give. When the catalytic change is complete the nickel is again momentarily free and one of several things might happen:

I. The nickel atom might take part in further momentary unions with unsaturated molecules.

II. It might remain suspended as a nickel sol in the liquid.

III. It might become reattached to the solid surface.

In the last named case, with unsupported nickel, it would, by analogy with adsorption data, catalyst poisons etc., be supposed to migrate most easily to the most exposed portion of the surface, and a state of average similarity to the original catalyst would be maintained.

Armstrong and Hilditch find evidence in support of their suggestion in the presence of fine colloidal suspensions of nickel in hydrogenated oils and in the fine deposit of nickel found on the interior of iron or copper vessels used for the hydrogenation of liquids. They further cite the roughening of a relatively smooth platinum or other metallic surface during such processes as catalytic oxidation in a gaseous system as obvious evidence of the actual transference of atoms of the metal from one position of the surface to another.

Definite experimental evidence that such losses from platinum occur is evident from the early studies of Hulett and Berger[2] on the losses in weight from ordinary platinum foil and also from pure platinum when heated in air or in oxygen-containing gases. Table I records the results of successive heatings at two temperatures for periods of two hours each. The increased loss following the etching with aqua regia is especially to be noticed.

---

[1] Proc. Roy. Soc., **108A**, 111 (1925); Deuxième Conseil de l'Institut Solvay, April (1925).

[2] J. Am. Chem. Soc., **26**, 1513 (1904). See also Nahrwold: Wied. Ann., **35**, 116 (1888); Stewart: *ibid.*, **66**, 88 (1898); Holborn and Henning: Sitzungsber. Berlin Akad., **1902**, 936; **1903**, 245.

TABLE I

Platinum foil, 530 sq. cm. Heated in air.

| Temperature | Time of heating | Loss in wt. | Remarks |
|---|---|---|---|
| 900°C. | 2 hours | 1.6 mg. | |
| 900 | 2 hours | 1.4 | |
| 900 | 2 hours | 0.9 | |
| 1020 | 2 hours | 1.5 | |
| —— | —— | 220 mg. | Foil treated with aqua regia |
| 1020 | 2 hours | 5.6 mg. | |

Burnishing with fine pumice had the same effect as treating with aqua regia. Pure platinum, as used in thermo-couple work showed the same effect. At 810°C. successive losses in 2 hours were 0.13 and 0.10 mg. At 870°C. the loss was 0.6 mg. in 2 hours. At 795°C. after aqua regia treatment, the loss was not measurable in 2.5 hours. Heated in vacuo or in oxygen-free atmospheres, no detectable losses were observed.

That the forces of adsorption are tremendously powerful in promoting the disintegration of solid bodies is very evident from the results of a recent research by Volmer and Mahnert[1] on the solution of solid bodies in liquid surfaces. In an effort to elucidate the well-known phenomenon of the erosion of camphor, partially immersed in water, at the water-air interface, Volmer and Mahnert have studied the mutual behavior of benzophenone and mercury surfaces. Benzophenone lowers the surface tension of mercury and is therefore adsorbed by the metal. By means of a micro-balance, these authors showed that a given solid sphere of benzophenone lost less than $1.5 \times 10^{-7}$g. per hour by evaporation in air. If the sphere were allowed to touch a surface of mercury, 20 cms. in area, for the space of one second, the loss in weight was $8 \times 10^{-7}$g. From this it is readily calculable that the surface of the mercury removes benzophenone from the solid sphere more than 18000 times more rapidly than this occurs by evaporation in air at the same temperature. From the vapor pressure at this temperature it can be also calculated that the loss by contact with a mercury surface is eight times more rapid than evaporation of the benzophenone into a perfect vacuum. The authors showed also, by an ingenious experiment, that the process occurring was not a solution process. Mercury was allowed to drop from a fine capillary in such a way that, at the moment of dropping, the mercury droplet touched a sphere of solid benzophenone. The mercury was collected in a vessel below. The total surface thus underwent a tremendous decrease which resulted in the excess benzophenone from the surface layers of the droplets collecting on the mercury surface in the larger vessel. It is evident therefore that the attractive forces operating between a mercury surface and solid benzophenone have the same influence traced out by Hulett and Berger in the platinum-oxygen case just considered, where the rate of evaporation was greater in the presence of oxygen

[1] Z. physik. Chem., 115, 239 (1925).

than in a good vacuum. The same should be true for all metal-adsorption complexes such as are met in catalytic change.

The fact that the extent of surface active in catalytic processes varies with the reaction catalysed militates against complete acceptance of the Armstrong-Hilditch standpoint, since it is difficult to believe that, in readily catalysed reactions, where practically the whole surface is active, any such detachment of atoms is involved. In certain cases, it is possible to see the reaction occurring on the surface, as, for example, in the manufacture of formaldehyde from methyl alcohol where the alternative oxidation and reduction of the copper catalyst is revealed by the constant colour change. Nor does it seem likely, with reactions catalysed by the platinum metals in the form of sols at ordinary temperatures, that the loss of atoms from the catalyst surface is involved. The same applies also to the case of the refractory oxides acting as catalysts. Armstrong and Hilditch believe that the exothermic nature of the reactions should result in a progressive devaluation of the catalyst in consequence of a series of localised exposures to high temperatures. They have never observed this, probably because their work has been mainly with supported catalysts raised to moderate temperatures before use. With unsupported catalysts, however, such progressive devaluation as a result of reaction has been well established by Russell[1], who showed that an unsupported nickel catalyst reduced at 250°, underwent steady deterioration when used for catalysis of hydrogen-carbon monoxide mixtures in the temperature range 200-260°C.. When, however, the catalyst was heat-treated at 400°C. no further loss in activity was noted by catalysis in the lower temperature range.

Larson and Smith[2] have shown, contrary to the opinion expressed earlier by Pease and Taylor, that the catalytic oxidation of hydrogen on nickel surfaces involves exactly the same behavior as in the case of the copper catalyst. "The experiments indicate that two distinct reactions take place during the catalytic formation of water on nickel and copper. One of these reactions involves the formation of an oxide that is not readily reduced by hydrogen if oxygen be present. During the synthesis, therefore, the reduction of this oxide probably contributes little to the total water being formed. The other reaction is most in evidence during the initial period of high activity. It is undoubtedly the faster reaction and as such accounts for the greater part of the water formed, not only initially but also during the period of low activity."

These results indicate very definitely that in the early stage of the catalysis at the lower temperatures and probably indefinitely at the higher temperatures the whole of the nickel or copper surfaces has catalytic activity and that this is poisoned by oxide formation. On the basis of the ideas put forward in the preceding theory the reactivity of adsorbed oxygen or oxide ions with hydrogen will be the greater the more isolated they are from one another. We can therefore picture the fast reaction as occurring between isolated adsorbed oxygen or oxide ions and impinging hydrogen molecules or with hydrogen

[1] J. Phys. Chem., 29, 1325 (1925).
[2] J. Am. Chem. Soc., 47, 346 (1925).

atoms or molecules. The chance that such individual groupings will grow into a film of oxide will be progressively less as the temperature is raised. This is in accord with the experimental facts. As Larson and Smith point out, the phenomena of ammonia synthesis parallel the hydrogen-oxygen case just discussed, a film of nitride acting to retard reaction. In such case a similar mechanism would hold for the synthesis process, namely reaction of impinging hydrogen molecules or adsorbed hydrogen with isolated adsorbed nitrogens.

## Promoter Action

In the Third Report the experimental data of Medsforth[1] and of Armstrong and Hilditch[2] on the promotion of nickel catalysts for methanation and for the hydrogenation of ethylenic compounds were presented. In the former paper Medsforth stressed a specific dehydration effect of the promoter, while, in the latter, promotion was attributed to extension of available catalyst surface. This clear-cut case of divergence was capable of test experimentally and this test has been carried out by Russell and Taylor[3]. An investigation was made of the action of thoria on nickel supported on pumice, in catalysing the interaction of carbon dioxide and hydrogen to form methane and water. Reaction velocities and extent of surface as measured by adsorption were studied on the same catalyst preparation. The experimental work on such supported catalysts shows that no proportionate increase in adsorption accompanies the activity shown by the promoted catalyst. It therefore appears that the surface of the catalyst has undergone a qualitative rather than a quantitative change. The actual experimental figures show that, whereas the promoted catalyst (Ni, ten per cent thoria on pumice) effects a given percentage reaction at a ten-fold increase in velocity over the non-promoted catalyst (Ni on pumice), the extension of surface as measured by adsorption of either the carbon dioxide or the hydrogen at reaction temperature only undergoes a twenty per cent increase. The harmony between this conclusion and the general considerations already put forward concerning the nature of the catalyst surface is at once evident. Even if it be assumed that the whole of the nickel surface capable of adsorbing hydrogen were catalytically active in the case of the promoted nickel catalyst, it would follow that not more than 10-12 per cent of the surface of the unpromoted catalyst surface adsorbing hydrogen would have any catalytic activity.

That such a percentage of active surface is only an upper limit, can be illustrated by an instructive calculation from the data of Medsforth. He found that a concentration of 0.5 per cent ceria in the nickel catalyst causes a ten-fold increase in reaction rate. Assuming uniform distribution of promoter in the catalyst, this represents one molecule of ceria in every 1130 atoms of nickel in the catalyst surface. This minute change in surface concentration brings about a ten-fold increase in catalytic activity. This strongly suggests

---

[1] J. Chem. Soc., **123**, 1452 (1923).
[2] Proc. Roy. Soc., **103A**, 586 (1923).
[3] J. Phys. Chem., **29**, 1325 (1925).

that in an unpromoted nickel catalyst the active nickel atoms are of the order of 1 in 11300 atoms. It should be noted that this represents a lower limit, since uniformity of distribution is assumed. Nevertheless it exhibits a state of affairs concordant with the data already set forth on the quantitative aspects of poisoning and on the theory of the catalytic surface generally.

In the case of unsupported catalysts the thoria acts not only as a promoter but also as a support to increase the extent of surface. This increase in extent of surface is shown by its increased adsorption values and by the greater apparent volume of the catalyst, its resistance to heat treatment. Russell's experimental results also show a specific action of thoria in increasing the relative amount of carbon dioxide adsorbed. A study by Hirst and Rideal of the promoter action of palladium on copper[1] also indicates an adjustment of ratio of adsorbed gases as well as the importance of the metal-promoter interface.

If a copper catalyst be promoted with small quantities of palladium and the ratio carbon monoxide to hydrogen determined for a series of such promoted catalysts, one of the following results may be anticipated: If the palladium causes no specific effect beyond a surface extension, the ratio $CO:H_2$ consumed will remain unaltered; alternatively, if promoting action is in reality an additive effect, then the $CO:H_2$ ratio will decrease with increasing palladium concentration and the ratio should be capable of accurate calculation from both the known ratios of $CO:H_2$ for the copper and the palladium each in the pure state and from the stoichiometric composition of the catalyst. If, on the other hand, the addition of small quantities of palladium promotes the activity of the oxidised copper for carbon monoxide, we should anticipate a higher $CO:H_2$ ratio for small additions of palladium, rising to a maximum with subsequent increase in the palladium concentration and finally falling to a $H_2:CO$ ratio higher than that for pure palladium at those concentrations where addition of copper promotes the palladium.

Hirst and Rideal found that small quantities of palladium, up to 1.70 per cent, increase the ratio of $CO:H_2$ burnt at any particular temperature in presence of a copper catalyst. A maximum occurs on the addition of 0.20 per cent. A promoted catalyst containing 1.70 per cent of palladium yields the same ratio as pure copper. Catalysts containing more than 1.70 per cent palladium yield a lower $CO:H_2$ ratio than copper, but higher than palladium. This increase in the ratio of $CO:H_2$ burnt on addition of small amounts of palladium is contrary to that which would be expected, as outlined in the preceding paragraph, either on the basis of extension of surface or of dilution of the catalyst surface with palladium. The result obtained is to be anticipated, however, if the reactivity of the oxidised copper at junctions such as Cu. Pd is affected.

To elucidate further the mechanism of the promoter action, Hirst and Rideal[2] studied the adsorption of hydrogen and carbon monoxide singly and

[1] J. Chem. Soc., **125**, 685 (1924).
[2] J. Chem. Soc., **125**, 694 (1924).

in various mixtures of copper, palladium and promoted catalysts. They conclude that the addition of palladium to copper produces an increase in the carbon monoxide adsorption and a decrease in the hydrogen adsorption as well as a relative increase in the carbon monoxide of the adsorbed phase in the presence of both gases. The relative increase in the adsorption of carbon monoxide was found to be in good agreement with the relative increase in the ratio $CO:H_2$ consumed in the catalytic combustion process. The specificity of the effect on adsorption produced by the palladium promoter is further evidence that the promoter action is not merely due to surface extension but involves the further factor of the nature of the interface between catalyst and promoter.

It is desirable to insist that these results do not exclude the possibility that, in addition to the several effects already discussed in connection with the function of the promoter, a promoter may also act by activating one of the reaction species. There is as yet no published evidence of any such case unequivocally demonstrated but there are several cases where it may exist. No evidence is yet forthcoming as to the mechanism whereby nitrogen is activated in the synthesis of ammonia from the elements. Some data by Taylor and Marshall[1], show that activation of the hydrogen alone as, for example, by excited mercury atoms, is not sufficient to bring about ammonia synthesis; whereas this is sufficient to cause reaction with ethylene and carbon monoxide. Certain of the promoters in ammonia-making catalysts may effect nitrogen activation, although with some, qualitative change in the surface of the catalyst by the added promoter is adequate to account for observed effects. It is possible that some information on this point may be achieved from the data on the heats of adsorption.

Larson and Smith, in the paper already cited, point out a further possible function of the promoter. They indicate that the addition of certain promoters decreases the amount or stability of the nitride accumulation, the result being a more reactive catalyst. This is in harmony with the concept that isolated molecular units have a higher reactivity than the material in bulk. The promoter in such case would act to isolate small units of the catalyst material giving them thereby enhanced reactivity, securing, in another manner, for the catalyst preparation, the advantages accruing from fineness of division.

The divergences between different substances used as promoters has also to be accounted for in any complete theory. It is apparent that the properties of the promoter used will in part determine its distribution in the catalyst, since solubility is one of the important factors which will determine the time of separation. Its lattice as compared with that of the lattice of the compound from which the catalyst is prepared will also affect distribution.[2] Many more experimental data are required on such points.

---

[1] J. Phys. Chem. 29, 1140 (1925).

[2] Concerning this point see Wyckoff and Crittenden: J. Am. Chem. Soc., 47, 2866 (1925).

One other aspect of the problem of promoters should also be placed on record. Considerable discussion of the reason for the desirability of oxygen in hydrogenation processes, especially at finely divided platinum surfaces in liquid systems, has taken place in the last few years. There are indications that a clue to the real cause has emerged from the studies of Adams and Carothers[1] on promoted platinum catalysts. They have shown that the reduction of benzaldehyde in presence of platinum is rapidly suppressed when pure platinum is used. They showed, however, that the presence of a very small amount of ferrous chloride enormously accelerates the platinum catalysis and that no reduction of activity is observed over considerable periods of reaction time. Their most recent paper supplements the list of promoters extensively, thirty-six other inorganic salts than iron having been studied with positive effects from many, including manganese, nickel, cobalt, zinc, copper and uranium salts. All alkalis accelerated the reaction. Mineral acids had little effect. Carothers and Adams now reject their earlier hypothesis, which was also that of Willstätter and Waldschmidt-Leitz, that the aldehyde deprived the platinum of the oxygen that is essential to its activity. They now believe that the most consistent explanation of the observed retardation with pure platinum is to be based on strong or irreversible adsorption of the aldehyde by the platinum. The utility of manganese, iron and nickel salts as promoters, themselves familiar as powerful oxidation catalysts, makes it improbable that they would, under the conditions of the experiment, have the opposite effect on the oxidation of the aldehyde associated with the platinum. The function of the oxygen as a regenerator would thus be to burn off strongly adsorbed aldehyde. With a promoted catalyst there should consequently be a better opportunity for both reactants to be present in favorable configuration on the catalyst surface. With pure platinum, the aldehyde is assumed by Adams and Carothers to be a self-poison, and the function of the promoter is in some way to bring about a desorption of the aldehyde and so permit a renewal of the platinum surface.

It should be borne in mind, however, that this is not the only possibility as regards self-poisoning of the surface although it appears at first to be the most plausible. There is a possibility that it is the hydrogen that is the self-poison and the arguments advanced above would hold almost equally well. It would account, moreover, for the adverse effects of pre-treatment with hydrogen in a number of other reactions earlier discussed[2]. This point of view is confirmed by a recent research of Kab[3] in Bredig's Laboratory. He shows that the activity of platinum black prepared by the method of electrical disintegration is conditioned by the gas in which it is prepared. If prepared in hydrogen it is quite inactive in the decomposition of formic acid to carbon dioxide and hydrogen. The removal, by continued evacuation, of hydrogen from the preparation is in itself an activation; treatment with oxygen, Kab

[1] J. Am. Chem. Soc., 45, 1071 (1923); 46, 1675 (1924); 47, 1047 (1925).
[2] Second Report, p. 814 et seq.,
[3] Z. physik. Chem., 115, 224 (1925). See also, Beans and Hammett: J. Am. Chem. Soc., 47, 1215 (1925).

finds, is not necessary though an available method of removing hydrogen. Carbon monoxide behaves like hydrogen. Disintegration in an oxygen atmosphere yields an inactive catalyst. Treatment, with oxygen, of an inactivated catalyst was shown to result in the removal of hydrogen with corresponding activation.

Promoter action, in such cases, where one of the reaction constituents acts as a self-poison, could therefore be ascribed to the effect of the promoter in altering the ratio of reactants adsorbed, a point of view originally suggested by Rideal and Taylor[1], some quantitative evidence for which has been obtained by Russell with promoted, unsupported nickel catalysts in the research already discussed.

### The Effect of Heat Treatment of Catalysts

It is possible, with the aid of the concept of the catalytic surface which has been developed to proceed to a semi-quantitative treatment of the phenomenon of sintering accompanied by loss of adsorptive capacity and reactivity on the part of the catalyst material[2]. The data of Pease on the effect of heating copper catalysts to successively higher temperatures was discussed in the preceding Report. They were characterised by the fact that "for each rise in temperature a noticeable decrease in activity occurred but further heating at the same temperature was without marked effect. There seems to be a stable condition of the surface corresponding to the highest temperature to which it has been heated." Russell has shown the same to hold true for both unsupported nickel and promoted unsupported nickel.

In a composite metal catalyst surface with atoms ranging in saturation from those almost completely saturated by surrounding atoms to those only held to the solid surface by a single metal-metal linkage, there will be a whole range of corresponding energy quantities, the heats of evaporation of individual atoms from the surface. These heats will increase as the atom becomes more saturated with neighbouring atoms and the increase will be approximately proportional to the number of atoms to which the given atom is attached. Thus, if Q be the heat of evaporation of a singly linked atom, 2Q will be that of a doubly linked atom and so on. Now, from the Boltzmann equation, the rate of evaporation will be proportional, for a singly linked atom, to the quantity, $e^{-Q/RT}$ and for a doubly linked atom, to the quantity, $e^{-2Q/RT}$ and so on. It is therefore evident that the rate of evaporation will fall off exponentially as the number of atom linkages increases. Thus, to cite an actual example, let us assume that Q for a single linkage has a value of 5000 calories and the sintering temperature T is 500°K. it is evident that the rate of evaporation of singly linked atoms will be proportional to $e^{\frac{-5000}{2\times 500}}$ or $e^{-5}$. For doubly linked atoms the rate will be proportional to $e^{-10}$. The rates of evaporation will

[1] "Catalysis in Theory and Practice," page 31, (1919).

[2] I am indebted to Dr. Langmuir for the suggestion of this approach to the problem of sintering.

therefore be in the ratio of $e^5$ : 1 or 148.4 : 1; in other words, at a temperature at which singly linked atoms leave the surface freely, doubly linked atoms are practically non-volatile. The relative rates for singly, doubly and trebly linked atoms will be 22046 : 148.4 : 1.

Herein lies the reason for the extraordinary temperature sensitivity of active catalytic agents, not only to the subsequent heat treatment but also to the thermal effects accompanying preparation and reaction. This is alone adequate to account for the divergences in catalysts preparations obtained by Adkins and Lazier[1] by reduction of nickel oxide with alcohol and with hydrogen. Since the thermal effect in the case of alcohol is less than that with hydrogen by an amount equal to the heat of dehydrogenation of alcohol, 11500 cals.[2], it is evident that the active centers—the detached atoms of nickel are subjected in the alcohol case to far less severe thermal treatment than in the hydrogen reduction. A more active surface, therefore, naturally results. The divergence is emphasised by the difference in speeds of reduction. With ethyl alcohol some sixty minutes are only required, as compared with twelve hours at the same temperature with hydrogen. When first used, therefore, marked divergences of efficiency are revealed. These are, however, not differences in "type" but differences in the atom linkage of the surface atoms. That such differences are of the most fundamental importance is very strikingly illustrated by some new work of Pease and Purdum[3], in which the lowering of the temperature of reduction of a sample of copper oxide from 200° to 150°C. made a product at the lower temperatures with which benzene could be hydrogenated whereas that prepared at the higher temperature was quite incapable of reducing the benzene nucleus. Failure to observe this accounts for Sabatier's[4] emphatic statement that benzene cannot be hydrogenated in presence of copper. Russell has shown that the heat of reaction alone is sufficient to cause a deterioration in the catalytic activity of an unsupported nickel catalyst prepared by reduction at 250°C. even though the working temperature, as measured by a thermometer bulb embedded in the catalyst mixture, never exceeded 265°C. Successive experiments between 200° and 250°C. showed steadily decrements in activity. An initial activity of fifty per cent methane formation at 225°C. fell to twenty per cent conversion when the catalyst had been used for 25 hours between 200° and 250°C.

It is the extra lattice atoms which possess the abnormal adsorptive power and abnormal volatility. This latter is well indicated by Langmuir's observation that a film of molybdenum vaporised on to a glass surface cooled in liquid air undergoes an irreversible change on warming to room temperature; that is, crystallisation is occurring, some 2500° below the melting point of the massive metal. The loss in adsorptive power has already been discussed.

---

[1] J. Am. Chem. Soc., 46, 2291 (1924).
[2] Rideal: Proc. Roy. Soc., 99A, 153 (1921).
[3] J. Am. Chem. Soc., 47, 1435 (1925).
[4] Sabatier-Reid: "Catalysis in Organic Chemistry", 511, 522 (1922).

## Specific Activation

The preceding sections attempt to give a conception of the catalyst surface which is consistent with the physical and chemical properties of such a surface and with independent observations from experimental work outside the immediate domain of catalysis. As was pointed out, however, in the Second Report, the effect of a catalyst does not depend exclusively on the increased concentration due to the attractive forces at the catalyst surface; all agree that the effect of the catalyst is specific. The problem of the specificity still remains to be solved.

In perhaps one direction, progress towards a solution of the problem may be definitely claimed. One feature of specificity which has been much stressed is that a given hydrogenation process may be effected with one hydrogenation catalyst but not with another. A good example of this type has been the hydrogenation of benzene. Sabatier was quite emphatic that hydrogenation of the benzene nucleus was not possible with a copper catalyst, but proceeded rapidly and smoothly with nickel. The research of Pease and Purdum already cited shows that the emphasis was unfounded since, with copper, hexahydrobenzene may be secured, though with less efficiency than with nickel. From the details of Pease and Purdum's results, some clue as to the cause of this presumed specificity may be obtained. They showed that it was necessary carefully to control the preparation of the copper catalyst. Reduction of a copper oxide sample at 200°C. gave an inactive copper. Reduction of the same kind of copper oxide at 150°C. gave a copper with which a forty per cent conversion could be secured. Now this alteration in preparation, as the initial sections of this report indicate, will yield a catalyst material in which the proportions of extra-lattice atoms capable of adsorbing more than one reacting molecule will be increased; in addition, it has been shown that, in the catalyst so produced, the adsorption ratio $H_2 : C_6H_6$ will be increased (heat treatment of a catalyst decreases this ratio; see earlier sections). Preparation of the catalyst at lower temperatures will thus have two effects, both favorable to reaction on the assumption that, with an ordinary copper catalyst, hydrogenation does not occur since the surface is practically exclusively monopolized by benzene. Pease and Purdum reach this conclusion from other evidence. In other words, specificity of catalytic action may arise from the unsuitability of the adsorption ratio of the two reactant gases on one hydrogenation catalyst as compared with that on another, abundant kinetic material now existing to show that variation in adsorptive capacities is associated with variation in catalytic activity. This thought emphasizes anew the necessity for obtaining experimental data on the adsorption of gases by catalysts from mixtures of gases. There are very few such data. Some obtained by Hirst and Rideal[1] indicate a very strange behavior, the total adsorption being far less than would be anticipated on the basis of the law of mixtures. Their work should be repeated with more adsorptive samples and other pairs of gases should be studied.

[1] J. Chem. Soc., 125, 694 (1924).

The idea that self-poisoning of the catalyst might account for specificity in the methanation process is also worth considering. On nickel, where methanation occurs readily, the adsorptions of hydrogen and carbon monoxide are comparable in magnitude. On copper, carbon monoxide is much more strongly and abundantly adsorbed than is hydrogen; and we might assume that the carbon monoxide poisons the methanation process on copper, especially in view of the fact, which the Pease-Stewart research[1] on ethylene-hydrogen combination in presence of carbon monoxide reveals, that, of the total adsorbing surface, only a very minute fraction is active in that reaction, a much more readily catalysed reaction than the methanation process. The disturbing aspect of this idea is, however, that there is marked specificity existing between nickel and copper, in the matter of the decomposition of carbon monoxide to carbon dioxide and carbon

$$2CO = CO_2 + C.$$

This reaction occurs readily with nickel and has not yet ever been observed by the writer even with quite active copper catalysts. Both adsorb carbon monoxide and there can hardly be a question of self-poisoning. But, we are so ignorant of mechanism even in a simple reaction of this kind that, as yet, there seems no satisfactory explanation available. Is this specificity to be associated with the ability to form carbonyl in the case of nickel and the absence of such compounds with copper? And if so, what is the difference between a carbon monoxide molecule adsorbed on a nickel surface and one on a copper surface? What methods are we to adopt to make clear such differentiations?

Dew and Taylor[2] have sought to establish such differentiation in the case of ammonia adsorbed on iron, nickel and copper, by determination of the heats of adsorption of ammonia on these metals at low partial pressures. The heat effect is greatest with iron and least with copper which is also the order of the catalytic efficiency of these metals in decomposing ammonia. But, it is not as yet clear what change in the molecule of ammonia is to be associated with these differences in the heat of adsorption.

That answers to such queries as those above might come from a study of the alternative decompositions of organic molecules has inspired a considerable amount of research in recent years, the substances studied including formic and other acids, alcohols, esters and amides. Many of the results of such studies have been included in the earlier reports. The most comprehensive studies have been those of Adkins and his co-workers[3], and these have led Adkins to what may be termed the 'spacing' theory of specific catalytic action.

Adkins found that the mixed dehydration and dehydrogenation of esters and of alcohols on alumina and titania surfaces was very sensitive to the nature of the catalyst material and the source from which it was obtained. From a

[1] J. Am. Chem. Soc., 47, 1235 (1925).
[2] Dew: Thesis, Princeton (1924).
[3] For literature references see 2nd Report and J. Am. Chem. Soc., 47, 807 (1925).

study of the activities of aluminas and titanias prepared from salts, acids and alkoxides, Adkins has formulated a 'spacial theory' in which the spacing of the "active points" plays a fundamental part. This spacing is thought to be secured by choice of the starting material for the preparation of the catalyst, by changing the size of the radical (e.g., OEt) attached to the aluminium atom when the compound goes (by hydrolysis) into the solid state. As an *ad hoc* hypothesis it can be made to fit the experimental facts in the case of the two reactions noted with considerable success. His work supplies an experimental basis for the theory which, however, involves difficulties when it comes to the problem of the experimental facts of the adsorption of reactant gases, taken singly, and of poisoning (see page 167).

Apart from the inherent improbability, judging by recent X-ray studies, that the distances between the atoms, molecules or "active points" of the catalyst can be modified in such a manner as claimed by Adkins, especially when the high temperature of use is borne in mind, certain other data of Adkins are hard to reconcile with his spacing theory. Thus, he has observed that, although the reactions already mentioned are sensitive to this assumed spacing in aluminas, this is not all true for such similar reactions as the dehydration of amides to yield nitriles, the decomposition of acids to ketones and the catalytic removal of hydrogen halides from alkyl halides. Similarly, formic acid decomposition on titania is as rapid on an ignited as an unignited catalyst.

This divergent behavior in these last four cases, quite inexplicable on the "spacing" theory, is strongly reminiscent of reactions in other fields of catalytic work, readily catalysed by a surface of almost any low activity, as, for example, with metals in the reduction of nitrobenzene. It suggests that every atom in the surface possesses catalytic activity—Langmuir's original assumption. On this basis, the abnormal behavior in the cases of alcohols and esters would arise by reason of the fact that only a certain fraction of the surface atoms were active in the decomposition processes. If this were so, the reactions would show sensitivity to poisons such as we have already discussed. The most likely poisons for acidic catalysts of this type will obviously be basic materials. An examination was therefore undertaken of Adkins' abundant experimental material to ascertain how far there was internal evidence of the operation of basic materials as poisons. The evidence which this revealed was arresting. Briefly, one can say that Adkins' catalyst data can be reinterpreted on the basis of possible contamination with poisons principally alkaline or salt poisons. This is so, since, as Adkins observes, titania from tetra-ethyl titanate is very different in its catalytic activity from Demarçay's oxytitanates—a fact which Adkins did not expect. He observes, however, in his experimental data that "the wash water (in the preparations from certain oxytitanates) reacted alkaline to phenol phthalein showing that some occlusion of sodium ethoxide had taken place in the crystallisation". These oxytitanates yielded the catalysts in which the ratio of $C_nH_{2n}/(C_nH_{2n} + H_2)$ was a minimum, in which also the absolute activity was a minimum. Similarly,

titania from sodium titanate gave a low ratio and a low absolute activity. In acetic acid decomposition these two were the most active. Furthermore, as evidence of sensitivity to poisoning, we may cite: "it has been found impossible to duplicate absolute activity in the preparation of certain catalysts." Charriou has shown[1] that the catalytic decomposition of ether by heating with alumina at 250°C., is inhibited if the alumina has adsorbed small amounts of other inactive substances. He showed that adsorbed lime was the most efficient of the inhibitors which he studied.

The most decisive evidence, however, that "spacing" is not the fundamental factor and that poisoning is, can also be cited from a recent paper of the Adkins series[2]. Bischoff and Adkins show that the decomposition of butanol at the titania surface, is modified profoundly by the presence of a basic agent in the gas phase, namely ammonia. They point out "an observation of no little importance," with titanias of two different "spacial" types, that the presence of the ammonia "materially altered the ratio of gaseous products, more butane and hydrogen and less butylene being formed. In fact, the effect of the ammonia was many times as great in shifting the reactions as was the equivalent of water." In other words, Adkins and Bischoff, here, by their own experiments prove that spacial distances between atoms, molecules or "active points" of the catalyst have no decisive influence on the ratio of reactions and that the presence of a poison does.

The concept of the solid catalytic surface developed in the earlier sections may therefore be utilised again to recast this concept of specific activity of catalytic materials. The surface is composite, with atoms, ions or molecules in the surface in varying degrees of lattice saturation. For some reactions, notably the decomposition of acids to yield ketones, amides to yield nitriles and alkyl halides to yield olefines and the corresponding hydrogen halides, the bulk of the surface atoms are to be considered active. For the decomposition of alcohols and esters, on the contrary, only a fraction of the surface and that, presumably, the less saturated lattice atoms, possesses catalytic activity sufficient to effect decomposition. The mode of decomposition and the nature of the products will, in such case, depend on the nature and arrangement of the extra-lattice atoms, which in turn will depend largely on the mode of preparation and subsequent treatment accorded to the catalyst. If such be true, it should follow, also, that the mode and extent of catalytic decomposition should be markedly sensitive to poisons in the case of alcohols and esters, and to a much less degree so sensitive for ketones, amides and alkyl halides. Alternative modes of decomposition would then be attributable to the differences in the molecular structure of the adsorbed reactant brought about by its attachment to the catalyst. What the nature of the changes in molecular structure so caused may be and the manner in which they may be established with certainty is not readily apparent. The possibility of their existence, however, is patent from observations on the effect of substituents, as for ex-

[1] Compt. rend., 180, 213 (1925).

[2] Bischoff and Adkins: J. Am. Chem. Soc., 47, 812 (1925).

ample, chloro and amino groups on the properties of organic fatty acids. In these cases, substitution at one end of a long hydrocarbon chain exercises a profound influence on the acidic property at the other end of the chain. For this reason also the chemical nature of the atoms or ions on which the reactant is adsorbed should also have a determining influence on the mode of reaction.

That poisons do determine the path of reaction is already well known; poisoning may be well utilized to yield a preferred product, and to such cases the term beneficial poisoning has been applied. A very obvious application is in the case where a catalytic process proceeds too far with an active catalyst. By minimising the activity of such a catalyst or poisoning the more highly reactive patches with the requisite poison, the reaction may be stopped at the desired stage. Many investigations into the conditions necessary to secure a good yield of a desired product may, in reality, be unconscious applications of this procedure of beneficial poisoning. An example suggestive of this may be quoted.

Armstrong and Hilditch[1] have shown that in the catalytic dehydrogenation of ethyl alcohol in the presence of copper, the presence of water in the alcohol improves the yield of acetaldehyde relative to that of hydrogen. Thus, at 300°C., whereas anhydrous alcohol only gave an aldehyde–hydrogen ratio of 67 per cent, alcohol containing 8 percent water gave a 95 per cent ratio. With the anhydrous alcohol there is a marked increase in the yield of gaseous products, principally methane, carbon monoxide and carbon dioxide in addition to the hydrogen. It is evident that, with the anhydrous alcohol, secondary decomposition of aldehyde is much more pronounced than with alcohol containing water. Thus, methane and carbon monoxide result from one such secondary decomposition.

$$CH_3CHO \longrightarrow CH_4 + CO.$$

Evidently, the water acts as a beneficial poison in that it poisons the catalyst for such secondary decompositions which apparently require a large energy of activation, in all probability as a result of a strong preferential adsorption on the catalyst surface. Armstrong and Hilditch showed, by passing aldehyde vapor together with water over a copper catalyst, that the water had a considerable protective influence on the aldehyde.

The dehydrogenation of alcohol in the presence of nickel occurs at lower temperatures than in the presence of copper but the secondary decomposition is very high. The data of Armstrong and Hilditch show that dehydrogenation occurred at 250°C. The aldehyde-hydrogen ratio was only 35.7 per cent and the evolved gas contained 60 per cent hydrogen, 20 per cent carbon monoxide and 15-17 per cent methane. Evidently, in this case, the 8 per cent of water in the alcohol used was not sufficient to protect the aldehyde produced. It would be interesting to extend this study of dehydrogenation with nickel in the presence of water to see whether the secondary decomposition could be largely suppressed by increase of water content in the alcohol, since the low yields obtained with copper at the higher temperatures could be partially restored by such an increase in water content.

[1] Proc. Roy. Soc., 97A, 262 (1920).

Palmer's study[1] of this same reaction in the presence of a copper catalyst indicates that alcohol itself plays the same role as the water in the experiments already cited. He showed that, below 300°C., the secondary products were negligible when the dehydrogenation of alcohol occurs; but, if a mixture of acetaldehyde and hydrogen is passed over the copper catalyst between 250° and 300°C., much of the aldehyde is decomposed. Bancroft has suggested that such cases might be called "protective poisoning".

The same procedure was used during the years 1917-1919 for the production of ethylene from alcohol in presence of kaolin. Instead of a low temperature process the reaction was conducted at red heat and the products were protected from decomposition by using alcohol-water mixtures, even though the process was dehydration. The researches of Rosenmund, Zetsche and Heise have been cited by Bancroft in an earlier report.

Recent work by Adams and his co-workers[2] indicates that the use of permanent poisons on the catalyst surface as well as temporary poisons in the gaseous reactants may also be used deliberately to direct a catalysis. Thus, with a platinum-iron catalyst, cinnamic aldehyde undergoes reduction to phenyl propyl alcohol. If the catalyst be suitably poisoned with zinc, the product is cinnamyl alcohol. The efficiency is very sensitive to the amount of zinc salt employed to poison the catalyst surface so that a question of the geometry of the platinum and zinc atoms in the surface as compared with that of cinnamic aldehyde may be involved in the explanation of the action of the poison. Armstrong and Hilditch see in such studies of selective hydrogenation a most promising field of research in heterogeneous catalysis[3].

Professor Adkins' comment on the point of view put forward in the preceding pages is worthy of record. "There appears to be little doubt that the atoms constituting the surface layers of a solid catalyst differ in the degree of their unsaturation. However, it is very doubtful if this fact, together with its resultant possibility of selective poisoning, offers any adequate explanation of the variations in ratios between simultaneous organic reactions, as studied in the Wisconsin Laboratory.

"In the case of ethanol there are at least five distinct reactions that take place at the surface of solid catalysts. The first four reactions take place over the same temperature range.

$$C_2H_5OH \longrightarrow \begin{cases} \nearrow CH_3CHO + H_2 & 1. \\ \rightarrow CH_3CH_3 + CH_3CHO + H_2O & 2. \\ \rightarrow CH_4 + CO + H_2 & 3. \\ \searrow CH_2 : CH_2 + H_2O & 4. \\ \searrow (C_2H_5)_2O + H_2O & 5. \end{cases}$$

The idea that Reaction 1 took place at the surface of those catalysts that strongly adsorbed hydrogen, and Reaction 4 with those catalysts that adsorbed water, is no longer held tenable even by its originator. The only other suggested mechanism is that the catalyst causes, through the formation of a

[1] Proc. Roy. Soc., 98A, 13 (1920).
[2] A. C. S. Spring Meeting, Baltimore (1925).
[3] Chimie et Ind., 12, No. 2 (1924); Deuxième Conseil, Institut Solvay (1925).

compound with the ethanol, a rearrangement of the electrons within the alcohol molecule, so that a split in the molecule occurs. On the basis of this idea, (which is due to Langmuir) one may say that copper forms a compound with ethanol so that the aldehyde rearrangement is the easier, which the alumina-ethanol compound most readily rearranges to give the alkene. One has then assumed that there are two distinct types of compound, one of which is liable towards the dehydrogenation reaction and the other towards the dehydration. Both reactions occur simultaneously over zinc oxide, the proportions not being a characteristic of zinc oxide but of the zinc compound out of which the oxide is prepared. Are there then *two* zinc oxide-ethanol compounds, one liable towards dehydrogenation and the other towards dehydration? Are there four iron oxide ethanol compounds, for Reactions 1, 2, 3, and 4 taking place simultaneously over that catalyst? On the basis of Dr. Taylor's hypothesis, a slightly unsaturated surface atom might induce one reaction, a more unsaturated one another reaction, etc. That is to say an atom of a catalyst produced dehydrogenation because it exerts a greater (or less) force than does one that produces dehydration. It seems to me more reasonable to believe that there are differences in kind rather than of degree of dislocation of the molecule. Instead of there being four or five kinds of catalyst-ethanol compounds or four or five degrees of unsaturation of catalyst atoms, the various reactions are dependent upon the relationship in space of the catalyst atoms which are *simultaneously* exerting their attractive forces upon the organic molecule, thereby distorting it in different ways. It seems probable that differences in the degree of unsaturation of catalyst atoms as well as the geometrical relationship of these active points are important factors in catalytic reactions.

"Emphasis should be placed on the fact that there are two distinct phases to these catalytic reactions, and that these two phases apparently have no relationship to each other. The one phase has to do with *how much* material reacts under a given set of conditions and the other phase has to do with the ratio of the reactions that take place. The first phase may very well have an intimate relationship to the adsorptive capacity of the catalyst. It varies with very slight changes in the method of preparation of the catalyst. In general this behavior of the catalyst is not readily duplicated with different preparations from the same materials. In marked contrast to this is the ease of duplication of the characteristics of the second phase; provided the catalyst is made by the same method, i.e. by ignition of a carbonate, dehydration of a hydroxide, hydrolysis of an alkoxide, etc. Two catalysts made from a butoxide may differ from each other by as much as a 100% in the *amount* of material that they will cause to react in unit time, but the proportion of the reactions induced will differ by only a per cent or so. The one characteristic of the catalyst is dependent, I believe, upon the number of active adsorbing centers, the other upon the characteristics of the surface at those active points. The distinctness of these two characteristics of catalysts has never been sufficiently realized.

"The titanias from the "oxytitanate" and from the sodium titanate were not duplicatable for a very simple reason. The "oxytitanate" was a mixture and the hydrolysis of sodium titanate gives a mixture of products. It is not surprising that the catalysts derived from different mixtures were not identical. If "alkaline or salt poisons" caused the differences in catalytic activity, what caused the differences between those catalysts that had been prepared by the hydrolysis of products that had been repeatedly distilled? The explanation given would only account for differences in the behavior of two catalysts out of twenty or more and seems of little importance when it is known that these catalysts were derived from impure mixtures."

## General Conclusions

. This report has attempted to demonstrate that, in so far as the contact agent itself is concerned, the experimental researches of the past five years have supplied a consistent, intelligible picture of its nature and of its special properties. This picture supplies a reason for much of the mystery with which the subject of contact catalysis has been surrounded hitherto. For, it shows that the properties of the contact agent are to be differentiated from the bulk properties of the substance of which the catalyst is composed; that it is rather the properties of the individual atoms or molecules of the catalyst, with the changes in these properties induced by position and arrangement in the catalyst particle, which are of importance in catalytic change. The ordinary general, inorganic, and organic chemistry of substances is concerned with the reactions and properties of many million millions of examples of such atoms or molecules, and the result given is a statistical average covering all the cases. The properties of the contact agent, especially in catalytic reactions difficultly achieved, are those of the aristocracy of the atomic or molecular species concerned, and are as different from the statistical average behavior of the crowd as the actions of an educated minority of people should be different from that of an indiscriminately collected mob.

That conclusion reached, however, oceans of uncharted knowledge open beyond. We seem to be forced to the conclusion that we know little or nothing concerning the effect which such aristocracies of atoms exercise on the impinging reactants. Our knowledge is almost negligible on the nature of the activation process induced in the reactant by its association with the catalyst. And it would seem that, before the whole problem can be solved, this must be learned. We return here to a sentence from the First Report, "the general problem of activation is of such fundamental importance that every chemist in the world, should be keeping it in mind so as to be ready to do his share in the solution." One would add to that the hope that he will not only keep it in mind but in hand as well, so that by experimental test the problem may achieve solution. The technique of the physicist in his study of sub-atomic phenomena is needed. The technique of the photochemist must be employed as an aid. Yet more and more experimental work, wisely conceived and accurately achieved, in the reactivity of molecules on contact catalysts is also indispensable.

# THE SORPTION OF VAPORS BY ALUMINA

BY L. A. MUNRO AND F. M. G. JOHNSON

## WATER

It has long been known that alumina would catalyse dehydration reactions, and this property of alumina has been extensively investigated by Sabatier[1]. Adsorption and catalysis may appear to be related phenomena, and several investigators have made a study of the sorptive power of different catalysts[2]. The sorptive power of alumina has, however, received very little attention[3]. It has been noted in the first part of this investigation[4] that alumina took up a greater amount of water than of any other vapor. This fact, in addition to the knowledge that alumina is such a good catalyst for dehydration of alcohols, etc., suggested that an accurate study of the sorption of water would be of interest. This research was undertaken with this object in view.

### Method

A dynamic method, such as that previously used[4], while of sufficient accuracy for a study of a general nature, is not suited for the measurement of sorption over a temperature range, nor can it be used when it is desired to obtain any great accuracy. In order that the study might still be pursued by a dynamic method it was necessary to design an apparatus which would give accurate measurements at different temperatures and concentrations. Such an apparatus has been constructed.

A known volume of air (measured directly by a specially designed gas meter), is saturated with vapor at a definite temperature, and the resulting mixture is passed through the sorption tube at a higher fixed temperature. The course of sorption is followed by weighing the sorbent at intervals. With this apparatus the weighing of the alumina is done without removing it from the bath and consequently at bath temperature. The great advantage of this is in the time saved. The amount of vapor supplied is calculated from the volume of air saturated, and the vapor pressure of the saturating liquid.

### Apparatus

The entire apparatus was constructed of glass with fused joints. In Fig. 1 are shown the Maass control[5] and counting device, which are mounted on a wooden stand. By means of the control M, attached to a water pump, alternate suction and pressure are applied to the miniature Töpler pump C,

---

[1] "Catalysis in Organic Chemistry."

[2] Guichard: Bull,, **31**, 647 (1922); Benton: J. Am. Chem. Soc., **45**, 887, 901 (1923); Beebe and Taylor: **46**, 43 (1924).

[3] Denver: Proc. Roy. Inst., **18**, 435 (1906); Munro and Johnson: Ind. Eng. Chem., **17**, 88 (1925); Pearce and Alvarado: J. Phys. Chem., **29**, 256 (1925).

[4] Munro and Johnson: Ind. Eng. Chem., **29**, 256 (1925).

[5] J. Am. Chem. Soc., **41**. 35 (1919).

(Fig. 2.) T, is a tap which serves to regulate the flow of mercury back into M, and thus adjusts the time interval between consecutive strokes of the pump C. The counter, operated by the piston P, counts the number of times the suction is released by M and thus the number of strokes of the pump. In order to prevent the mercury column in the U tube from hitting the piston P with too much momentum when the suction is broken, a large plug of glass wool is inserted at X. This greatly reduces the velocity of the fall.

The other parts of the glass apparatus are shown in Fig. 2. No. 1 and 2 are thermostats, no. 1 being at a temperature greater than no. 2. These are

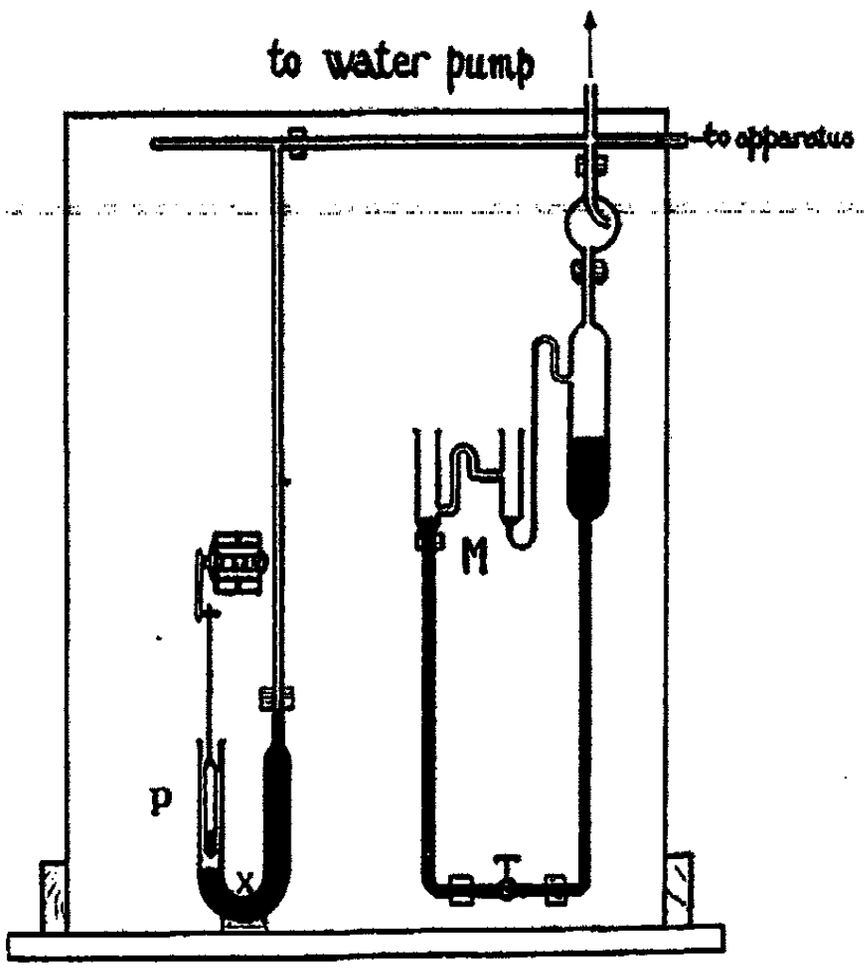



FIG. 1

joined by a tube at M. The baths and the connecting tubes were heavily lagged with asbestos paper. When suction is applied, the mercury in C is drawn into the bulb B, filling it. Air, free from $CO_2$ and water, enters C through A, at atmospheric pressure. As the suction continues, a small volume of mercury rises in the capillary tube, reaching the level x′, at which time the suction is broken by the control M, (Fig. 1), and atmospheric pressure restored. The mercury flows back into C, cutting off the air at the same point each time and rising to the fixed level in the very fine capillary D.

The air then passes through the mercury valve E. It enters a piece of apparatus designed to make the flow of air continuous, and at the same time to have it under uniform pressure. This is accomplished in the following way: A capillary of sufficient fineness to give the desired rate of flow of the entering air, is inserted at J. The air from E has two routes available at F; through J at the definite rate, or through the tube F. The large amount enters the

vessel G through the latter tube. G acts as a gas reservoir and can move upward and downward in the chamber I. The entering air forces G upward against the pressure due to the head of mercury in H. The rising tube is guided at the top and the bottom as shown in the diagram. Mercury fills I to the level X making a seal between F and G. As soon as the air ceases to enter E the reservoir G begins to descend, due to the weight of mercury in H, the air escaping through J. Since G is made from very thin glass the difference in pressure due to the difference in volume of the glass immersed in the mercury at any time is negligible compared to the pressure caused by H. By adjusting the mercury in H, the rate of flow of air through J may be regulated.

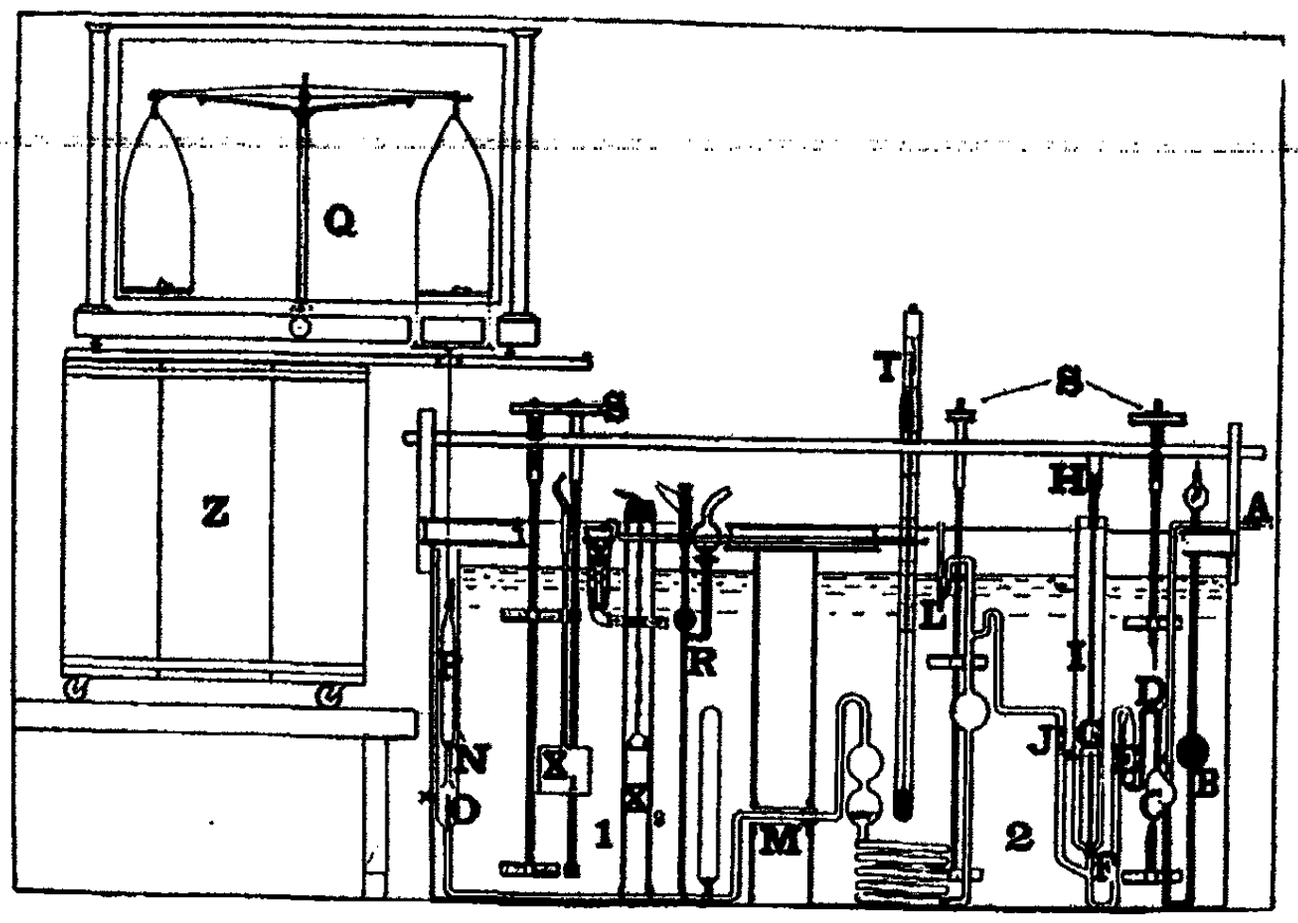



FIG. 2

The air next passes to a wide glass spiral containing glass beads and filled with the saturating liquid. Bubbles are formed at the bottom of the spiral. These travel a considerable distance (90 cm) in contact with the liquid and become saturated. The mixture passes along to M where it enters a region of higher fixed temperature, in bath 1.

Beyond M the mixture goes to the sorption apparatus N. P, the tube containing the alumina is provided with a narrow tube at each end. The upper tube is bent and a little glass hook is affixed to the side, so that the tube may be suspended vertically in the tube N. The lower tube is of just sufficient width to admit the tube O and has a flanged end which serves as a guide for the tube O when P is being lowered. A closed connection is made between O and P by means of a mercury seal. The tube P can be raised and suspended to one arm of the balance Q, by means of a silver wire. Q is mounted on a moveable stand Z, so that on the completion of a weighing, P can be de-

tached from the balance wire and then lowered over O by another wire when the balance is moved out of the way. R is a thermo-regulator. The stirrers are denoted by S. T is a Beckmann thermometer. $X_1$ and $X_2$ are heaters. Y is a constant level arrangement for bath 1.

The saturator can be refilled by means of the device L. The mercury in L is removed by a pipette and the saturating liquid is poured into the long arm, siphoning over into the saturator. This filling can be done without getting any air into the apparatus, because the short branch of L can be kept full of liquid since it is above the surface of the warm bath. Hence the mercury level is brought just below the branch tube, the short tube is still sealed by liquid which siphons over when more liquid is added. The mercury is replaced and the short arm remains filled with liquid. The thermo-regulator and heating units for thermostat no. 2 and the thermometer for no. 1 are not shown in the diagram.

## Possible Sources of Error in the Apparatus

It is necessary to make a critical survey of the apparatus in order to get a reliable estimate of the accuracy obtainable.

The first thing to be considered is the volume of air delivered by C. The same amount of air must enter and the same amount must be discharged each time. The factors which will affect this will be the pressure of the entering air and the relative position of the mercury in C at the beginning and end of each up stroke. The expansion of the mercury in B and C over a temperature range of 30° is not great enough to affect the level to which the mercury falls in C. If initially the level to which the mercury fell was just below the air inlet and subsequent lowering of temperature caused the level to sink well down in the tube leading to B, some error might be introduced. Under experimental conditions however, this never happens. Differences in temperature will make very little difference in the height to which the mercury will rise in the capillary D, because the diameter of the bulb E is so large that an expansion of 10 per cent would only cause a slight change in level. The capillary D is of a very fine bore so that any such change in level would have practically no effect on the volume of air delivered.

The volume of air entering E is also independent of the pressure in other parts of the apparatus. The air enters C at atmospheric pressure and shuts off at the same point each time. If the pressure in E did vary, the air in the capillary D would expand or contract, but the effect of as much as one centimetre pressure variation in E would be negligible.

The expansion of the glass over the temperature range used (25-45°) can be neglected.

Calculations of the amount carried over depend on the assumption that the water vapor is of normal density and that Dalton's law is followed by the mixture. That this assumption is justifiable has been shown by Menzies[1]. There is therefore no error inherent in this part of the apparatus.

[1] J. Am. Chem. Soc., 42, 978 (1920).

The amount of vapor which the air will carry over will depend on the temperature of the liquid and the pressure at M. The latter has been reduced to atmospheric pressure by using the sorbent in the form of relatively coarse grains and a loose plug of asbestos to retain the alumina.

The other place in the apparatus which may introduce experimental error is the arrangement for weighing the sorbent. On raising P from the mercury, a volume of air equal to the volume of the inlet tube O will be drawn into the upper part of P. In order that this air might not come in contact with the alumina and change the concentration of the equilibrium mixture, the tube was never completely filled with alumina. This entering air would therefore have no effect and would be expelled by the exit gases, if not by the replacement of the tube over O.

In order that the guiding flange of P might not entrap air when lowered into the mercury, with a resulting dilution of the entering gas, a small hole was blown in the wall of the tube just above the flange. This allowed the air to escape. Hence error caused by the dilution of the vapor has been eliminated.

### The Temperature Control

The temperatures are controlled by thermostats. Bath no. 2 in which the apparatus A to M is placed, is heated electrically. Temperature variation in this bath was shown by a Beckmann thermometer to be $<.02°C$. The temperatures of the baths were set by a standard thermometer.

Thermostat 1 was heated by $X_1$ and $X_2$, and the temperature kept constant by varying the resistance in the $X_1$ circuit by means of a relay in series with the thermo-regulator R. At 80° the temperature variation was less than 0.1°, while at lower temperatures it was less than 0.05°.

When N was open to the air, as in the case when a weighing is being made, the temperature in N at a point 2.5 cm below the surface of the bath was found to be 0.5° below the temperature of the bath (80°). Five cm. below the surface, the temperature was 80°. This means that even during weighings, the alumina was kept at constant temperature.

The chief source of error is the weighing of the tube P. The tube can be weighed to within ± .0002 g. This may amount to as much as a few percent of the increase in weight between consecutive weighings, but seldom introduces an error of more than .1% in the saturation value.

The amount of vapor supplied by one stroke of the pump is given by the product:

$$\frac{273 \cdot p \cdot V \cdot M.}{T. (760-p) .22400}$$ grams. Where p is the vapor pressure of the liquid,
V, the volume of air supplied,
M, the molecular weight of the vapor,
T, the absolute temperature.

p is the factor involving the greatest error, which may in some cases be as high as 0.5%. Any back pressure caused by the alumina in P will introduce some error, but the total error in this product is not greater than 1%.

The preparation of the alumina, its subsequent treatment and its age, all affect its sorptive power. When the gels are prepared in the same manner accurate results can be obtained, and these results can be reproduced.

## Calibration

The pump C was calibrated by measuring the volume of air at constant temperature delivered by a known number of strokes of the pump. Three consecutive determinations gave the values 13.18, 13.17, 13.18 c. c. as the volume of air delivered per stroke. This was checked a month later and the value 13.18 c.c. obtained.

## Preparation of the Alumina

At first the alumina was prepared from the hydroxide obtained from the Mallinckrodt Chemical Co. This was found to be too fine for use in this type of apparatus as it caused considerable back pressure. The alumina used in this work was prepared by precipitating the hydroxide from a hot solution of 300 g. of the nitrate in two litres of water, by concentrated ammonium hydroxide. It was then diluted to 6 litres and boiled until there was no odor of ammonia. After settling the gel was washed with distilled water until free from nitrates as shown by the phenol sulphonic acid test. Any traces of ammonium nitrate remaining would be decomposed at the temperature used for dehydration. The gel was then dried for twenty-four hours at 100° after which a known weight of the gel (10-16 mesh) was placed in a sorption tube and heated in an air bath for one hour at 300°. The total water content was determined by blasting a separate sample of gel for several hours. The state of hydration is determined from the loss in weight of the alumina tube.

## Composition of the Gel

Kuhn[1] distinguishes between "water capacity" and "water intensity" of gels. The intensity is determined by the strength of the attraction between the water molecules and the molecules or particles of gel. It is probable that water intensity of alumina is much greater than that of silica gel since the latter forms no definite hydrates whereas several hydrates of alumina occur in nature. Martin[2] and von Bemmelen[3] have shown that the true hydroxide is obtained when an aluminate is decomposed by HCl. Milligan[4] has found that the true hydroxide is stable up to 145°. Hagewaka[5] has shown that the water of crystallization changes to sorbed water at 200° and Fricke and Wever[6], on the other hand, have found that alumina gel slowly changes to the crystalline hydrargillite, and if heated at 100° for some time, shows a tendency to revert to microcrystalline bauxite.

[1] Kolloid-Z., 35, 276 (1924).
[2] Mon. Sci., 5, 225 (1915).
[3] Rec. Trav. chim., 7, 75 (1888).
[4] J. Phys. Chem., 26, 247 (1922).
[5] Kolloid-Z., 32, 1154.
[6] Z. anorg. Chem., 135, 321 (1924).

The question as to the composition of alumina gel has received the attention of a number of investigators and the opinion of most of these has been that the gel is not $Al(OH)_3$. Willstätter[1] has recently published a series of papers on alumina gel, in one of which he describes the drying curves for gels prepared by different methods. In almost every case the water content of the sample remained constant as the temperature was raised to 120°. These different gels had dissimilar properties, which he attributed to the presence of a different number of alumina-water complexes in each. He supposed that the $Al(OH)_3$ is the primal hydrate which loses water, leaving partially dehydrated molecules. These being possessed of strong residual fields unite to form molecular groups with varying amounts of water. These groups may be represented by the general formula $Al_n(OH)_{3n}.xH_2O$. It is therefore probable that when water comes in contact with this molecular complex it will be attracted by forces that are distinctly chemical.

It is impossible however to imagine that all the water in the gel is held by residual valences; some must certainly be held by capillary condensation, beyond the range of the unsaturated forces of the alumina complexes. Foote and Richards[2] consider that the gel contains both "chemically combined" and sorbed water. By the term "chemically combined" they doubtless mean that the water is held by what Langmuir calls "primary valence". Since the difference between the forces that bring about chemical combination and those that cause adsorption is a quantitative rather than a qualitative one, it is sufficient to state that the water in alumina gel is bound by chemical forces and by condensation in the capillaries. Experimental results previously described[3] show that alumina takes up a greater amount of water than of any other vapor. This fact supports the theory of selective adsorption. The results to be described in this paper show that capillary condensation also plays an important part in the sorption of water vapor by alumina.

## Results

It has been found that better agreement between the results for different samples of alumina is obtained when the results are expressed as mg. per gram of *active* $Al_2O_3$ instead of *sorbent* ($Al_2O_3 . xH_2O$). The amount of active $Al_2O_3$ is readily calculated from the dehydration when the original water content of the gel is known[4]. The results of this investigation are expressed in this manner.

## Sample Calculation

Two typical examples of the results obtainable with this apparatus are given in detail (Tables I and II) in order to show the method of calculation and the agreement between the calculated and observed values of the amount of vapor supplied.

[1] Ber., 57, 58 (1924).
[2] J. Am. Chem. Soc., 38, 588 (1916).
[3] Munro and Johnson: Ind. Eng. Chem., 17, 88 (1925).
[4] Munro and Johnson: Ind. Eng. Chem., 17, 88 (1925).

TABLE I

Tube 3. Weight of tube 16.0460 g. Gel. .2.469 g. Active $Al_2O_3$, 1.464 g.
Bath no. 1 at 80.0°C. Bath no. 2 at 45.00° ± .02
Rate 1 stroke / min.
Vapor pressure 72 mm
Amount of vapor supplied per 100 strokes of pump =

$$\frac{18 \times 72 \times 13 \,.\, 18 \times 273}{224 \times 689 \times 318} = .0941 \text{ g}$$

| Total strokes | Weight supplied | Amt. supplied in mg/g $Al_2O_3$ | Gain in wt. of alumina | Amt. sorbed in mg/g $Al_2O_3$ | Hours |
|---|---|---|---|---|---|
| 65 | 0.0612 | 41.7 | 0.0610 | 41.7 | 1.1 |
| 110 | 0.1035* | 70.7 | 0.1030 | 70.7 | 1.8 |
| 200 | 0.1882 | 128.5 | 0.1562 | 106.7 | 3.3 |
| 370 | 0.3418 | 238.0 | 0.1675 | 114.4 | 6.2 |
| 460 | 0.4330 | 296.0 | 0.1765 | 120.5 | 7.7 |
| 770 | 0.7246 | 495.0 | 0.1806 | 123.4 | 12.8 |
| 1370 | 1.2900 | 880.0 | 0.1850 | 126.0 | 22.8 |
| 1752 | 1.6480 | 1126.0 | 0.1864 | 127.0 | 29.2 |
| 2060 | 1.938 | 1324.0 | 0.1872 | 128.0 | 34.3 |
| 2360 | 2.921 | 1517.0 | 0.1900 | 130.0 | 39.3 |

*Sorption is probably complete, since difference between calculated and observed values, is less than 0.5%.

TABLE II

Tube 5* Weight of tube 15.1452 g. Gel. 1.810 g. Active $Al_2O_3$, 1.054 g.
Alumina (Bath no. 1) at 40.0° Saturator (Bath no. 2) at 30.0°
Rate 1 stroke per minute
Partial pressure 31.8 mm.
Amount of vapor supplied per 100 strokes of pump =

$$\frac{18 \times 31.8 \times 13 \,.\, 18 \times 273}{224 \times 730 \times 303} = .0416 \text{ g.}$$

*(Resistance to air flow, 1.5 mm)

| | | | | | |
|---|---|---|---|---|---|
| 65 | 0.0269 | 25.6 | 0.0268 | 25.6 | 1.11 |
| 175 | 0.0728 | 69.0 | 0.0730 | 69.2 | 2.9 |
| 280 | 0.1165 | 110.5 | 0.1162 | 110.4 | 4.7 |
| 380 | 0.1580 | 150.0 | 0.1400 | 133. | 6.3 |
| 500 | 0.2080 | 197.0 | 0.1534 | 147. | 8.3 |
| 630 | 0.2630 | 249.0 | 0.1640 | 156. | 10.5 |
| 862 | 0.3585 | 340.0 | 0.1720 | 163. | 14.4 |
| 1142 | 0.4750 | 451.0 | 0.1768 | 168. | 19.0 |
| 1397 | 0.5812 | 551.0 | 0.1800 | 171. | 23.3 |
| 1435 | 0.5968 | 566.0 | 0.1832 | 174. | 23.9 |
| 2207 | 0.9180 | 871.0 | 0.1864 | 177. | 36.8 |
| 2590 | 1.077— | 1022.0 | 0.1866 | 177. | 43.2 |

TABLE III

| Alumina at 80° | Partial pressure 72.7 mm. | |
|---|---|---|
| Amt. of vapor supplied, in mg./g. $Al_2O_3$ | Amt. of vapor sorbed, in mg./g. $Al_2O_3$ | Time in hours |
| 40.1 | 40.1 | 1.0 |
| 64.3 | 61.0 | 1.67 |
| 109.2 | 71.1 | 2.83 |
| 161. | 73.7 | 4.16 |
| 642. | 78.4 | 16.7 |

TABLE IIIa

| Alumina at 80° | Partial pressure 72.7 mm. | |
|---|---|---|
| Amt. of vapor supplied, in mg./g. $Al_2O_3$ | Amt. of vapor sorbed, in mg./g. $Al_2O_3$ | Time in hours |
| 32.1 | 32.1 | .83 |
| 64.2 | 60.9 | 1.67 |
| 141.3 | 72.9 | 5.60 |
| 212. | 75.3 | 5.50 |
| 578. | 77.8 | 15.0 |
| 994. | 82.1 | 25.8 |

TABLE IV

| Alumina at 80° | Partial pressure 55 mm. | |
|---|---|---|
| 24.3 | 23.4 | .85 |
| 50.9 | 51.0 | 1.75 |
| 97.0 | 65.2 | 3.33 |
| 170. | 68.0 | 5.83 |
| 509. | 71.4 | 17.5 |
| 580. | 71.4 | 20.0 |

TABLE V

| Alumina at 80° | Partial pressure 42.2 mm. | |
|---|---|---|
| 19.1 | 20.5 | .66 |
| 43.9 | 43.7 | 1.55 |
| 134. | 57.4 | 4.67 |
| 430. | 61.6 | 15.0 |
| 28. | 28.0 | 1.33 |
| 111. | 58.0 | 5.33 |
| 151. | 59.3 | 7.25 |
| 471. | 62.9 | 22.6 |

TABLE VI

| Alumina at 80° | Partial pressure 31.8 mm. | |
|---|---|---|
| 54.2 | 45.6 | 2.3 |
| 79.8 | 49.9 | 3.3 |
| 459. | 54.4 | 19.1 |
| 558. | 55.8 | 23.3 |
| 660. | 53.9 | 27.6 |

VII

| Alumina at 60° | Partial pressure 55 mm. | |
|---|---|---|
| 29.4 | 29.6 | 1.0 |
| 62.8 | 62.5 | 2.2 |
| 353. | 114.5 | 12.2 |
| 546. | 115.7 | 18.8 |
| 677. | 115.7 | 23.4 |

TABLE VIII

| Alumina at 60° | Partial pressure 42.2 mm. | |
|---|---|---|
| 24.3 | 24.7 | .83 |
| 76.8 | 73.9 | 2.63 |
| 120. | 87.9 | 4.16 |
| 170. | 94.4 | 5.90 |
| 259. | 97.4 | 9.00 |
| 341. | 98.9 | 11.2 |
| 715. | 110. | 24.8 |

TABLE IX

| Alumina at 60° | Partial pressure 31.8 mm. | |
|---|---|---|
| 61.2 | 62.6 | 2.58 |
| 90.6 | 77.0 | 3.83 |
| 122.4 | 80.8 | 5.17 |
| 428. | 89.2 | 18.1 |
| 580. | 89.2 | 24.5 |

TABLE X

| Alumina at 50° | Partial pressure 72.7 mm. | |
|---|---|---|
| Amt. of vapor supplied, in mg./g. $Al_2O_3$ | Amt. of vapor sorbed, in mg./g. $Al_2O_3$ | Time in hours |
| 64.4 | 63.0 | 1.4 |
| 96.7 | 94.7 | 2.5 |
| 226. | 195. | 4.2 |
| 907. | 294. | 16.8 |
| 1360. | 316. | 25.1 |
| 1720. | 330. | 31.8 |
| 2626. | 346. | 48.2 |
| 2980. | 349. | 55.0 |
| 3190. | 352. | 58.9 |
| 4645. | 376. | 83.9 |
| 4745. | 378. | 87.6 |
| 5428. | 379. | 100.3 |
| 5595. | 383. | 103.3 |

TABLE XI

| Alumina at 50° | Partial pressure 55 mm. | |
|---|---|---|
| Amt. of vapor supplied, in mg./g. $Al_2O_3$ | Amt. of vapor sorbed, in mg./g. $Al_2O_3$ | Time in hours |
| 69.7 | 69.9 | 1.32 |
| 199. | 142.2 | 3.78 |
| 247. | 149.0 | 4.7 |
| 343. | 158.6 | 6.5 |
| 455. | 165. | 8.6 |
| 1054. | 170. | 20.0 |
| 1260. | 172. | 23.9 |

TABLE XII

| Alumina at 50° | Partial pressure 42.2 mm. | |
|---|---|---|
| 34.5 | 34.5 | .87 |
| 61.1 | 61.1 | 1.53 |
| 130.2 | 117.9 | 3.27 |
| 193.9 | 128.8 | 4.87 |
| 305.5 | 135.1 | 7.68 |
| 390. | 138. | 9.80 |
| 465. | 139. | 11.7 |
| 558. | 139.4 | 14.0 |
| 1127. | 141. | 28.3 |

TABLE XIII

| Alumina at 50° | Partial pressure 31.8 mm. | |
|---|---|---|
| 19.7 | 19.7 | .61 |
| 42.6 | 42.7 | 1.26 |
| 61.8 | 61.6 | 2.00 |
| 100.3 | 91.0 | 3.25 |
| 116. | 97.2 | 3.75 |
| 143. | 105.3 | 4.63 |
| 175. | 107.4 | 5.65 |
| 270. | 112.0 | 8.75 |
| 642. | 117. | 20.8 |

TABLE XIV

| Alumina at 50.1° | Partial pressure 23.5 mm. |
|---|---|
| 26.6 | 1.15 |
| 89.8 | 3.88 |
| 169. | 7.38 |
| 380. | 16.5 |
| 480. | 20.9 |
| 647. | 28.1 |

TABLE XV

| Alumina at 40° | Partial pressure | at 40 |
|---|---|---|
| 32.0 | 32.0 | 0.2 |
| 105.6 | 105.6 | 3.8 |
| 167. | 169. | 5.9 |
| 486. | 330. | 17.0 |
| 643. | 382. | 22.5 |
| 690. | 396. | 24.2 |
| 790. | 424. | 27.7 |
| 862. | 450. | 30.2 |
| 1195. | 526. | 41.8 |
| 1282. | 547. | 45.0 |
| 1348. | 561. | 47.2 |
| 1500. | 593. | 52.5 |
| 1640. | 620. | 57.3 |
| 1990. | 678. | 69.5 |
| 2070. | 691. | 72.5 |
| 2220. | 719. | 77.6 |
| 2310. | 738. | 81.0 |
| 2720. | 752. | 110. |

TABLE XVI

| Alumina at 40° | Partial pressure 52.5 mm. | |
|---|---|---|
| Amt. of vapor supplied, in mg./g. $Al_2O_3$ | Amt. of vapor sorbed, in mg./g. $Al_2O_3$ | Time in hours |
| 49.3 | 49.3 | 1.05 |
| 94.2 | 94.2 | 2.01 |
| 197.4 | 182.4 | 4.22 |
| 253.3 | 209. | 5.42 |
| 311.8 | 232. | 6.67 |
| 357. | 249. | 7.64 |
| 598. | 315. | 12.8 |
| 669. | 335. | 14.3 |
| 1260. | 432. | 27.0 |
| 1345. | 435. | 28.7 |
| 1449. | 451. | 31.0 |
| 1825. | 502. | 39.0 |
| 2468. | 559. | 52.8 |
| 2877. | 608. | 61.5 |
| 3137. | 628. | 67.1 |
| 3774. | 675. | 80.7 |
| 4300. | 717. | 92.0 |
| 4613. | 764. | 98.6 |
| 4937. | 782. | 105.2 |
| 5392. | 802. | 115.3 |

TABLE XVII

| Alumina at 40° | Partial pressure 49.7 mm. | |
|---|---|---|
| Amt. of vapor supplied, in mg./g. $Al_2O_3$ | Amt. of vapor sorbed, in mg./g. $Al_2O_3$ | Time in hours |
| 47.3 | 47.3 | 1.3 |
| 120. | 120. | 3.2 |
| 190. | 175. | 4.2 |
| 238. | 196. | 5.2 |
| 310. | 220. | 6.5 |
| 324 | 243. | 7.0 |
| 376. | 258. | 8.2 |
| 417. | 265. | 9.1 |
| 1043. | 350. | 22.6 |
| 1139. | 364. | 24.7 |
| 1297. | 376. | 27.4 |
| 1381. | 387. | 29.9 |
| 2220. | 473. | 48.1 |
| 2430. | 484. | 52.4 |
| 2540. | 498. | 55.3 |
| 2750. | 513. | 59.8 |
| 2870. | 520. | 62.4 |
| 3390. | 549. | 73.5 |
| 3650. | 565. | 79.3 |

TABLE XVIII

| Alumina at 40° | Partial pressure 43.3 mm. | |
|---|---|---|
| 48.3 | 48.3 | 3.3 |
| 129. | 115.8 | 8.9 |
| 275. | 177.3 | 19.0 |
| 301. | 184.4 | 20.8 |
| 348. | 196.5 | 24.0 |
| 411. | 213. | 28.4 |
| 452. | 220. | 31.2 |
| 611. | 234. | 42.2 |
| 712. | 242. | 49.1 |
| 811. | 249. | 56.0 |
| 927. | 257. | 64. |
| 1019. | 258. | 72. |
| 1086. | 259. | 75. |
| 1276. | 266. | 88. |
| 1390. | 270. | 96. |
| 1469. | 272. | 101. |

TABLE XIX

| Alumina at 40° | Partial pressure 23.5 mm. | |
|---|---|---|
| 28.3 | 28.3 | 1.67 |
| 48.1 | 45.5 | 2.83 |
| 166. | 109.1 | 7.5 |
| 159. | 116.6 | 9.3 |
| 229. | 126.7 | 13.5 |
| 275. | 129.7 | 16.2 |
| 331. | 131.8 | 19.5 |
| 399. | 132.0 | 23.1 |
| 589. | 134. | 34.6 |
| | 134. | 44.7 |

TABLE XX

| Alumina at 35.5° | Partial pressure 31.8 mm. |
|---|---|
| Amt. sorbed in mg./g. | Amt. supplied in mg./g. |
| 111.5 | 113.1 |
| 115.2 | 155.7 |
| 158. | 183. |
| 185. | 263. |
| 211. | 386. |
| 236. | 715. |
| 251. | 1097. |
| 264. | 1520. |
| 266. | 1782. |
| 267. | 2372. |

In Tables III-XIX are given the results for alumina at 80, 60, 50 and 40° and for partial pressures of from 72.7 to 23.5 mm. The curves for 40° (Tables XV-XIX) are given in Fig. 3. These are typical, and the curves for the other temperatures are therefore omitted in order to save space. The broken line in Fig. 3 is the total sorption line, which the curve follows when the alumina is 100% efficient.

The sorption was first measured when the alumina and saturator were both at 40° i.e. p/P = 1. Other experiments (Tables XVI and XVII) were carried out in order to find how the sorption varied with small changes in con-

centration of vapor near the saturation pressure. The results are shown graphically in curves 1, 2 and 3, Fig. 3. In the experiments with water at a partial pressure of 52.5 mm and 55 mm it was observed that the gel became transparent before the last few points shown on the curves (1 and 2) were reached. Owing to the proximity of the temperature of the alumina and the saturator, condensation of the vapor is brought about by very slight changes in temperature and it is therefore very difficult to determine the true saturation value.

Curves 4, 5 and 6 are for partial pressures of 42.2, 31.8, and 23.5 mm. respectively. In one experiment the alumina was kept at 35.5°, the partial pressure of the vapor being 31.8 mm. The curve is shown in Fig. 3 (No. 7) in order that the results may be compared with those obtained when the alumina was at 40°.

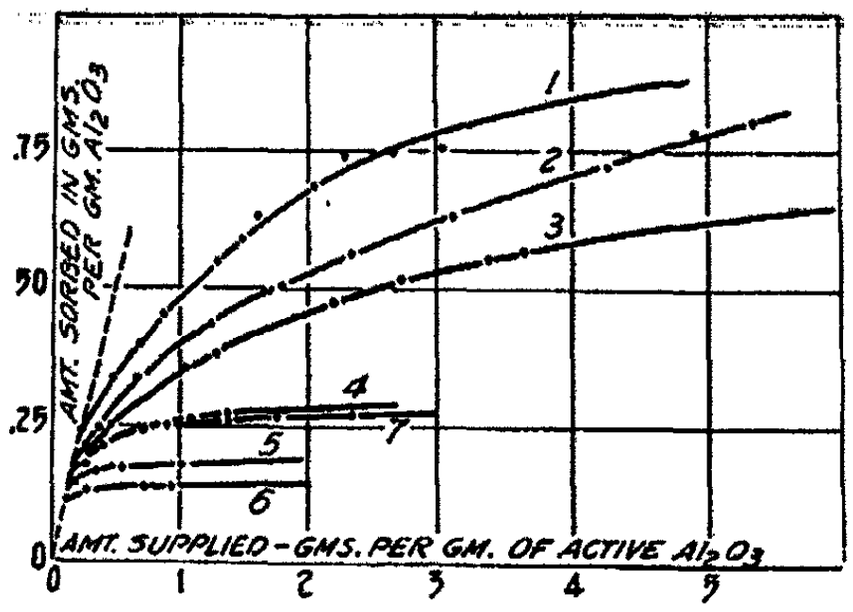



FIG. 3

## The Sorption Isotherm

The saturation value represents the amount of vapor held by the sorbent when in equilibrium with a certain partial pressure of water vapor. By plotting these values against the partial pressure, typical isotherms are obtained. In Fig. 4 are given the isotherms for 80, 60, 50, and 40°. The curves for 80 and 60° as well as the lower part of the 50° isotherm resemble the curves obtained by other investigators for the sorption of gases on charcoal and silica gel by static methods. Freundlich's equation was therefore applied to these curves and it has been found that when the log of the saturation value is plotted against the log of the partial pressure straight lines are obtained. (Curves 1 and 2, Fig. 5).

Patrick[1] related the volume of *liquid* sorbed to the relative partial pressure of the vapor and the surface tension of the liquid at the temperature of the sorbent. His equation, which is a modification of the Freundlich equation involving new constants, reads; $V = K (Sp/P)^{1/n}$ where p is the partial pressure of vapor, P is the vapor pressure of liquid at the temperature of the sor-

[1] J. Am. Chem. Soc., 38, 588 (1916).

bent, S is the surface tension of liquid at the temperature of the sorbent, and K and $n$ are constants. His equation also demands a straight line when log V is plotted against log Sp/P.

The different values of these factors are given below:

| Temperature. | Sp/P | | | | | V. | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 80° | 5.58 | 7.41 | 9.65 | 12.64 | | 55.6 | 64.4 | 73.9 | 84.5 | |
| 60° | 14.1 | 18.6 | 24.3 | 31.8 | | 90.2 | 105.1 | 120. | 132. | |
| 50° | 17.2 | 23.3 | 30.9 | 40.3 | 52.8 | 103. | 118. | 143. | 174. | 386. |

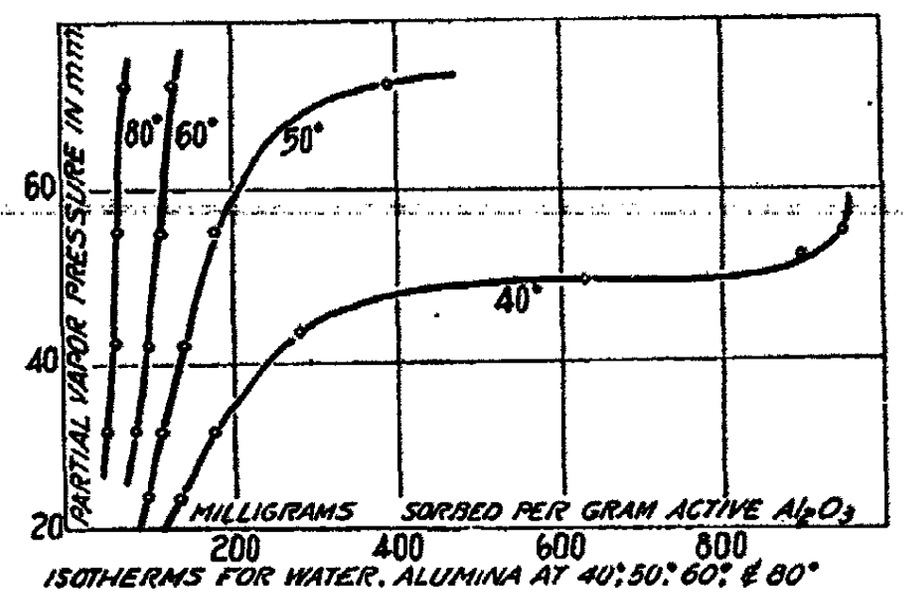



FIG. 4

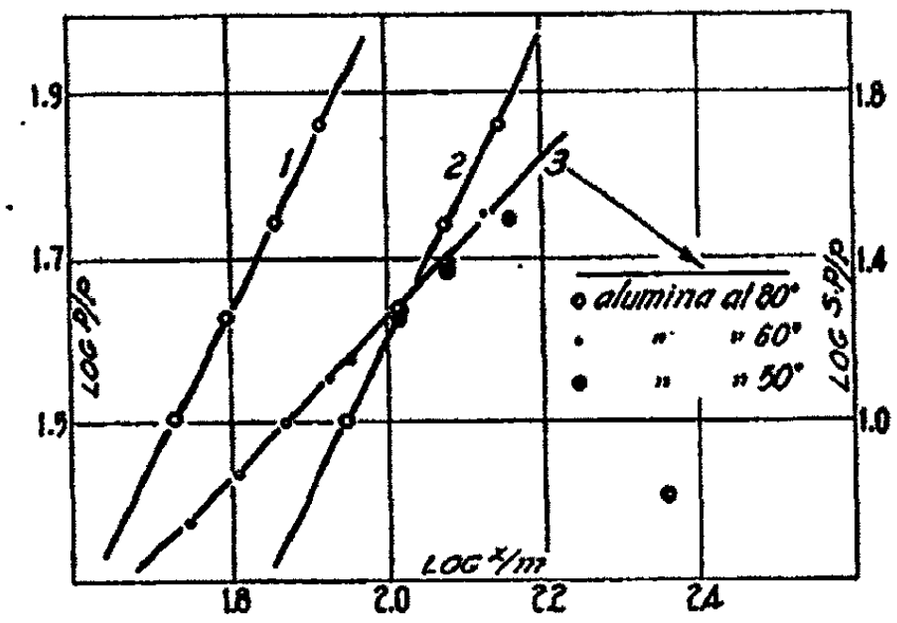



FIG. 5

The curve constructed from the logs of these is given in Fig. 5 (curve 3). Patrick's equation therefore applies to the 80° and 60° isotherm.

It will be noted that the 40° curve, Fig. 4 changes direction and flattens as the partial pressure of the vapor approaches the vapor pressure of the liquid at the temperature of the alumina. This undoubtedly represents the filling of the minute capillaries of the alumina with water. Neither Freundlich's nor Patrick's equation applies to this curve.

Trouton's equation which Anderson[1] used to calculate the radius of the capillaries in silica gel cannot rightly be applied to the curve for 40°, since in this case the curve represents the filling of the capillaries, and as Anderson and others have shown, when air is present the capillaries fill at a higher partial pressure than that at which they are emptied. The radius as determined by applying Trouton's equation to this curve will therefore be much smaller than the true radius.

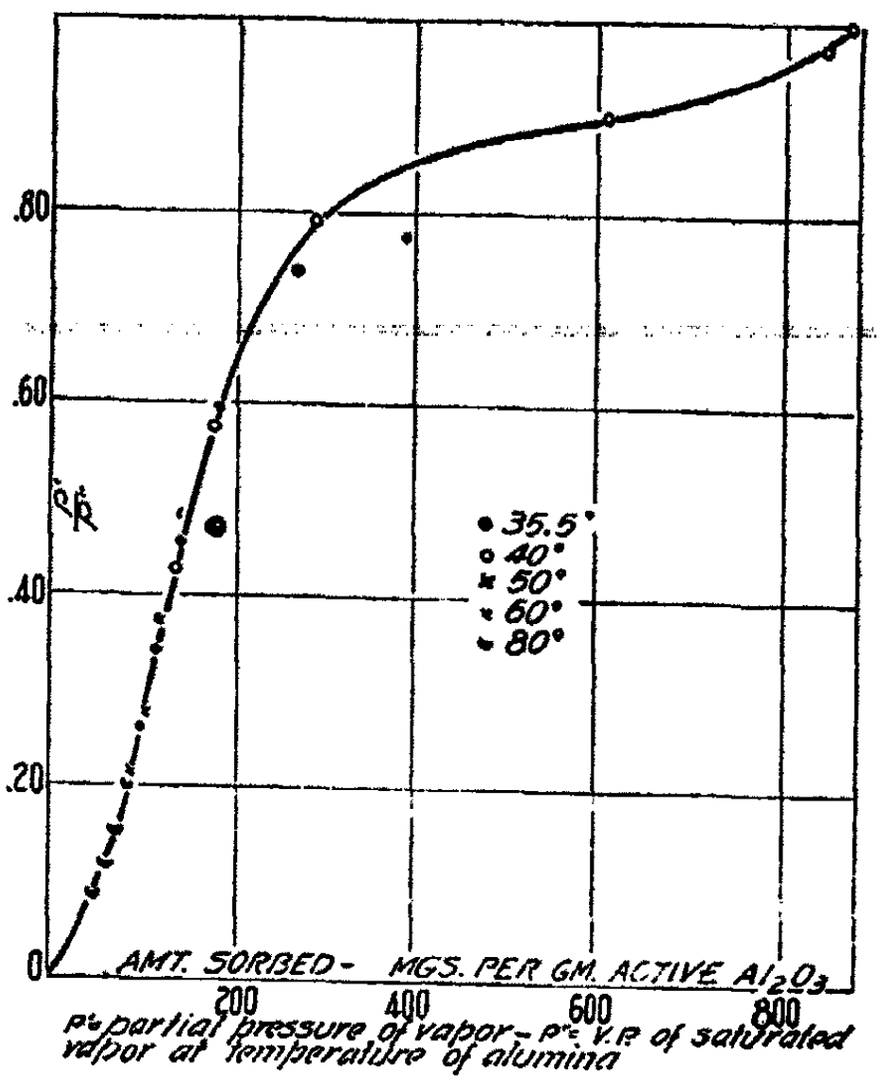



FIG. 6

## Trouton's Sorption Rule

Trouton[2] considered that the amount of vapor taken up is independent of the temperature but dependent solely on the ratio of the partial pressure of the vapor to the saturation pressure of the vapor at the temperature of the sorbent. The saturation values have been plotted against the ratio p/P in Fig. 6. It will be seen that all the points fall on approximately the same curve. Trouton's rule may therefore be considered to hold approximately.

## Relative Sorption Velocity

In Fig. 7 are shown the relative rates of sorption of water by alumina at 50° for different concentrations. These curves are similar in appearance to

[1] Z. physik. Chem., **88**, 191 (1914).
[2] Proc. Roy. Soc., **77**, 292 (1906).

those obtained by Harned[1] for the adsorption of gases by charcoal, but of course a quantitative comparison cannot be made since the velocity of flow and the dimensions of the tubes were not the same. In these experiments the rate of flow was 13 cc/min. and the cross section of the tube .39 sq. cm. Similar velocity curves can also be constructed for the other temperatures.

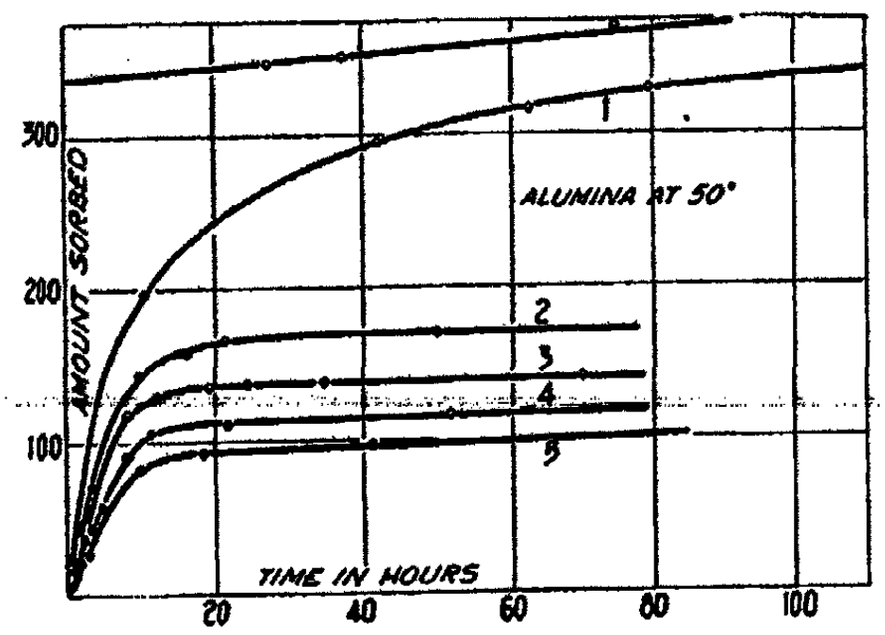



FIG. 7

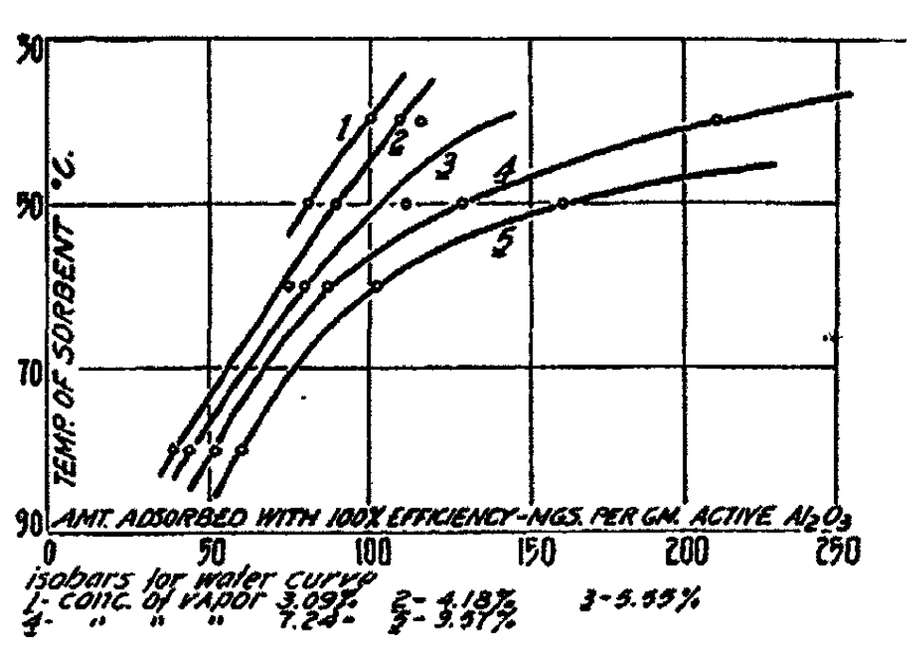



FIG. 8

## Efficiency of the Alumina

A knowledge of the efficiency of a sorbent under different conditions is of very great importance in any technical process. This is particularly true of gas mask sorbents where the efficiency must be high enough to reduce the concentration of gas to below .0001% in a very short period of time. In other applications of the sorptive power of solids the demands are not so rigorous, but the efficiency of the sorbent is still of importance. Any technical process using alumina as a drying agent would require information on the variation

[1] J. Am. Chem. Soc., 42, 920 (1920).

of the efficiency of the alumina with time, temperature and concentration. The efficiency of other vapors will depend on the relative sorption velocities under the same conditions.

The way in which temperature affects the amount which the alumina will take up before the break point is reached, given by the amount of water sorbed with 100% efficiency, is shown in Fig. 8. In this figure curve

1. represents a concentration of 3.09%
2. " " " " 4.18%
3. " " " " 5.55%
4. " " " " 7.24%
5. " " " " 9.57%

water in the entering air-vapor mixture.

In many cases information as to the efficiency of the sorbent during the whole sorption process is of interest. There are several ways in which such information may be obtained. Bohart and Adams[1] give transmission curves which show the percent of entering vapor which is unsorbed or transmitted at any time, and give equations to fit their curves. The same information is given by the curves for water (Fig. 3) since the amount transmitted or unsorbed is given by the distance between the curve and the total sorption line. Efficiency-time curves can be constructed from the data given in the tables.

## Summary

1. The sorption of water vapor has been measured at different temperatures and concentrations.

2. Both Freundlich's and Patrick's equations apply to the isotherms for 80 and 80°C. Neither applies to those isotherms obtained when the partial pressures approach the vapor pressure of the liquid at the temperature of the sorbent.

3. Trouton's rule holds approximately.

4. Curves are given showing the change in efficiency with temperature and concentration.

5. Sorption-time curves of the ordinary type are obtained.

## Acknowledgment

This research was carried out under tenure of a studentship from the Research Council of Canada, which is hereby gratefully acknowledged.

*Department of Chemistry,*
*McGill University,*
*Montreal.*

---

[1] J. Am. Chem. Soc., 42, 523 (1920).

# EQUILIBRIUM IN COLLOID SYSTEMS

BY OSCAR KNEFLER RICE

Some years ago Tolman[1] wrote two articles in which he developed a generalized phase rule, and applied it to divided and dispersed systems. He considered systems in which a phase might be divided into several regions—for example, two pieces of ice form two regions but only one phase. He developed a special phase rule for the cases where some of the regions were identical; and he found that in any one-component system two regions must either be identical or have at least two variables differ in value, while in a two-component system two regions must be identical or have at least three variables different. In the ordinary two-component colloid systems a colloid particle, which is a region, can change in two independent variables only—size, say, and concentration of one component. (Tolman assumes, and I shall always, that the particles are spherical.) Hence for equilibrium all the particles must be identical. In the case of electrically charged particles, however, another possibly independent variable is introduced. It is the purpose of the present article to develop a generalized phase rule in a form in which it possesses the practical advantage of giving the proper number of degrees of freedom without the previous consideration of identical phases, and then to apply it to the case of electrically charged colloids, showing that the possibility of various electrical conditions does not introduce extra degrees of freedom. It is also desired to consider the dynamics of the above cases, with especial regard to the criterion of stability, which I believe to be different from the one Tolman has given.

## The Phase Rule

The number of variables we choose to consider in the development of our phase rule is a somewhat arbitrary matter; but we must choose them to completely determine the system. Inclusion of extra unnecessary variables leads to an equal number of extra equations, and so makes no difference in the phase rule. In a system of $c$ components and $r$ regions we will take the following as variables:

1. The $c$ concentrations in each of the $r$ regions, $cr$ in all.
2. The $c$ fugacities in each of the $r$ regions, $cr$ in all.
3. The temperature, which is assumed to be the same throughout all the regions.
4. The $n$ other variables in each of the regions (including the pressure which is not assumed necessarily to be the same throughout) which serve to specify the state of the regions, $nr$ in all.
5. Any other variables, $v$ in number, which cannot be associated with any particular regions or which affect only a few regions.

[1] Tolman: J. Am. Chem. Soc., 35, 307-333 (1913).

At times we may neglect certain variables, which have very little effect on the problem at hand. This is continually done in phase rule work, and its permissibility for purposes of approximation is discussed in Tolman's articles[1].

We have, then $2cr + nr + 1 + v$ variables.

There are the following equations:

1. One equation for each region, stating that the sum of all the concentrations, expressed in per cent, gives 100 per cent; $r$ in all.

2. $r - 1$ equations for each component, stating that the fugacity in each region is the same; $(r - 1)c$ in all.

3. $r$ equations for each component stating that the fugacity is a function of the other variables, $rc$ in all.

4. Any other equations which may exist but which are not included in the above, $e$ in all.

The total number of equations is $r + (r - 1)c + rc + e$.

The number of degrees of freedom is, therefore, given by

$$f = 1 - r + c + nr + v - e \qquad (1)$$

We will first attempt to apply this phase rule to colloids which are not electrically charged. We have here two components, one of which chiefly makes up the dispersed phase, the other the dispersing phase, thus making $c = 2$. $n = 1$, for, as we have mentioned above, in this case there is but one independent variable, other than concentration and temperature, for each region; this may be taken as the size of the particle, and for the dispersing phase the pressure. The pressure inside each particle is uniquely determined by the surface tension, the radius, and the external pressure, while the surface tension is determined by the radius of the particle and the other variables. It is seen, then, that either pressure or surface tension might just as well have been taken as the independent variable, and we will use these quantities in many cases interchangeably. We have yet another variable to consider. It is known that the fugacity of the constituents of the dispersing phase and perhaps of the other regions depends on the number of colloid particles per unit volume. Or, instead, we may use as variable the ratio of the total amounts of the two components, which, with the other variables, determines the number of particles per unit volume. So $v = 1$. There are no additional restrictions or relations between the variables, so $e = 0$. Substituting now into (1) $f = 4$. We have completely specified our system if we give temperature, pressure on the dispersing medium, radius of *one* particle, and the ratio of total amounts of the two components. From this we would infer that at equilibrium there is one size of particle, or, at least, only a small number of definite sizes.

We shall now pass to the case where the colloid particles may be charged. Here the fugacities of the various substances concerned will be completely determined if, besides temperature and external pressure, their concentrations, the concentration of electricity, and the surface conditions, electrical and otherwise, are known. It may be necessary to use several variables to specify the

[1] Tolman: loc. cit.

conditions at the surface but at equilibrium they will each have a definite value for given concentrations of the components and electricity in the particle and surrounding region, for given geometrical conditions (which we assume are determined by the size of the particle to which the variables relate), and for a given particle density. They are, therefore, not independent, and cannot affect the number of degrees of freedom, under the assumptions made, which would seem to hold very approximately. So $n = 1$, as before. The above discussion naturally intimates that we are going to treat electricity as a component. (Only one kind of electricity is a component, for the electricity is involved in an equilibrium with matter, $A \longrightarrow A^+ +$ an electron, which brings in an equilibrium equation). This necessitates the addition of another equation stating total charge is zero. We now have $c = 3$, $e = 1$, while $v = 1$, as before, so we again have $f = 4$.

If the electrical charge is due to ionization the case is not essentially different. One of the ions is then taken as the extra component.

This result may be obtained in another way. Suppose we divide our system into a large number of small regions, within each one of which conditions are approximately uniform[1]. Then conditions in any one region are determined by the temperature, its pressure, its concentrations of substances and electricity, and similar variables for other surrounding regions. The regions are of course battered around in the Brownian movement, but if the particles do not change appreciably when in a state of equilibrium the regions may be considered to maintain their identity, at least for a time, while the effect of surrounding regions, which is doubtless small, is to some extent a statistical mean. If there is a certain definite number of regions each having a definite composition, the ratio of components may no longer be regarded as an independent variable, and if we call $v = 1$ we must add an equation. But the same definiteness in number of regions and their composition fixes the amount of electricity present and eliminates the necessity of another equation stating total charge is zero, so the number of degrees of freedom is the same as before. The rigor of the above treatment may be questioned owing to the Brownian movement and the fact that a region may have a small number of molecules. In fact, all the previous considerations are more or less open to the former objection, as Tolman noted in his treatment of the subject, but the value of results obtained by neglecting Brownian movement will appear later.

The next interesting case is that of a colloid dispersed in a salt solution. Here, counting the electricity as a component we have $c = 4, n = 1, v = 1$ (particle density, say) and $e = 1$ (total charge zero). Hence $f = 5$. So we must fix, say, temperature, outside pressure, relative amounts of colloid substance, solvent, and salt, and the radius of one particle.

From these results it is again to be inferred that a condition of equilibrium is realized when the particles are all of one size, or of a small number of definite sizes. This inference can be readily generalized.

---

[1] See Beattie: J. Am. Chem. Soc., **46**, 2213 (1924).

## Stability of the Equilibria

Since in the cases above considered the size of the particles can be fixed at any desired size there will be many such equilibria, but not all of them will be stable. If the equilibrium is unstable its free energy will be a maximum, and any infinitesmal displacement will cause a change in free energy which is zero to the first order of infinitesmals and negative to the second. The condition for stability is that the total free energy of the system shall be a minimum, i.e., that any infinitesmal displacement in the system shall cause a second order increase of free energy. We may have a family of such minima. In this case there may be one or more of these minima which is less than all others immediately adjacent. The stability which exists at any one of the minima in the family we shall designate as temporary stability; if it corresponds to one of the particular minima which is less than its immediate neighbors we shall refer to it as permanent stability; for we would anticipate that a system in which there was thermal agitation would sooner or later revert to stability of the latter type; it must not be forgotten, however, that the words as used here have a special technical meaning. As a matter of fact, in practice we would never expect to see temporary stability, while a system in a permanently stable state would be subject to statistical fluctuations. Experimentally known systems in which the particles all come to a certain stable size[1] are presumably in a permanently stable state in the sense used.

What we shall have to say in the following applies to all colloids which can change continuously in size, and we will reserve the right to use such words as particle and drop, colloid and emulsion, indiscriminately.

There are three distinct kinds of changes possible in ordinary colloid systems: (1) Changes involving transfer of material from the colloid particles into the dispersing medium and *vice versa*, without change in the number of particles (drop-solution changes); (2) changes involving interchange of material between various particles without change in their number (drop-to-drop changes); (3) interchange of material involving change in the number of particles (drop-density changes).

In order to visualize these phenomena better we will devise a process whereby the changes may be effected. It should be emphasized that these changes take place within a given system, and that whatever steps our hypothetical process may take us through we always have in the initial and final states exactly the same total amount of each component. The machine we will use will merely be a set of reversible cells each of which can transfer one of our components from place to place in our system, or into a standard region to be specified. Thus if we wish to transfer material from one drop to another we have electrodes in each of the drops. If we wish to have a greater number of drops we can have various electrodes in different drops all connected in parallel and connected to an electrode which is in an infinitesmal drop, which we can then build up to the desired size at the expense of the others. This

[1] Tolman: loc. cit.

shows that a change from one state to another in which the number of drops is different can never be an infinitesmal displacement in the dynamical sense, for if the drop to be made or removed is of finite size it requires the transference of a finite amount of material. This point should be emphasized, as it carries important consequences. Systems stable with respect to drop-solution and drop-to-drop changes are stable in the way we have called temporary, while if they are also stable with respect to drop-density changes they are permanently stable, as will appear.

We will now consider the stability of equilibria in which all the particles have the same size and are similar. One condition for stability is that reversible drop-solution transfers of material shall cause an increment of free energy which is zero to the first order and positive to the second. The same must be, true for free energy changes accompanying reversible drop-to-drop changese with or without change of composition. By examining in detail the case whern there is a drop-to-drop transfer of one component only we can get certain criteria of value.

Let $F_i$ be the free energy[1] of the $i$th drop, referred for convenience to a standard state in which composition and all other variables are the same as in the drop except that there is no pressure due to surface effects, $m_{ij}$ the mass of the $j$th component in it, $v_i$ its volume, and $s_i$ its surface.

Then, in order for the system to be stable $\Sigma_i \delta F_i > 0$ to the second order of small quantities, and $\Sigma_i \delta m_{ij} = 0$, where the summations are to be taken over all the drops. We may then write

$$\Sigma_i \delta F_i = \Sigma_i \frac{\partial F}{\partial m_{ij}} \delta m_{ij} + \tfrac{1}{2} \Sigma_i \frac{\partial^2 F_i}{\partial m_{ij}} (\delta m_{ij})^2$$

to the second order by Maclaurin's expansion. For the case where the particles are alike we may drop the subscripts $i$ and write the derivatives outside the summation sign, thus:

$$\Sigma \delta F = \frac{\partial F}{\partial m_j} \Sigma \delta m_j + \tfrac{1}{2} \frac{\partial^2 F}{\partial m_j^2} \Sigma (\delta m_j)^2 \qquad (2)$$

The first term drops out as $\Sigma \delta m_j = 0$, and since $\Sigma (\delta m_j)^2$ must be positive, for stability $\partial^2 F / \partial m_j^2$ must also be positive. Since under the conditions stated $v$ and $s$ are functions of $m_j$ we may change variables and write

$$\frac{\partial^2 F}{\partial m_j^2} = \frac{\partial}{\partial m_j} \left( \frac{\partial F}{\partial v_j} \frac{\partial v}{\partial m_j} \right) = \frac{\partial^2 F}{\partial v_j^2} \left( \frac{\partial v}{\partial m_j} \right)^2 + \frac{\partial F}{\partial v_j} \frac{\partial^2 v}{\partial m_j^2} > 0 \qquad (3a)$$

$$\text{or} \quad \frac{\partial^2 F}{\partial m_j^2} = \frac{\partial}{\partial m_j} \left( \frac{\partial F}{s_j} \frac{\partial s}{\partial m_j} \right) = \frac{\partial^2 F}{\partial s_j^2} \left( \frac{\partial s}{\partial m_j} \right)^2 + \frac{\partial F}{\partial s_j} \frac{\partial^2 s}{\partial m_j^2} > 0 \qquad (3b)$$

where $v$ and $s$ are written $v_j$ and $s_j$ where necessary to indicate that the amount of the $j$th component is the only independent variable. We can consider $\partial F / \partial s_j$

[1] This free energy may be either one of the two free energies, called respectively A and F by Lewis and Randall in "Thermodynamics and Free Energy of Chemical Substances", p. 155, for it will be observed that the changes we deal with are the same in both, not involving the part wherein they differ at all. It must be borne in mind that Lewis and Randall's P is the external pressure, while the $p$ we later use is the excess pressure in the drops due to surface effects.

as the surface tension corresponding to the $j$th component and $\partial F/\partial v_j$ as the pressure $p_j$ due to this surface tension. There seems to be no need for the various surface tensions and pressures for different components to be equal.

If the jth component has constant partial volume, $\partial v/\partial m_j$, the last term in (3a) drops out and since $\left(\frac{\partial v}{\partial m_j}\right)$ is positive the inequality becomes

$$\frac{\partial p_j}{\partial v_j} > 0 \qquad (4)$$

Now in order to have stability we must have the solubility of a particular component in a drop increasing when the amount of it accidentally increases and decreasing when it decreases, otherwise large drops would get larger and small drops smaller, so they would continue to diverge in size. So the above equation states in effect that if the component is incompressible or nearly so its solubility increases with the "pressure".

No such simplification is possible with (3b) which explains why we would rather talk in terms of pressure and volume than surface and surface tension.

We can also imagine our changes to take place so that no change in composition occurs. If we let F be the free energy of a drop referred to a standard state as above, $m$ the *total* mass of a particle, $v$ its volume, $s$ its surface, $\gamma$ its surface tension, and $p$ its pressure, then the same reasoning as applied before, remembering that all differentiations are to be taken with composition constant, will lead to inequalities like (3a, b), thus:

$$\frac{\partial p}{\partial v}\left(\frac{\partial v}{\partial m}\right)^2 + p\frac{\partial^2 v}{\partial m^2} > 0 \qquad (5a)$$

$$\frac{\partial \gamma}{\partial s}\left(\frac{\partial s}{\partial m}\right)^2 + \gamma\frac{\partial^2 s}{\partial m^2} > 0 \qquad (5b)$$

and for the incompressibility the inequality

$$\frac{\partial p}{\partial v} > 0 \qquad (6)$$

$p$ and $\gamma$ are now what are ordinarily considered the "real" pressure and "real" surface tension, respectively. In this case it would be almost inconceivable for inequalities (5a, b) not to hold if (6) does, in the light of the explanation following (4), for we could scarcely imagine a decrease of fugacity of any component accompanying an increase of pressure without change in composition.

It will be noticed that the requirements for stability are such that they will be met in general by a continuous range of sizes. We are therefore prompted to look for sizes of permanent stability, but first we must consider the case where we have several sizes in equilibrium. We will assume incompressibility. We have, for transfer of the $j$th component, since $p_{j1} = \partial F/\partial v_{j1}$, ...

$$\Sigma\delta F = p_{j1}\Sigma\delta v_1 + p_{j2}\Sigma\delta v_2 + \ldots + \tfrac{1}{2}\,\partial p_{j1}/\partial v_j\,\Sigma(\delta v_1)^2 + \tfrac{1}{2}\,\partial p_{j2}/\partial v_j\,\Sigma(\delta v_2)^2 + \ldots \qquad (7)$$

where the subscripts 1, 2,... refer to the different sizes, and where we have taken such things as we may out of the summations, and where each summation is to be taken over all particles of the proper size. The first order terms must

add to zero (adding together all the first order summations), the sum of the second order parts must be positive. The $\delta v$'s are arbitrary, subject only to the condition $\Sigma\delta v_1 + \Sigma\delta v_2 + \ldots = 0$. Hence

$$p_{j1} = p_{j2} = \ldots . \qquad (8)$$

Again the arbitrariness of the $\delta v$'s and the positiveness of their squares necessitates for stability

$$\frac{\partial p_{j1}}{\partial v_j} > 0, \quad \frac{\partial p_{j2}}{\partial v_j} > 0, \ldots . \qquad (9)$$

But even though particles of different sizes exist in equilibrium together there might be much energy released if all the particles of one size could pass over to the other size, because such a change would involve a change in the number of particles, and would involve the free energy of building up or removing whole particles. On account of something analogous to an energy of activation the change might be slow, or the system might be going over to some still more stable state. That two sizes which exist in equilibrium should have the same energy content per unit mass is an extremely improbable circumstance. We are justified, then, if, in our considerations of permanent stability, we take into account only systems in which the drops are all of the same size.

In order to find the criterion of permanent stability we need to consider how we can go from one state of temporary stability to another by means of our standard process. We will have the material of each of the particles simultaneously removed at the same rate and without change of composition, into a phase which differs only from the dispersed phase in that there is no pressure due to surface tension, till they are completely gone. We will then build up the system, creating the proper number of new particles still without change in composition, till we have put all our material back, giving a different number and a different size of drops. The particles thus formed, being of the same composition as the previous ones will not now be in equilibrium with the solution, but an infinitesimal change of composition will bring them into equilibrium. The free energy change involved will be a second order infinitesimal, if the change of the mass of the particles between initial and final states is a first order infinitesimal, as it is a change to equilibrium. But the work done in the whole change from one state to the other will later appear to be in general of the same order of magnitude as this difference of mass, and in order to find the position of maxima or minima of free energy we may set it equal to zero to the first order, neglecting the work done in the final change which gives equilibrium in composition. We must use great caution in *distinguishing* between maxima and minima, for that involves the second order terms.

If there is an appreciable amount of surface layer which is different from the rest of the particle we will not consider it to be part of the particle, but will allow it to change so as to be in equilibrium with the liquid, and as it is always maintained at equilibrium these changes may be neglected also, as we will show. Now we are considering intermediate steps in our process. Say

we remove a small part of each of our drops to our standard phase, making them all smaller in size. We did an amount of work in this process which is of the order of magnitude of the mass removed, while the work involved in reversible changes which bring the surface into equilibrium with the solution is again a second order infinitesimal. If we did not allow this change in the surface layer we see that as the particle got smaller and smaller the surface layer would get thicker and thicker, and finally when all the interior of the particle was gone we would be confronted with the problem of removing this surface part and redistributing it among a different number of particles. Our final result would, of course, be the same. I believe that the process chosen is as simple as any that may be found—in the light of the above two paragraphs we see that it requires only that we calculate the work due to surface tension involved in removing and adding material in the drops without change in composition. The difficulty is in knowing the surface tension or the pressure in the drops under the unnatural conditions used. We will be led, however, to certain approximations, and will obtain a perspective which will enable us to estimate the range of their validity.

Let us start with some particular size in which the particles all have a mass $m$. Let F be the free energy which is *lost* by one particle when all of its material is transferred as part of our process to the standard state described (it is then the free energy gained in the reverse process), and let F′ be the free energy *gained* when a particle is regenerated by this process to a mass m′ which it has in an adjacent state, or rather which it would have were it not for the subsequent transfer of material which is necessary to get back to equilibrium. The total free energy lost by removing all the drops is $\Sigma F = \Sigma (F/m)m$ where the summation is taken over all the particles. As F and $m$ are the same for all particles this may be written $F/m\ \Sigma m$. Similarly the total free energy gained in the particles' regeneration is $F'/m'\ \Sigma m'$, where the summation is again taken over all the particles, there being now a different number of them. The total change in free energy, which we may denote as $\delta\Sigma F$ is given by

$$\delta\Sigma F = F'/m'\ \Sigma m' - F/m\ \Sigma m$$

But as $\Sigma m = \Sigma m'$ we get letting $F'/m' - F/m = \delta\,(F/m)$ and $m' - m = \delta m$

$$\delta\Sigma F = \left(\delta\frac{F}{m}\right)\Sigma m = \left[\frac{\frac{\partial F}{\partial m}}{m}\delta m - \frac{F}{m^2}\delta m\right]\Sigma m \text{ (to the first order).}$$

Hence as a necessary but not a sufficient condition for permanent stability

$$\frac{\frac{\partial F}{\partial m}}{m} - \frac{F}{m^2} = 0 \qquad (10)$$

where it is understood that all the differentiations are taken with constant composition, as explained.

Now $\partial F/\partial m$ may be separated into two parts. When a single particle is removed by our process a certain amount of work is done. Now suppose we change the number of particles, and regenerate them till each has a mass equal to that it had in the *initial* state. The work to regenerate each particle to this

mass might be different from that it did in being removed, due to the effect of the different number of particles. We will designate this difference as $\left(\frac{\partial F}{\partial m}\right)_1 \delta m$, $\delta m$ having the meaning of the previous paragraph. *Now* in order to get to the proper final state a certain amount of material must still be removed or added, and this work, done against the pressure due to surface tension and depending on the volume change in this final process, we will call $\left(\frac{\partial F}{\partial m}\right)_2 \delta m$, so $\frac{\partial F}{\partial m} = \left(\frac{\partial F}{\partial m}\right)_1 + \left(\frac{\partial F}{\partial m}\right)_2$ while $\left(\frac{\partial F}{\partial m}\right)_2 = p \frac{\partial v}{\partial m}$. It is now to be noted that in systems where the density of colloid particles is very small $\left(\frac{\partial F}{\partial m}\right)_1$ tends to vanish, while $p \frac{\partial v}{\partial m}$ remains finite. Hence for dilute colloidal solutions the necessary condition for permanent stability becomes

$$\frac{p}{m}\frac{\partial v}{\partial m} - \frac{F}{m^2} = \frac{p}{m}\frac{\partial v}{\partial m} - \frac{\int_0^v p dv}{m^2} = 0 \qquad (11)$$

In this case and in all others (unless specifically noted to the contrary) all quantities which appear under the integral sign are to be considered as functions of the variable of integration, and when they appear outside the integral sign they have the values corresponding to the upper limit.

We now turn to the consideration of other necessary conditions. In the first place our point must be a point of minimum, not maximum, free energy. This being the case the derivative of the expression $\frac{\partial F/\partial m}{m} - \frac{F}{m^2}$ with respect to the number of particles must be negative. The negative sign is explained if we consider, for example, a state in which the number of particles is *smaller* than in the critical maximum or minimum state. This means the particles are arger. They must have a tendency to become smaller if the critical point is to be a stable point. But they tend to get smaller $\frac{\partial}{\partial m}\left(\frac{F}{m}\right)$ or $\frac{\partial F\, \partial/m}{m} - \frac{F}{m^2}$ is positive, and so has *increased* from its zero value at the critical point. This derivative must include changes due to changes in composition, as these cannot be ignored in considerations where second order differentials enter.

For one particular case, when the dispersed and dispersing phase are practically mutually insoluble, as regards all their components, there is no appreciable change in composition, and dm/dn, where $n$ is the number of particles, is a negative constant. In this case we can differentiate with respect to $m$ and our condition becomes

$$\frac{\partial\left(\frac{\partial F/\partial m}{m} - \frac{F}{m^2}\right)}{\partial m} = \frac{\frac{\partial^2 F}{\partial m^2}}{m} - 2\frac{\frac{\partial F}{\partial m}}{m^2} + 2\frac{F}{m^3}$$

$$= \frac{\frac{\partial^2 F}{\partial m^2}}{m} - \frac{2}{m}\frac{\partial\left(\frac{F}{m}\right)}{\partial m} = \frac{\frac{\partial^2 F}{\partial m^2}}{m} > 0 \qquad (12)$$

$\frac{\partial(F/m)}{\partial m}$ being, of course, zero at a maximum or minimum. For the particular case considered the criterion (5a, b) becomes the same as this. Hence the conditions for temporary stability coupled with (10) are both sufficient and necessary for permanent stability.

For incompressibility $\partial v/\partial m = v/m$ and (11) and (12) become (multiplying through by $(m/v)^2$ and $(m/v)^3$ respectively)

$$\frac{p}{v} - \frac{\int_0^v p dv}{v^2} = 0 \text{ and } \frac{\partial p/\partial v}{v} > 0 \quad (13) \text{ and } (14)$$

Recapitulating, these hold (1) if the particles are incompressible, (2) if the density (number per unit volume) of particles is so small that the condition of any one of them is independent of their number, and (3) if the dispersed and dispersing regions are mutually insoluble. The last of these assumptions removes the difficulty, of which we previously spoke, of evaluating $\gamma$ and $p$ under the unnatural conditions of our process. For no matter what system we consider, provided only the dispersed regions and dispersing phase separately have definite proportions of their particular components, when we arrive at a certain size drop in the course of our process it has a certain composition, which is indeed the only one any drop in that set of systems can have, and with assumption (2) above granted we can say that the surface tension of a drop depends, for a whole series of systems which satisfy the condition outlined, only on its size. Insofar as this is not true (13) will give incorrect results; and as (13) itself is an approximation from (11) this is another source of error. We have already noted that if (6) or (14) hold it is almost inconceivable that (5a, b) or (12) should not, but the validity of (12) as a condition for *permanent* stability rests on the assumption of insolubility. If this assumption is not correct it might have the peculiar effect of causing us to make a mistake in deciding whether (13) represents a maximum or minimum of free energy

Tolman[1] takes as his criterion of (presumably permanent) stability for the ideal case considered $\frac{\partial\left(\frac{\partial F}{\partial m}\right)}{\partial\left(\frac{\partial s}{\partial v}\right)} = 0$. As $\frac{\partial s}{\partial v}$ is a function of $m$ this amounts to $\frac{\partial^2 F}{\partial m^2} = 0$. Knapp[2] does a somewhat similar thing. Needless to say, I think this is wrong, and that the error is due to neglect of the fact that drop-density changes are far-reaching and profound.

## Theory of Coagulation

Just how far we can apply equilibrium principles to an explanation of coagulation is perhaps to be questioned. Certainly other factors enter, but we will proceed to an investigation of our equations when the particles are large, and a discussion of our results will show, I believe, that we have at least a valuable guide.

[1] Tolman: loc. cit.

[2] Knapp: Trans. Faraday Soc., 17, 457-465.

First notice that if F/m and $\partial F/\partial m$ remain finite that $\frac{\partial(F/m)}{\partial m}$ vanishes when $m$ is infinite. This means that energy changes in the neighborhood of $m$ infinite are small, that is, if a drop is large enough, it does not greatly matter just how large it is, a well known fact. This may explain why colloids when precipitated do not come down and form one continuous mass, but stay in flocks and clumps of "small" adhering particles; which has not been offered as an explanation as far as I know, though it is always stated that "surface energy becomes important only when the surface is large." As Brownian movement ceases at something like ten thousand molecular diameters, and as this is presumably near the size where more or less rapid settling occurs, it may well be that coagulation occurs when the particles are practically infinite in size as regards energy changes, though still microscopic as regards visual observation.

Because conglomeration represents the upper limit of particle size, whether it will be stable or not depends only whether larger or smaller particles have less free energy. Hence applying the discussion preceding equation (10) for a stable conglomerate $\frac{\partial(F/m)}{\partial m}$ or $m\,\frac{\partial(F/m)}{\partial m}$ which is $\frac{\partial F}{\partial m} - \frac{F}{m}$ must be less than zero when $m$ is large. Hereafter we will write (compare (11) and (13),

$$p - \frac{\int_0^v p\,dv}{v} < 0 \qquad (15)$$

for the condition of a stable conglomerate, making all the assumptions implied therein, i.e., fairly dilute colloidal solution, incompressibility, mutual insolubility of phases.

It is not necessary, and in fact, as we shall see, impossible under the assumptions we will make for large particles to be even temporarily stable if the conglomerate is stable. We will discuss this later.

Let us consider now the case of a colloid dispersed in salt solution. It seems that by far the greater effect of the salt lies in its electrical action, and we shall attribute it all to that, assuming that $\gamma_0$, the surface tension of the colloid solvent boundary as distinct from the electrical surface tension is independent of the salt concentration, and independent of the size of the particle unless the size is small.

Let us suppose that our charged particle may be considered to approximate to an electric double layer. Let us also assume that as long as the distance between the layers is small compared with the radius $a$ that both it and the surface density of charge may be considered constant for a given composition. In the range where this holds we may write for $q$, the total charge on the particle

$$q = ka^2 \qquad (16)$$

where $k$ is a constant related to the surface density and depending on the salt concentration, and for $\Phi$, the difference of potential between the drop and the solution

$$\Phi = \frac{q}{Ka} - \frac{q}{K(a+h)}$$

$$= \frac{qh}{Ka^2}, \text{ approx.} \qquad (17)$$

(neglecting $h$ as compared with $a$) where $h$ is the distance between the electric layers for large particles, and also depends on the salt concentration and where K is the dielectric constant.

From (16) and (17) $\qquad kh = K\Phi \qquad (18)$

The pressure $p_e$ due to the electric charge is given by

$$p_e = -\frac{q^2}{8\pi Ka^4} + \frac{q^2}{8\pi K(a+h)^4}$$

$$= -\frac{q^2h}{2\pi Ka^5} \text{ , approx.} \qquad (19)$$

(again neglecting h compared with a). Substituting for q from (16)

$$p_e = -\frac{k^2h}{2\pi Ka} \qquad (19a)$$

If $p_t = 2\gamma_o/a$ is pressure due to non-electrical surface tension

$$p = p_t + p_e = \frac{2\gamma_o}{a} - \frac{k^2h}{2\pi Ka} \qquad (20)$$

This holds when the particles are large. We write as a more general expression $p_e = \frac{k^2hf_2(a)}{2\pi Ka}$ and put $\gamma_o = \gamma_o^\infty f_1(a)$, where $\gamma_o^\infty$ is the non-electrical surface tension of a large drop, and assume as an approximation which certainly will not affect the general character of our results that $f_1(a)$ and $f_2(a)$ are independent of $k$ and $h$. Then, remembering that $k$ and $h$ are quantities belonging to large drops and are constant for any given system, and that $v = 4/3\,\pi a^3$, we have for large particles

$$p - \frac{\int^v pdv}{v} = \frac{2\gamma_o^\infty}{a} - \frac{k^2h}{2\pi Ka} - \frac{6\gamma_o^\infty}{a^3}\int_o^a af_1(a)da + \frac{3k^2h}{2\pi Ka^3}\int_o^a af_2(a)da$$

$f_1(a)$ and $f_2(a)$ are 1 when $a$ is large, but they may vary when $a$ is small. We can take account of this fact by setting $\int_o^a af_1(a)da = \int_o^a ada + c_1/6$ and $\int_o^a af_2(a)da = \int_o^a ada + c_2/6$, where $c_1$ and $c_2$ are constants, since in the range of large particles the values at the upper limit of $\int_o^a af_1(a)da$ and $\int_o^a af_2(a)da$ are equal to that of $\int_o^a ada$, while the lower limit does not vary. Making these substitutions, performing the intergations, and collecting terms we get

$$p - \frac{\int_o^a pdv}{v} = -\frac{\gamma_o^\infty}{a} + \frac{k^2h}{4\pi Ka} - \frac{\gamma_o^\infty c_1}{a^3} + \frac{k^2hc_2}{4\pi Ka^3} \qquad (21)$$

We do not know the values of $c_1$ and $c_2$, but when $a$ becomes *very* large we may neglect the terms with $a^3$ in the denominator. We then see that if

$\frac{k^2h}{4\pi K} < \gamma_o^\alpha$ (15) is satisfied and a coagulated mass is stable. Otherwise it is not.

Changing the concentration of salt might affect $h$ simply due to variation in the number of ions, but we would expect its chief effect to be one on $k$ due to adsorption of ions. Adsorption of ions of opposite sign would cause $k^2h/4\pi K$ to finally become smaller than $\gamma_o^\alpha$ and precipitation would occur. But if enough ions were added there might be reversal of the effect, there being a point where $k$ and $\Phi$ would pass through zero and change in sign. Since $k$ and $\Phi$ must vary in the same direction $k^2h$ which varies as $k\Phi$ must also have the same general trend, and the three quantities will be zero together. So we see that small values of $\Phi$ will be marked by coagulation, and that there will be certain limiting values of $\Phi$, positive and negative, between which coagulation will always occur.

If $\Phi$ exceeds this critical value we can attempt to form an idea of the relation between $\Phi$ and $a$ by a setting (21) equal to zero and solving for $k^2h$, getting

$$k^2h = 4\pi K\gamma_o^\alpha \frac{1 + c_1/a^2}{1 + c_2/a^2}$$

(Unfortunately we can get a relation between $\Phi$ and $a$ only if we have one between $h$ and $k$.) Since this only holds if $a$ is fairly large anyhow we may perform the indicated division, neglecting higher terms, and get

$$k^2h = 4\pi K\gamma_o^\alpha \left(1 + \frac{c_1 - c_2}{a^2}\right) = 4\pi K\gamma_o^\alpha \left(1 + \frac{c}{a^2}\right) \quad (22)$$

where $c = c_1 - c_2$.

If $\frac{k^2h}{4\pi K} > \gamma_o^\alpha$ we see by differentiating (20) that (6), the condition for temporary stability, must hold, and (22) has a real solution if $c$ is negative, and as $a$ becomes great $\frac{k^2h}{4\pi K}$ approaches $\gamma_o^\alpha$, its limiting value. If $c$ is positive there is no solution when $\frac{k^2h}{4\pi K} > \gamma_o^\alpha$ in the region where the assumptions on which (21) is based hold, but there might be points of permanent stability possible elsewhere. In the one case coagulation would occur after gradual increase of the size of the drops to infinity, while in the other it is hard to tell just what would happen.

One possibility that we have quite neglected in treating of coagulation is that in a given system there should be at the same time other stable conditions possible, outside of the range of large particles. If the conditions of an experiment were not such as to exclude these possibilities anomalous results might be obtained. If (15) holds then (6) cannot, and any large drop will tend to distill into the conglomerate mass, becoming smaller itself. It may continue to do this till it disappears, or it may reach a size such that it can exist in equilibrium with a coagulated mass, the condition (8) being satisfied and (9) being satisfied for the drops. If there were a large mass of the conglomerate material we would expect it to exert a sort of stabilizing influence by

maintaining the composition of the solution constant, being particularly effective if (9) held, for the particles, over a long range around the equilibrium size. Knapp[1] quotes examples which answer this description.

It should be brought to the reader's notice that $\gamma = \gamma_o^\alpha + \frac{k^2 h}{4\pi K}$ for the large particles and conglomerates we have been considering. Thus if $\gamma$ is positive the coagulated mass is stable, otherwise not. This is also Tolman's conclusion, which he got by assuming the surface tension not to vary or to vary only slightly, which is essentially what we did for the case of very large particles (and only for them). But Tolman, as far as I am aware, does not point out that this entails a critical potential, nor does he have anything to indicate, as equation (22) does, that this limiting potential is approached asymptotically as a approaches infinity (if a solution of this equation is possible when $\gamma$ is negative.)

## Interpretation of Experiments

A critical potential below which coagulation occurs has been found by Powis in experiments with oil emulsions[2] and arsenious sulfide[3], and numerous other such cases are given by Northrup[4]. While nothing very conclusive is to be learned from the experiments, it does seem probable that coagulation is brought about by an increase in the size of the particles. Ellis[5] has measured the size of oil particles supposedly in equilibrium in solutions of various concentrations of hydrochloric acid and sodium hydroxide and has found that as the potential is lowered the size of the particle increases more and more rapidly, the increase becoming very large at a definite potential, in qualitative agreement with (22).

One difficulty in interpreting the experiments is that we are never really sure whether equilibrium is established; but even if it is not it is still very likely that the equilibrium conditions would be controlling factors in the general course of events. Even the fact that hardly any colloids keep indefinitely is not a fatal objection to the theory outlined, for while there might be very slow changes taking place which would eventually result in precipitation these can be disregarded as compared to more rapid changes of another nature, in the applications of the principles of equilibrium; and, indeed, it is generally recognized that coagulation is a different kind of thing than very slow settling. It would be quite possible, for, example, to have some very slow chemical process taking place which would alter the change on the particles; this is an explanation Northrup suggests for slow settling after an initial period of stability. While this kind of change would not affect the equilibrium at any one time, it might cause a gradual change in the equilibrium size. Of course, any

[1] Knapp: loc. cit.

[2] Powis: Z. physik. Chem., 89, 186-212 (1915).

[3] Powis: J. Chem. Soc., 109, II, 734-744 (1916).

[4] Northrup in Bogue's "Theory and Application of Colloidal Behavior", Vol. I, Chap. III

[5] Ellis: Z. physik. Chem., 80, 579 (1915).

colloid whose precipitation can be explained by equilibrium principles really should be a reversible colloid. Merely changing the concentration of the salt after arsenious sulfide has been precipitated will not bring it back into colloidal solution. Just why this is, is hard to say. It may have something to do with the fact that the Brownian movement is present during the precipitation process, but not after precipitation, or it may be a result of slow diffusion and hence slow establishment of equilibrium in the flocks of precipitated particles, or something else may happen to the precipitated particles. And it must be remembered that our theory refers only to spherical, hence free, particles, though how much difference this might make is hard to tell.

Weiser and Nicholas[1], Burton and Bishop[2], and Bach[3] have found effects of colloid concentration on the concentration of electrolyte necessary to cause coagulation, contrary to what would be expected on our theory. It is true that sometimes there are about 100 mols of colloid to every mol of electrolyte at coagulation, so that it might be argued that the adsorption could actually change the concentration of the salt in the solution, and then besides the colloid would not be "dilute" in the sense defined, after all, and our whole treatment would be invalidated. But this should not be the case for large particles, if the adsorption is truly a surface effect, and so would not make any difference in the critical potential or concentration.[4] Powis observed his arsenious sulfide solutions[5] over a period of several months, and found, for example, that if the solution were .3 millimolal in barium chloride there was no precipitate in that time, while in a .4 millimolal solution a precipitate appeared in a day or two. The results of the others would vary with the time they let their solutions stand.[6] Also, none of the other writers ever found less salt necessary to coagulate than Powis did, except that Bach once found very slightly less, and usually they needed much more. So it seems probable that Powis was observing equilibrium effects; and the others rate of reaction effects as they, themselves, would probably agree. Powis, himself, did not come as close to

---

[1] Weiser and Nicholas: J. Phys. Chem., 25, 742-757 (1921).

[2] Burton and Bishop: J. Phys. Chem., 24, 701-715 (1920).

[3] Bach: J. Chim. phys., 18, 52 (1920).

[4] In order to get some idea of the general order of magnitude of $\left(\frac{\partial F}{\partial m}\right)_t$, as used in the paragraph immediately preceding equation (11), we may note (using primes to distinguish the variables in the integration from their values at the upper limit, as confusion might arise in this case) that (for incompressibility)

$$\left(\frac{\partial F}{\partial m}\right)_t = \int_0^v \frac{\partial p'}{\partial v} dv' = \frac{d}{dv}\int_0^v p'dv' - p \quad (23)$$

But $p = \frac{2\gamma}{a}$, and if, for large values of $a$, $\gamma$ is approximately constant(which is the case if the adsorption is truly a surface effect, for then, for large values of $a$ the adsorption should not be able to appreciably change the concentration of salt in the solution). $\frac{d}{dv}\int_0^v p'dv' = \frac{2\gamma}{a}$, so $\left(\frac{\partial F}{\partial m}\right)_t$ obviously becomes zero faster than $p$, as is seen by putting these values, which become more and more approximately correct as $a$ becomes large, in (23).

[5] Powis: J. Chem. Soc., 109-2, 734-744 (1916).

[6] See Weiser and Nicholas: loc. cit. (page 750).

observing equilibrium effects as he might have, as he did not consider precipitation to have taken place till the concentration of the barium chloride was .5 millimolal, but the only effect this can have is to cause the measured magnitude of the critical potential to be slightly too low.

## Summary

The phase rule has been deduced in a form in which it can be directly applied to colloids, and by its use it has been inferred that both where the particles are electrically charged and where they are not that equilibrium exists only if the particles are all of one size, or of a few definite sizes.

The stability of the equilibria has been examined, and two distinct types of stability, temporary and permanent, have been found. The conditions for stability, and the relation between the two kinds of stability have been considered in detail.

These considerations have been applied to coagulation, and an attempt has been made to interpret experiments with their aid.

I wish to thank Professor R. C. Tolman of the California Institute of Technology and Professor J. H. Hildebrand of this laboratory for valuable suggestions.

*Department of Chemistry,*
*University of California,*
*Berkeley, California.*

# ANTIMONY SULPHIDES

BY LAUCHLIN MACLAURIN CURRIE

## I. Composition of the Antimony Sulphides

Stibnite was known five centuries ago, and recognized as a mixture or combination of sulphur and antimony[1]. It was in 1812 that Davy[2] first showed by analyses that stibnite is the trisulphide of antimony, and corresponds to the formula $Sb_2S_3$. The quantitative study of the antimony sulphides really began with Davy's work. Others followed closely behind him.

Faraday[3] supposed that he had prepared the disulphide. Unger[4] claimed to have prepared a disulphide according to the reaction $3Sb_2S_3 = Sb_2S_5 + {}_2Sb_2S_2$. This so-called disulphide was never separated. Dammer[5], Pélabon[6], and Moissan[7] all agree that the existence of such a compound is very unlikely. Gmelin-Kraut[8] states that a sulphide containing less sulphur than that required by the formula $Sb_2S_3$ does not exist.

H. Rose[9] concluded that from a solution of antimonic acid a mixture of trisulphide of antimony and sulphur would be thrown down by $H_2S$. Bunsen[10] disagreed and recommended the precipitation of antimony as the pentasulphide for the quantitative estimation of the element. Neither Willm[11], Mourlot[12] nor Thiele[13] could check with Bunsen's work. All found that the sulphide as precipitated contained sulphur easily extractable with a sulphur solvent. Bosek[14] did much towards clearing up the question, by showing that only if Bunsen's directions are carefully followed will pure pentasulphide be formed. He also made a study of the factors affecting the reaction.

Berzelius[15] in 1822 stated that antimony tetrasulphide could be prepared by passing hydrogen sulphide through a solution of $Sb_2O_4$. Since that time there has been much discussion as to the existence or non-existence of the tetra- and penta-sulphides of antimony. Considerable work has been done but relatively little since that of Klenker[16] who left the question far from settled.

---

[1] Abegg: "Handbuch anorg. Chem." **3** III, 573, 596 (1907); Mellor: "Modern Inorganic Chemistry", 607 (1917).

[2] Phil. Trans., **1812**, 196.

[3] Pogg. Ann. **23**, 314 (1831).

[4] Arch. Pharm. (2) **147**, 193 (1871); **148**, 2 (1871).

[5] Dammer: "Handbuch anorg. Chem." **2** I (1) 213 (1894).

[6] Compt. rend., **130**, 911 (1900); Chem. News, **81**, 202 (1900).

[7] Moissan: "Traité de Chimie minerale," **2**, 42 (1905).

[8] Gmelin-Kraut: Handbuch anorg. Chem., **3** II, 698 (1908).

[9] Pogg. Ann., **107**, 186 (1859).

[10] Ann., **192**, 305, 317 (1878).

[11] Z. anal. Chem., **30**, 428-443 (1891).

[12] Compt. rend., **123**, 54-55 (1896).

[13] Ann., **263**, 371 (1891).

[14] J. Chem. Soc., **67**, 515 (1895).

[15] Schweigger's J., **39**, 58 (1822).

[16] J. prakt. Chem., (2) **59**, 150, 353 (1899).

The object of this study was two-fold: (1) the determination of the nature and number of phases in so-called antimony pentasulphide; (2) the study of the colors of antimony sulphides—particularly the trisulphides—and the factors affecting the colors.

Antimony pentasulphide is referred to here as "so-called", meaning, in this case, any substance that on analysis gives 60% antimony and 40% sulphur. One may easily calculate that this might be a trisulphide plus 16% excess sulphur, a tetrasulphide plus 8% excess sulphur, a pure pentasulphide, or a mixture of the three sulphides plus the required amount of excess sulphur.

Analytical methods alone can tell one little as to the composition of such a substance; a mixture of 0.840 gm. of stibnite plus 0.160 gm. of sulphur will on analysis show exactly the same composition as will pure pentasulphide, or a mixture of 0.420 gm trisulphide, 0.460 gm tetrasulphide plus 0.120 gm of sulphur.

Most of the early research, taking note of the effect of different sulphur solvents on the sulphides, was done with especial care to note the exact amount of sulphur extracted under definite conditions, and the exact composition of the resulting residue. Early workers carefully noted the *amount* of sulphur extracted, but failed to get any idea as to the *way* in which sulphur was extracted, and so failed to distinguish between sulphur present in the original sample as a separate solid phase and that formed by subsequent decomposition of the sample.

The method as adopted for this study is not a new one. It has been used successfully by Allen[1], Foote[2], Thiel[3], Miller and Kenrick[4], and others. It is based on the variation in concentration of a solution in equilibrium with a solid phase of varying composition. When concentration of solution is plotted against composition of the total solids, the resulting curve will give an idea as to the nature of the material studied.

The problem here studied differs radically in one important detail from the work mentioned above. All the work required that equilibrium be reached. The previous studies dealt with reversible equilibrium, where the equilibrium may be reached by approach from either direction. In the problem here studied, equilibrium could be reached from one direction only, the side corresponding to the higher sulphide.

The study is, therefore, one of an irreversible equilibrium. Just why this should be true is by no means clear. To date, however, all attempts to replace sulphur after removal from a sulphide have resulted in failure.

The method as usually used calls for the treatment of the sample with successive portions of solvent, allowing sufficient time to reach equilibrium, and determining the composition of the solid and solution phases. In this case, the method was changed to suit the problem. In the first place, instead

[1] Am. Chem. J., 25, 307 (1901).
[2] Am. Chem. J., 29, 203; 30, 339 (1903); 32, 246, 251 (1904).
[3] Z. physik. Chem., 43, 641 (1903).
[4] J. Phys. Chem., 7, 259 (1903).

of treating the same sample with successive portions of solvent, equal samples were treated with increasing amounts of solvent, allowed to reach equilibrium, and the composition of the two phases determined. This method was found to be much faster, allowing the study of several samples at one time. Other factors also influenced our choice of this method. In the repeated treatment of the same small sample, errors are cumulative and so soon tend to equal the changes in results due to natural causes. The use of volatile solvents—and most sulphur solvents are quite volatile—necessitates rapid handling, and any loss of solvent in handling introduces appreciable error into the calculation of results.

The results as obtained by treating equal samples with increasing amounts of solvent, were calculated back to the same basis as though obtained by repeated treatment of the same sample with small amounts of solvent.

It is possible in this way to show that true antimony pentasulphide may, under certain conditions, be prepared pure, but as ordinarily made it consists of a mixture of antimony pentasulphide, antimony trisulphide, and sulphur. It was also found that the so-called antimony pentasulphide, as prepared by decomposing thioantimonates with dilute acids, is a mixture of free sulphur and a solid solution of sulphur in antimony tetrasulphide. Both tetra- and pentasulphides of antimony were found to be decomposed by heating, breaking down finally to antimony trisulphide and sulphur.

*Method of Procedure:*

The sample was weighed into a tared test tube. Varying quantities of the solvent chosen were added to the test tube containing the sample of sulphide, and the amount determined by weighing tube and contents. This was then allowed to stand at the temperature chosen, with shaking at frequent intervals, until equilibrium was reached.

When equilibrium was reached, the contents of the tube were allowed to settle as much as they would, and the supernatant liquid transferred to centrifuge tubes, care being exercised to prevent losses of solvent by evaporation, tubes being immediately corked tightly. The centrifuge tubes were then centrifuged until perfectly clear, the liquid transferred to a weighed weighing bottle, and weighed. The solvent was then evaporated from the solution at a temperature of less than 80°C. The amount of sulphur in the sample of solution taken was then determined by weighing the weighing bottle and crystallized sulphur to constant weight.

This method for determining sulphur was chosen after considering several others. It was found superior to weighing the sulphide before and after extracting and calculating the sulphur by difference. This latter method has the disadvantages of including in the sulphur so determined any other soluble compounds, any moisture in the sample, and errors due to loss of material. Calculations of the amount of sulphur removed, by determining the increase in the percentage of antimony in the sulphide, gave too widely varying results for small amounts of sulphur removed. Determination of removed sulphur

by calculation after converting sulphur to barium sulphate was used in a few cases only.

Drying and weighing the dissolved sulphur was found to be comparatively rapid, and accurate enough for the purpose. Sulphur has such a low vapor pressure at the temperatures used that its loss is negligible[1]. Samples were dried to constant weight in three hours or less. Continued heating for a second three-hour period showed losses of sulphur averaging less than half percent of the sulphur weighed.

This procedure will hereafter be referred to as our standard procedure.

In the experimental part of this work, samples of antimony sulphides were prepared by several different methods, and the composition of the different samples determined. All the samples on analysis showed very close agreement with the theoretical analysis of pure pentasulphide, 60% Sb, 40% S.

The samples prepared by different methods and under different conditions showed very different properties, and compositions. These will be taken up in detail under separate heads.

## Pure Pentasulphide

*Experimental:*

Bunsen's method[2] was followed in the preparation of a supposedly pure pentasulphide. (Compare also Bosek[3], and Klenker[4].) The precipitate was filtered out, washed with water, alcohol, carbon disulphide and alcohol, then dried in a vacuum desiccator over sulphuric acid. When dry the resulting pigment was thoroughly mixed, sampled and analyzed.

Analysis: Pigment 7.

| | |
|---|---|
| Antimony | 60.05% |
| Sulphur | 39.41% |
| Moisture | 0.38% |
| Chlorides | 0.08% |

Color: Good rich orange.

This analysis shows that the sample corresponds to that of an antimony pentasulphide slightly deficient in sulphur. Refluxing samples of this pigment with chloroform and carbon disulphide for three hours removed 10.1 and 12.6 mg of sulphur per gram of sample. Standing in these solvents for three weeks at room temperature, samples showed losses of 0.0 and 0.9 mg respectively, proving that there was practically no free sulphur in the substance.

Concentrated HCl liberated sulphur equivalent to 16.02 percent by weight. (Theoretically only 15.39%. Difference is probably due to occluded salts.)

Heating this pigment showed little visible effect until temperatures around 100°C. were reached, when a dulling of the color was noted. At 135° the pig-

[1] Jones: J. Soc. Chem. Ind., **31**, 815 (1912); Luff and Porritt: **40**, 275T (1921).
[2] Bunsen: Ann., **192**, 305, 317 (1878).
[3] J. Chem. Soc., **67**, 519 (1895).
[4] J. prakt. Chem., (2) **59**, 150, 353 (1899).

ment had darkened appreciably to a brown, and at 150°C. traces of black color appeared.

This sample was used for subsequent work as a pure pentasulphide.

In order to determine the exact composition of this pigment the effect of sulphur solvents was tried in several ways and over a long period of time.

The results of these tests may be summed up as follows:

Cold carbon bisulphide, chloroform, carbon tetrachloride, benzene, and toluene have practically no effect on pure pentasulphide. These same solvents at their boiling points have slightly more effect—particularly the carbon bisulphide. Boiling acetone has but slight effect, although it has a higher boiling point than the bisulphide.

Samples of the pentasulphide when heated as a dry powder to temperatures above 75°C., showed larger amounts of sulphur dissolved. A sample heated above 157°C for three hours lost 15.51% by weight to $CS_2$, the residue after extraction analyzing pure trisulphide.

From the work done on this material, it is reasonable to conclude that:

(1) Antimony pentasulphide unquestionably exists.

(2) The pentasulphide decomposes on heating, liberating sulphur.

(3) It is practically unaffected by cold sulphur solvents, and but slightly so by the hot solvents.

(4) The effect of hot carbon bisulphide is due to the higher temperature of the boiling solvent, and also to the very great solubility of sulphur in this solvent. The statement of Esch and Balla[1] that only impure carbon bisulphide affects antimony pentasulphide could not be substantiated. The further the concentration of the sulphur in solution from the saturation value, the lower its potential and the greater the power of the solvent to decompose the sulphide[2].

## So-called Pentasulphide

In order to test the so-called antimony pentasulphide, samples of pigment were made by passing a stream of hydrogen sulphide through solutions of pentavalent antimony.

The conclusions of Bosek[3] were verified. Some of the pentavalent antimony is reduced, evidently to the trisulphide direct, and sulphur is liberated. Long continued passage of the current of $H_2S$, high temperatures, and low acid concentrations were found to favor the formation of the trisulphide. At temperatures above 95° the precipitate was largely trisulphide. A sulphide precipitated by a slow stream of $H_2S$, passed for 5 hours through a boiling antimonic chloride solution, filtered, washed with water, alcohol, carbon bisulphide, and alcohol, then dried in a vacuum desciccator, showed on analysis 69.06% antimony. This corresponds to a maximum of 8% antimony pentasulphide in the mixture.

---

[1] Esch and Balla: Chem. Z., 28, 595 (1904).

[2] Cf. Weber: "Chemistry of Rubber", 186 (1906); Luff and Porritt: J. Soc. Chem. Ind., 40, 275T (1921).

[3] J. Chem. Soc., 67, 526 (1895).

Treating pure antimony pentasulphide with successive portions of solvent show that, after the extraction of a *very* small amount of sulphur, the concentration of the sulphur in solution on further treatment drops to zero. This result agrees with that obtained by Hutin[1] and Dubosc[2]. Pure pentasulphide is practically unaffected by the solvent.

The so-called antimony pentasulphide behaves entirely differently with reference to the solvent. Some sulphur is dissolved, giving a solution saturated with sulphur. See Fig. 1. Further treatment with solvent extracts more sulphur, the concentration remaining constant—saturated solution—until all the sulphur as a separate solid phase disappears. The concentration of sulphur in the solution then drops to zero. The position of the break depends upon the method used in preparing the sample of pigment. Curves "efg", "efcd", and "efchi" on Fig. 1 show diagrams of three different samples. These samples are considered mixtures of the penta- and trisulphides with some sulphur. Sloping lines in place of lines "fg" and "hi" would indicate the existence of solid solutions, while vertical lines as obtained might be taken to indicate definite compounds. Line "cd" would indicate the presence of antimony tetrasulphide. But since the drop from the saturation value of sulphur in solution to a zero value is practically vertical, and since the positions of the breaks and lines "fg", "cd", and "hi" may be altered almost at will by changing conditions of precipitations, one is safe in assuming that the residue in each case is simply a mixture of the penta- and trisulphides and not a single compound or solid solution. The curve "efcd" indicates that the residue was composed of equal parts of penta- and trisulphide.

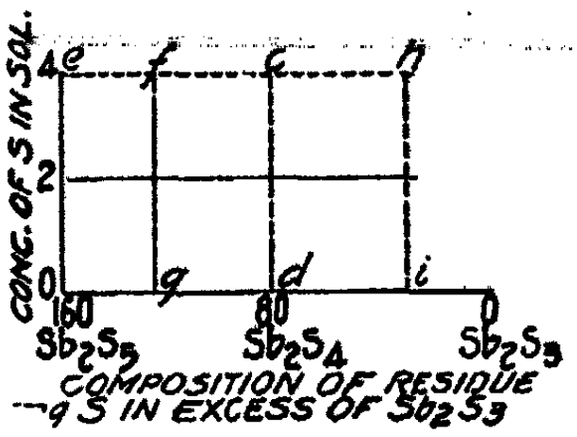



FIG. 1

Mixed $Sb_2S_5$, $Sb_2S_3$ and S

*Sulphides from Thioantimonates.*

The next group of sulphides studied was that made by decomposing thioantimonates with acids. The equation for this reaction is usually written

$$2Na_3SbS_4 + 6HCl = Sb_2S_5 + 6NaCl + 3H_2S$$

The study of this group showed that actually the reaction does not give pure pentasulphide, but always gives more or less free sulphur. The object of this study was to determine the composition of the other solid phase or phases.

Pure sodium thioantimonate (Baker and Adamson's C. P.) was recrystallized and dissolved in cold water, 85 grams of the salt per liter of water. The thioantimonate was then decomposed by dilute acid solution, thoroughly cooled. The acid concentration used was less than 5%. In all cases the resulting precipitate was washed by decantation, filtered, washed well with water

[1] Ann. chim. anal., 21, 32 (1916).

[2] Le Caoutchouc et la Gutta Percha, 8886, 8958 (1916).

and alcohol, and thoroughly dried. Several samples were made with slightly varying conditions. Of these, the following are typical.

Golden 3. Dilute sulphuric acid poured into thioantimonate solution. Washed precipitate dried at 105°-110°. Yield of approximately 96% of theoretical value. Color—rather dull orange.

Golden H. Using dilute HCl. Excess $H_2S$ removed by slow stream of air. Dried at less than 70°C. Yield 95% of theoretical. Color—good rich orange.

Golden A. Same as Golden H, except that excess $H_2S$ was not removed by air, and a temperature of less than 55°C. was used. Yield 97% of theoretical. Color—good rich orange.

Golden B. Exactly same as Golden A, except for the fact that the thioantimonate solution was poured into the acid, rather than the acid into the thioantimonate solution. Dried in the same way as Golden A. Gave same yield. Color—slightly darker than Golden A.

Golden D. Exactly same as Golden A, except temperature of drying. The washed filter cake was dried in a vacuum desiccator over sulphuric acid. Required 23 days to get the moisture content less than half of one percent. Color—rather dull tan.

The analyses of these samples were as follows:

| | Golden 3 | Golden H | Golden A | Golden B | Golden D |
|---|---|---|---|---|---|
| Antimony | 59.60% | 59.2% | 59.84% | 59.51% | 59.59% |
| Sulphur | 40.5 | 40.8 | 39.96 | 40.17 | 39.75 |
| Moisture | 0.16 | 0.04 | 0.39 | 0.32 | 0.47 |
| Chlorides | trace | trace | ——— | ——— | trace |
| Excess S | 0.76% | 1.34% | 0.06% | 0.50% | 0.04% |

The excess sulphur was figured from the antimony content on the dry basis.

The above listed samples were treated with a solvent according to our standard method of procedure. All the data in Tables I-IV are calculated on the basis of one gram sample of sulphide used. The solvent chosen for this set of experiments was a mixture of two parts by weight of chloroform to one of acetone, giving a mixture of specific gravity 1.256 at 23°C.

TABLE I — Golden 3. — FIG. 2.

| Solvent added grams | Sulphur removed milligrams | Conc. of S in soln. | Analysis of residue: mg S in excess of $Sb_2S_3$ |
|---|---|---|---|
| 0.0 | 0.0 | 0.0 | 167.6 |
| 4.6 | 17.5 | 3.81 | 150.1 |
| 1.4 | 5.2 | 3.72 | 144.9 |
| 3.5 | 12.5 | 3.57 | 132.4 |
| 5.5 | 20.0 | 3.64 | 112.4 |
| 8.5 | 19.8 | 2.33 | 92.6 |
| 6.5 | 7.0 | 1.07 | 85.6 |
| 14.5 | 2.6 | 0.18 | 83.0 |
| 64.0 | 1.4 | 0.02 | 81.6 |

| Table II. | Golden H. | | Fig. 3. |
|---|---|---|---|
| Solvent added grams | Sulphur removed milligrams | Conc. of S in soln. | Analysis of residue: mg S in excess of $Sb_2S_3$ |
| 0.0 | 0.0 | 0.0 | 173.4 |
| 6.27 | 23.2 | 3.70 | 150.2 |
| 2.70 | 10.1 | 3.74 | 140.1 |
| 3.63 | 13.4 | 3.69 | 126.7 |
| 6.4 | 22.1 | 3.45 | 104.6 |
| 2.9 | 8.2 | 2.83 | 96.4 |
| 3.4 | 9.2 | 2.71 | 87.2 |
| 5.9 | 7.8 | 1.32 | 79.4 |
| 16.4 | 1.0 | 0.06 | 78.4 |

| Table III. | Golden A. | | Fig. 4. |
|---|---|---|---|
| 0.0 | 0.0 | —— | |
| 4.74 | 17.2 | 3.62 | 160.4 |
| 0.99 | 3.6 | 3.64 | 143.2 |
| 3.52 | 12.7 | 3.60 | 139.6 |
| 4.25 | 14.5 | 3.41 | 126.9 |
| 1.50 | 4.7 | 3.15 | 112.4 |
| 12.0 | 20.3 | 1.70 | 107.7 |
| 3.1 | 3.7 | 1.20 | 87.4 |
| 20.8 | 4.5 | 0.21 | 79.2 |
| 20.7 | 0.2 | 0.00 | 79.0 |

| Table IV. | Golden B. | | Fig. 5. |
|---|---|---|---|
| Solvent added grams | Sulphur removed milligrams | Conc. of S in soln. | Analysis of residue: mg S in excess of $Sb_2S_3$ |
| 0.0 | 0.0 | —— | 165.0 |
| 5.45 | 19.6 | 3.60 | 145.4 |
| 3.83 | 14.2 | 3.70 | 131.1 |
| 5.3 | 16.4 | 3.10 | 114.7 |
| 2.95 | 7.7 | 2.61 | 107.0 |
| 15.7 | 14.1 | 0.90 | 92.9 |
| 14.6 | 5.3 | 0.36 | 87.6 |
| 12.1 | 0 | 0.0 | 87.4 |

The data for these samples of sulphides are perhaps best understood when considered from their graphical statements. All four of these samples have some noticeable points in common.

All four samples show that the concentration of sulphur in solution remains constant for a certain length, then the concentration decreases more or less abruptly, and in all the cases approximates a zero concentration when the composition of the solids is equivalent to that of antimony tetrasulphide.

The fact that the concentration of sulphur in solution remains constant indicates that there are two solid phases present. The fact that this constant

concentration represents the solubility of sulphur, indicates that sulphur is one of these two phases. When the concentration of sulphur begins to decrease, one is safe in concluding that a solid phase has disappeared.

If the remaining total solids were antimony pentasulphide plus some antimony trisulphide, the disappearance of the free sulphur would cause the concentration of sulphur in the next solution to fall to zero, for it has already been shown that the pure pentasulphide is not decomposed by the solvents.

With a sloping curve from the constant value down to zero at approximately $Sb_2S_4$, one best explains conditions by assuming the existence of a solid solution of sulphur and $Sb_2S_4$. In all four cases here, further treatment of sample with solvents, showed no extraction of sulphur after the composition corresponding to $Sb_2S_4$ was reached.

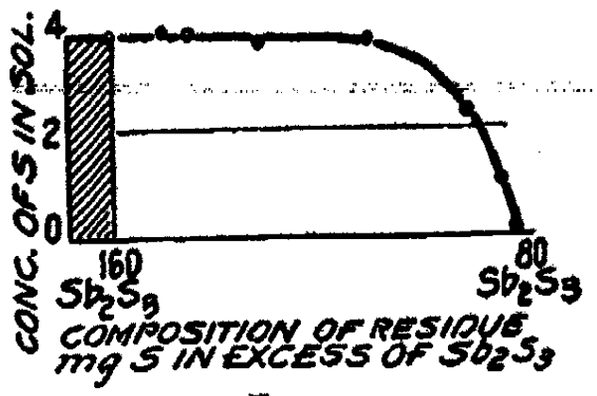



FIG. 2
Pigment Golden 3

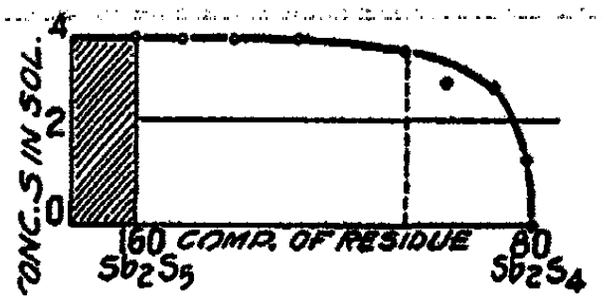



FIG. 3
Pigment Golden H

The shaded areas on the curves for Golden 3, B, and H (Figs. 2, 5 and 3) show presence of sulphur in excess of that required by pure antimony pentasulphide. This sulphur may have come from either of two sources: the recrystallized thioantimonate may have occluded some excess sulphur, or sulphur may have been formed by the oxidation of the hydrogen sulphide given off in the decomposition of the thioantimonate. This latter is much more likely to be the true explanation for the recrystallized thioantimonate gave clear crystals, which showed on analysis an antimony content of 25.00% and 24.97%. The theoretical value is 25.04%. The fact that removing the excess hydrogen sulphide with a stream of air, as in the case of Golden H, also showed a larger excess of sulphur, further confirms the statement that the hydrogen sulphide is the source of most of the excess sulphur.

The analysis of Pigment A corresponds to that of a pure antimony pentasulphide. These data, however, show that this sample consists of a solid solution of sulphur and antimony tetrasulphide, with just the amount of excess sulphur to bring the analysis up to that of pure pentasulphide.

Comparison of the diagrams for Golden A and B shows a general similarity, and indicates that, in general, the phases present in the samples are the same. The position of the break in the curves show that Pigment A has a larger amount of free sulphur, as compared with the amount of solid solution. This fact may be stated in another form by saying that the solid solution formed in Golden B is richer in sulphur than the solid solution in the case of A. The

different methods of preparation would account for this difference. In the case of the Golden A, pouring the acid into the thioantimonate gives a precipitate formed largely in the presence of thioantimonate in excess. When a particle of precipitate is formed, it tends to adsorb acid. When subsequently the particle is stirred through the thioantimonate solution, the adsorbed acid is neutralized by more thioantimonate and more precipitate is formed, with the evolution of hydrogen sulphide, either actually in the original particle, or in close contact with it. This hydrogen sulphide tends to reduce any of the higher sulphides of antimony (see later), thus forming more free sulphur as a separate phase.

In the case of Golden B, the particles formed still tend to adsorb acid, for acid is always in excess. But the particle is later stirred through the acid solution and no further reaction takes place, for dilute acid is always in excess.

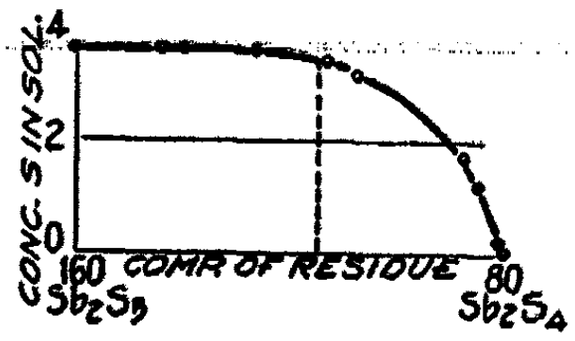



FIG. 4
Pigment Golden A

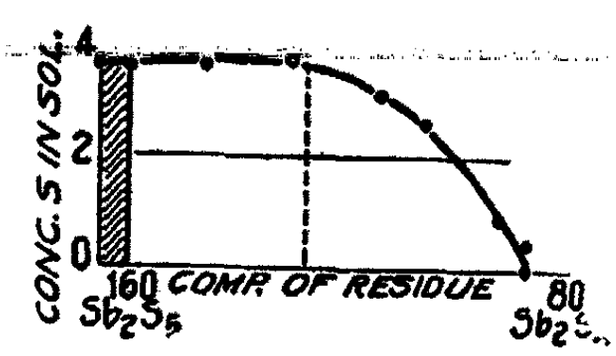



FIG. 5
Pigment Golden B

So the tetrasulphide and sulphur are formed all at the same instant, and so form a higher percentage of solid solution and less of free sulphur as a separate phase. There is a possibility that some antimony pentasulphide is formed here in small amounts. Most of it is decomposed by the hydrogen sulphide and acid, but a very small amount may remain in the material. The fact that the curve for Golden B intersects the axis of abscissae on the left side of the value corresponding to pure tetrasulphide, may be accounted for by supposing the presence of a small amount of antimony pentasulphide, which has been shown to be unaffected by the solvent used.

The difference between pigments Golden A and Golden B calls attention to the possibility of changing the composition of the solid solution formed between $Sb_2S_4$ and sulphur. Goldens 3, H and A show the presence of a solid solution of about the same composition in each case. This composition corresponds to that of two atoms of sulphur and five molecules of the tetrasulphide. Golden H has slightly less than this amount of sulphur: the difference may be due to decomposition of the solid solution by the passage of the stream of air. This point was checked qualitatively.

Several factors were found to affect the composition of the solid solution. Among these factors, increasing temperature of the reaction or of drying, passage of a stream of air or hydrogen sulphide, and precipitation from thioantimonate solutions containing free alkali, all showed some increase in the amount of free sulphur (present as a separate phase) formed at the expense of the sulphur in solid solution.

Curves similar to the preceding were not run on samples of Pigment Golden D. The sulphur extracted by chloroform and carbon bisulphide, refluxing three hours, amounted to 8.05 and 8.20% respectively. The residue insoluble in boiling 1:2 HCl amounted to 16.09%.

Similar treatment of Golden H gave 9.54% sulphur extractable by refluxing carbon bisulphide, and 17.2% residue with HCl.

These figures check with the conclusions drawn from the equilibrium curves. The solvents remove the sulphur present as a free solid phase, and that in solid solution with the tetrasulphide. The acid decomposes the antimony tetrasulphide, freeing any other atom of sulphur, and leaving as a residue all the sulphur in excess of that required to form antimony trisulphide. This sulphur is evolved as hydrogen sulphide.

From the above studies it may be concluded that the decomposition of sodium thioantimonate by dilute acid does not yield antimony pentasulphide, but a mixture of sulphur and a solid solution of sulphur and antimony tetrasulphide. The upper limiting composition of this solid solution corresponds approximately to the formula $Sb_2S_{4.66}$.

### Trisulphide

It was considered worth while next to spend a little time upon antimony sulphides prepared from other materials.

Supposedly pure trisulphide was prepared by passing hydrogen sulphide slowly into a hydrochloric acid solution of freshly distilled antimony trichloride. A rich yellow precipitate separated. This was filtered out, washed, and dried at 105-110°C. The color of the pigment darkened a little on drying but was still a rich golden yellow. The analysis showed an almost pure trisulphide, containing but 0.6% excess sulphur. This was evidently produced by the oxidation of some of the hydrogen sulphide. When the pigment was tested with solvents, as in the case of the pentasulphides, it lost but 0.6% sulphur, checking exactly with the analyses. This sample was called Pigment E.

The formation and action of trisulphides of antimony showed nothing new nor unusual. This sample was used in work later on.

Several samples of the so-called antimony "crimson sulphide" (variously called "antimony cinnabar", "vermilion") were prepared from the interaction of a dilute solution of antimony trichloride (in hydrochloric acid) with a solution of sodium thiosulphate. The object of this set of experiments was to determine the nature of the sulphide material formed, and to study the factors affecting it.

According to Fehling[1] the interaction of trivalent antimony in dilute acid, with solutions of sodium thiosulphate, gives a pigment which is an antimony oxysulphide, and not the trisulphide. Von Szilagyi[2] agrees with this idea, but also states that some antimony pentasulphide may be formed. Bayer and

---

[1] Fehling: "Neues Handwörterbuch Chem.," 1, 686 (1874).
[2] Z. anorg. allgem. Chem., 113, 69 (1920).

Company[1] obtained a patent which purports to obtain some pentasulphide from this reaction. Von Hahn[2] also claims that some pentasulphide is formed. On the other hand, Baubigny[3], Dammer[4], and Gmelin-Kraut[5] state that it is the trisulphide that is formed.

Varying the conditions of precipitation were found to have marked effects on the composition and color of the precipitate. (The color effects will be taken up in detail later.) Increasing percentage of sulphur was obtained by increasing temperature of mix, by increasing percent acidity of final mix up to a certain limit (about 30%), by increasing the ratio of thiosulphate to trichloride, and by increasing the concentration of the thiosulphate solution used.

Samples of this precipitate—of varying color, and with a wide range of sulphur content (2-52%)—were tested according to our standard procedure, using the acetone-chloroform mixture. In every case of the pigments precipitated from the sodium thiosulphate and antimony trichloride solutions, they were found to consist of antimony trisulphide with free sulphur as a separate solid phase. If sufficient acid were present to prevent all hydrolysis of the antimony chloride, the analyses showed a total of 100%,—antimony, sulphur, moisture and trace of chlorides being the only substances present. No evidence was found as to the formation of any pentasulphides, oxysulphides, or solid solutions.

In order to determine what the reaction would be if antimony trisulphide were treated with sulphur at the melting point of the latter, a sample of finely divided trisulphide (pigment E) was mixed with finely ground flowers of sulphur, and the mixture heated in a test tube placed in a bath of molten sulphur, just above its melting point. The color of the trisulphide slowly deadened and darkened, finally becoming black before the sulphur in the test tube was at its melting point. The mix was held at a temperature of 124°C. for an hour, then removed and cooled slowly.

The analysis of the mix showed the composition was: antimony 61.0%, sulphur 38.78%, moisture—trace, chlorides (HCl) 0.08%.

Samples of this blackened pigment F were extracted with chloroform under the reflux condenser. 14.3 and 14.35% of sulphur were removed. Carbon bisulphide removed 14.35% sulphur. The original analysis showed that the pigment contained 14.39% sulphur in excess of the trisulphide.

Other samples of this material were tested according to our standard procedure. They showed clearly that this material consisted simply of black crystalline antimony trisulphide and free sulphur. There was no evidence of any compound or solid solution between the two.

All attempts to add sulphur (other than mechanically) to trisulphides resulted in failures. Extracted samples of pigments E and F (golden and

[1] Brit. Pat., 14355, June 19 (1912); Chem. Abs., 7, 4050 (1913).
[2] Kolloid-Z., 31, 200 (1922).
[3] Compt. rend., 119, 687 (1894).
[4] Dammer: "Handbuch anorg. Chem.," 4, 341 (1903).
[5] Gmelin-Kraut: "Handbuch anorg. Chem.," 3 II, 703 (1908).

black trisulphides, respectively) were allowed to stand in contact with solutions of sulphur solvents saturated with sulphur. The golden trisulphide (Pigment E) removed less than 0.3% of its weight of sulphur from the solution. The crystalline trisulphide did not remove a detectable amount. The sulphur removed by Pigment E was likely held by adsorption or occlusion. The samples were so finely divided that such surface effects would be easily possible. Pigment F, being crystalline, and much coarser, naturally showed less, if any, effect.

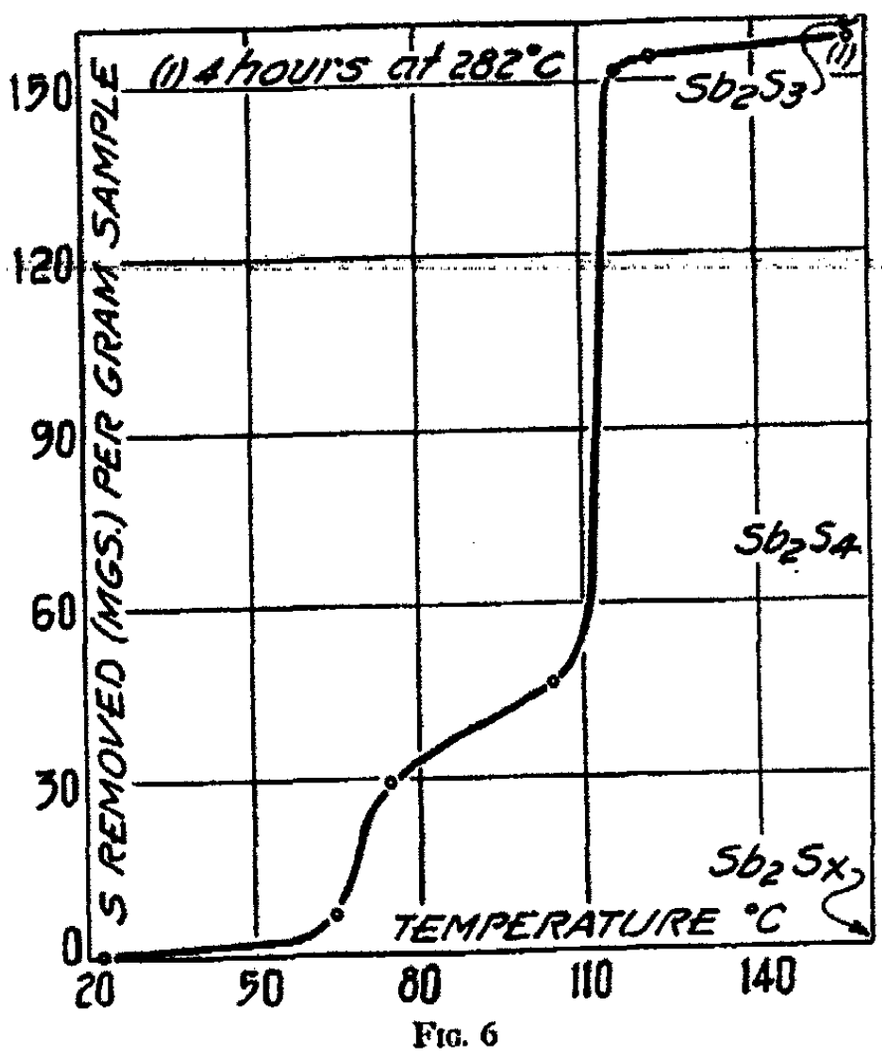



FIG. 6

Pigment 7. Heated eight hours. Effect of temperature on sulphur extracted.

Solutions nearly saturated with respect to sulphur, when in contact with antimony sulphides containing excess sulphur, remove sulphur from the sulphide up to the point of saturation of the solution. Pigments Golden 3, H, B and samples of the crimson trisulphide all showed this effect.

These few experiments showed that, if to a system of antimony sulphides, sulphur and sulphur solvent—at equilibrium conditions with the solvent saturated with sulphur—more sulphur be added, the excess sulphur is thrown out as a free solid phase, with no evidences of any addition or combination with the antimony sulphides.

The effect of the heat on the sulphides of antimony was next considered and studied. To date there has been considerable variety in the results and conclusions reached by the different investigators. Klenker's work[1] published

[1] Klenker: J. prakt. Chem., (2), 59, 150, 353 (1899).

in 1899 was very carefully performed and showed definite results, but has been rather frequently overlooked. Klenker noted that pure pentasulphide was decomposed by heat, and several of his experiments showed that temperatures of 85-90°C. were sufficiently high to give a noticeable breaking down. Von Bacho[1], von Zani,[2] Luff and Porritt[3], and many others have also given the question some consideration.

It was thought likely that a phase rule study of the question might give some insight as to the conditions and products of the decomposition of antimony sulphides.

Samples of the pure pentasulphide were placed in carefully cleaned and dried test tubes, corked, and then subjected to heat at various temperatures for periods of eight hours each. After cooling the tubes, the samples were extracted with chloroform.

The data for these samples are shown in Table V. They are shown graphically in Fig. 6. This curve shows that the rate of decomposition is very low at low temperatures, is appreciable at temperatures around 75°C. and increases very rapidly at temperatures above 100°C. At 120°C. the decomposition is practically complete.

TABLE V. Pigment 7, Heated 8 Hours. FIG. 6.

Effect of Temperature on Sulphur extracted.

y = milligrams extracted sulphur per gram sample.

| Temp. | y | Temp. | y |
|---|---|---|---|
| 23° (room) | 0.0 | 117° | 152.0 |
| 65 | 7.0 | 123 | 154.0 |
| 75 | 29.8 | 158 | 156.8 |
| 105 | 46.6 | 282 | 161.2 |

The last sample was heated for four hours in an atmosphere of $CO_2$. The value of sulphur extractable was determined by difference, and includes any volatilized matter other than sulphur, moisture, and any oxidation.

TABLE VI. Effect of Continued Heating on Amount of Sulphur extractable from Pigment 7. FIG. 7.

| Time of Heating | Temp. 65°C. | Temp. 75°C. | Temp. 105°C. | Temp. 123°C. |
|---|---|---|---|---|
| 8 hours | 7.0 | 29.8 | 46.6 | 154.0 |
| 24 hours | 11.2 | —— | 79.1 | 156 |
| 48 hours | —— | 48.2 | —— | 158 |
| 5 days | —— | 58.0 | —— | —— |
| 1 week | 14.1 | 60.2 | 89.1 | 158 |
| 2 weeks | 15.0 | 70.0 | 91.0 | 158 |
| 3 weeks | 15.4 | 77.2 | —— | —— |
| 4 weeks | —— | 83.3 | —— | —— |

[1] Ann. Chim. applicata, 12, 143-152 (1919).
[2] Chem. Abs., 4, 1947 (1910).
[3] J. Soc. Chem. Ind., 40, 277T (1921).

Since the slope of the curve showing relative decomposition of pure pentasulphide at different temperatures is rather uncertain at temperatures below 75°C., another series was run in which samples were heated at constant temperature for different lengths of time. Series were run at temperatures of 65°, 75°, 105°, and 123°C. Data for these series are given in Table 6, and the results plotted on Fig. 7.

Continued heating at 65° (Curve D) shows a very small amount of sulphur liberated in 3 weeks by the decomposition of antimony pentasulphide. Heating at 75° (Curve C) shows a much more rapid decomposition at first, but

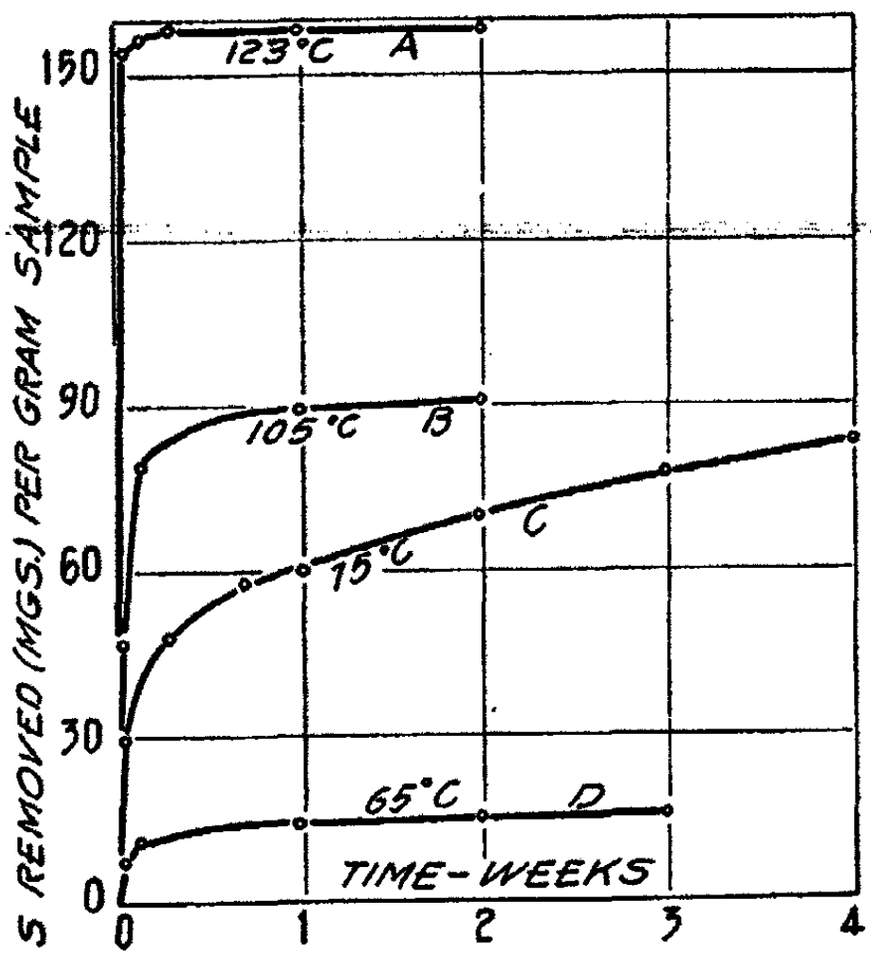



FIG. 7

Effect of continued heating on sulphur extracted from Pigment 7

later slows down appreciably. Sulphur corresponding to one atom per molecule of pentasulphide is rather easily extracted, indicating that the first product of the decomposition of the pentasulphide by heat may be the antimony tetrasulphide.

Heating samples at 105° (Curve B) for 24 hours showed that the pentasulphide would furnish approximately one atom of sulphur as a separate phase, but further heating showed little effect. Temperature of 123° (Curve A) and above caused rapid decomposition of the pentasulphide, decomposition to the trisulphide being complete.

The results obtained here agreed in general with those obtained some twenty-odd years ago by Klenker[1]. Klenker found that 24 hours at 140°-150° gave complete decomposition to the trisulphide, while at temperatures above

[1] J. prakt. Chem. (2) 59, 193 (1899).

150°, oxidation of the sulphur and sulphide began to occur in noticeable amount.

From the work here described it may be concluded that pure pentasulphide will be more or less completely decomposed to the tetrasulphide if heated at temperatures 70-75°C. The tetrasulphide formed is slightly decomposed at 105° and rapidly so at 155-120°. These values for temperatures of decomposition are both slightly lower than those given by Klenker, and although requiring long periods of heating, are believed to be more correct.

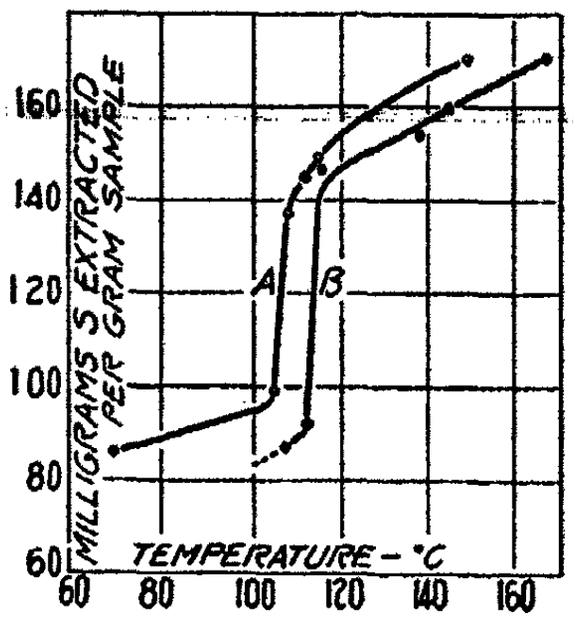



FIG. 8
Effect of Temperature on Pigment 3

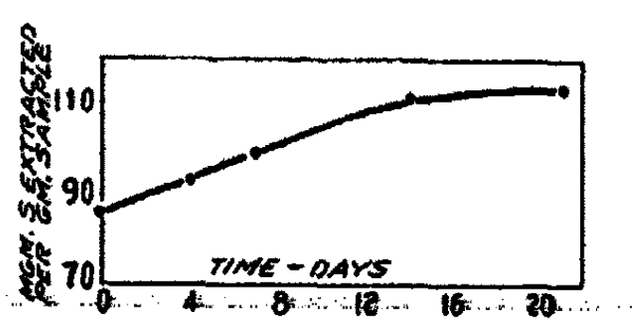



FIG. 9
Pigment 3 heated at 105°

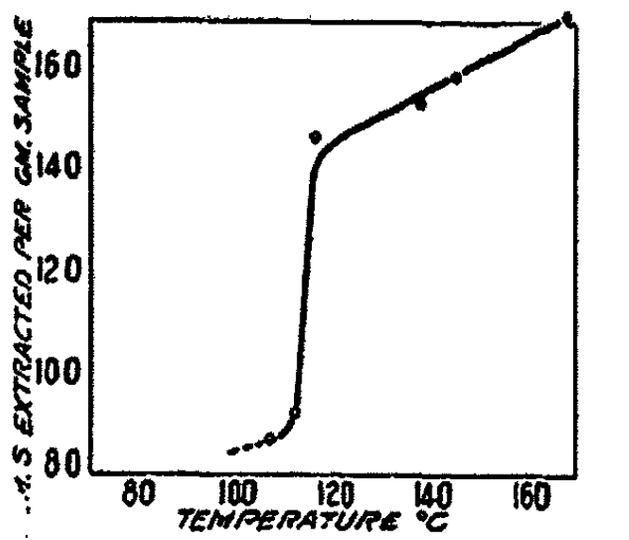



FIG. 10
Effect of Temperature on Pigment 3—168 hours

Similar study was given to the so-called antimony pentasulphide made by acidifying sodium thioantimonate. Pigments Golden 3 and Golden H were the samples used. Samples were heated at different temperatures, the time of heating being kept the same for each sample. The results of these tests are given in Tables VII-X, and are shown graphically in Figs. 8, 9, and 10.

TABLE VII. Effect of Temperature on Pigment H Heated 48 Hours. FIG. 8 Curve A.

y = milligrams sulphur extracted per gram sample

| Temp. | y | Temp. | y |
|---|---|---|---|
| 70° | 86.0 | 112° | 145.0 |
| 105 | 99.2 | 115 | 149.0 |
| 108 | 137.0 | 150 | 169.0 |

The last sample was heated but four hours.

TABLE VIII. Effect of Temperature on Pigment Golden 3. Heated 27 Hours
y = milligrams sulphur extracted per gram sample

FIG. 8. Curve E

| Temp. | y | Temp. | y |
|---|---|---|---|
| 107° | 87.0 | 138° | 154.5 |
| 112 | 92.0 | 145 | 159.5 |
| 116 | 147.2 | 168 | 171.5 |

TABLE IX. Effect of Heat on Pigment Golden 3. Heated 168 Hours.
y = milligrams sulphur extracted per gram sample

FIG. 10.

| Temp. | y | Temp. | y |
|---|---|---|---|
| 105° | 99.2 | 135° | 167.0 |
| [illegible] | 147.0 | 150 | 160.0* |
| 120 | 164.0 | | |

*Sulphur was subliming rapidly, and some was probably lost.

TABLE X. Effect of Heat on Pigment Golden 3 Heated at 105°C—varying time.
Time in days
y = milligrams sulphur extracted per gram sulphur

FIG. 9.

| Temp. | y | Temp. | y |
|---|---|---|---|
| 0° | 86.0 | 14° | 111.0 |
| 4 | 93.6 | 21 | 113.0 |
| 7 | 99.2 | | |

The work listed above on Pigments Golden 3 and Golden H agrees very well with that described by Klenker, and also with that done on the pure pentasulphide. The solid solutions of antimony tetrasulphide and sulphur are stable up to temperatures above 100°, the rate of decomposition being very slow at 105°–108°C. At temperatures above 112–115° the decomposition of the material is quite rapid, and practically complete at 150°, even in a few hours.

The solid solutions evidently decompose rather easily, forming sulphur and antimony tetrasulphide as separate phases and this tetrasulphide decomposes at 115–120°C.

The main reactions that take place when antimony pentasulphides are heated are evidently as follows:

At temperatures up to approximately 110°

$$Sb_2S_5 \text{ (+ heat)} = Sb_2S_4 + S$$

From temperatures around 110° up to 150°

$$Sb_2S_4 \text{ (+ heat)} = Sb_2S_3 + S$$

Above 150°, the reaction is largely oxidation, or in the absence of air, subliming of the sulphur, with an accompanying change in the physical properties of the trisulphide formed.

The reactions for the pigments made from thioantimonates are similar to those of the tetrasulphide formed from the pentasulphides. The tetrasulphides are practically stable at temperatures up to approximately 110°. The change below those temperatures is very very slow.

In drying the residues after extracting sulphur from samples of pigment Golden 3, it was noted that some residues darkened in color much more rapidly than did others, and that this effect is most noticeable in the cases where the amount of sulphur removed is greatest. In order to check this point up, a whole series of samples was tested.

Samples of the pigment (Golden 3) were treated with varying amounts of the acetone-chloroform solvent, as in our standard procedure. The solvent was then filtered off, the residues washed with acetone, alcohol and water, and dried at 100°C. The dried residues were then placed in corked tubes, and subjected to a temperature of 130° in a hot air oven. They were observed at intervals, to note any sign of blackening, or subliming of sulphur onto the walls of the tube. These times, along with those at which blackening was complete, were noted, and are shown in Table XI.

TABLE XI. Effect of Heat on Pigment Golden 3 after Partial Extraction of Sulphur.

| S Extracted Mgs. | Blackening started | Blackening completed | Sulphur separating |
|---|---|---|---|
| 78.5 | 1st 18 hrs. | First | |
| 75.6 | 2nd 24 hrs. | Second | 36 hrs. |
| 75 | 2nd 24 hrs. | Third | |
| 55.2 | 3rd 36 hrs. | Fifth | |
| 44.9 | 4th 36 hrs. | Sixth | |
| 26.9 | 5th 144 hrs. | Seventh | 96 hrs. |
| 16.6* | 4th 36 hrs.* | Fourth* | |

*This sample is the only one out of order in the series. This exception is probably due to the fact that the tube was broken in handling, and the pigment recovered as well as possible. Impurities may have been introduced which accelerated the blackening.

The change in color of the pigment under these conditions is evidently a physical one only. The solid solution of antimony tetrasulphide and sulphur, and all the tetrasulphide itself is broken down, at this temperature in the first 24 hours, to trisulphide and more sulphur. The change in color is due to change in the physical condition of the trisulphide.

This change in the color of the antimony trisulphide takes place rapidly at higher temperatures. (See this paper, page 229). The excess sulphur liberated in the decomposition of the tetrasulphide evidently decreases the velocity of the reaction. This effect may be due to some actual chemical effect of the excess sulphur, but it is much more likely that its effect is due to a purely physical effect, namely, separating the particles of the trisulphide by forming a thin layer between the particles. Its effect may also be due in part to the fact that the higher percentage of sulphur present may mask the first slight color change, and prevent the darkening from showing up at the time it would otherwise be noted.

## Summary

(1) Antimony pentasulphide may be prepared by following carefully the directions given by Bunsen and Bosek. All the antimony must be carefully oxidized, the acidity adjusted, solutions kept cool, and the saturated hydrogen sulphide water added rapidly to excess. The working limits for the reaction are rather narrow.

(2) Pure antimony pentasulphide is not decomposed by cold sulphur solvents.

(3) Pure pentasulphide is decomposed by temperatures above 70°C., and quite rapidly by temperatures around 100°C. Hot sulphur solvents, especially carbon bisulphide, have some decomposing effect. Long heating breaks the pentasulphide down, liberating one atom of sulphur, and forming antimony tetrasulphide.

(4) Passing a slow stream of hydrogen sulphide through an antimonic acid solution reduces some of the antimony, forming antimony trisulphide and free sulphur.

(5) The decomposition of sodium thioantimonate with dilute acid does not form antimony pentasulphide, but a mixed pigment consisting of sulphur and a solid solution of sulphur in antimony tetrasulphide. The amount of solid solution present may be changed by changing the conditions of the decomposition reaction. The composition of the solid solution may be varied between that corresponding to $Sb_2S_{4.66}$ and $Sb_2S_4$.

(6) The solid solution of sulphur in antimony tetrasulphide is decomposed by heating at temperatures above 100°C. The tetrasulphide is rapidly decomposed into trisulphide and sulphur when heated above 115°C.

(7) The pigment formed by the interaction of trivalent antimony in acid solution and sodium thiosulphate does not contain antimony pentasulphide or antimony oxy-sulphide. The pigment is trisulphide and sulphur alone. There are no evidences of the formation of any solid solution.

(8) Removal of sulphur from the higher sulphides of antimony is a relatively simple matter, but the addition of sulphur, other than mechanically, has not been feasible.

(9) The presence of intimately mixed sulphur appears to have a retarding effect on the decomposition of antimony tetrasulphide by heat, and the subsequent change in physical properties of the trisulphide formed.

(10) A method is given for the study, from a phase rule point of view, of an irreversible equilibrium, enabling one to determine the composition of the material when a chemical analysis will not answer.

## II. Colors of the Antimony Sulphides

The first part of this paper dealt with the nature and number of phases in so-called antimony pentasulphides. This latter half will be taken up with a study of the colors of antimony sulphides. The object of this study will be to account for the different colors found in the sulphides.

Antimony trisulphides may be prepared which vary in color over a wide range. The tetra- and pentasulphides of antimony do not show such a variety of colors. The trisulphides will be taken up first.

Antimony trisulphides have long been divided into two classes—the natural variety, and the artificially prepared varieties. In general, the latter class includes all the colored trisulphides.

The natural variety of antimony trisulphide is the mineral stibnite. It is the most important source of antimony. Stibnite is crystalline—either hexagonal[1] or rhombic[2]. It is variously described as black, (steel-gray, gray, etc.) brittle needles which melt at about 550°C. Dana[3] states that it possesses a metallic luster. Stibnite is a poor conductor of electricity. On exposure to light it shows a voltage effect like that shown by some selenium compounds.

In addition to the well-known stibnite, there also exists a natural brick-red antimony trisulphide, said to be amorphous[4]. This is known as meta-stibnite. It will not be considered here.

The artificial trisulphides vary widely in color and other properties, depending on methods of preparation. From any of these artificial trisulphides, a black crystalline trisulphide may be prepared. This latter variety is very similar to stibnite: later in this paper, it will be shown that the two are identical. (See page 237)

The other artificial trisulphides may be prepared, varying in color from a very light yellow, through a series of shades of orange, red, maroon, and brown to black. The red and maroon shades can not be prepared in the ordinary way. The presence of hydrogen sulphide in the solutions from which the sulphide is precipitated is found to prevent the formation of these shades.

Williams[5] has recommended that the artificial trisulphides be divided into two sub-groups. The first group should include all those sulphides of antimony precipitated in the presence of hydrogen sulphide. This includes all the sulphides precipitated by hydrogen sulphide direct, those formed by the interaction of acids with thioantimonites or thioantimonates, and those precipitated by treating stibnite with sulphur in sunlight. This group may be called the "antimony goldens".

The second group of artificial trisulphides should include those formed in the absence of hydrogen sulphide. This is the group that gives us our greatest variety of colors. Although much lighter sulphides may be formed, those formed by these methods at moderate temperatures are usually some shade of red. This group may be called the "antimony crimsons."

Williams[6] showed that the color of the precipitate obtained was, in general, darkened by increasing the temperature, acidity, or the length of time of the reaction. All these factors may cause the formation of larger particles or agglomerates. This makes it appear likely that a large part, if not all, of the difference in the colors of antimony trisulphides may be explained or accounted for simply by this change in particle size. A series of experiments was run to test out this point.

The addition of any substance which would tend to cause the formation of a larger particle would be expected, according to this idea, to form a darker

[1] Olsen: "Chemical Annual", pp. 184-5 (1922).
[2] Moissan: "Traité de Chimie minerale", 2, 42 (1905).
[3] Dana: "A System of Mineralogy", p. 36.
[4] Becker: Am. Phil. Soc., 25, 168 (1888).
[5] Unpublished report—privately communicated.
[6] Unpublished report—privately communicated.

colored pigment. Antimony sulphides as sols are stated to be negatively charged[1]. The addition of an acid or a salt giving an easily adsorbed positive ion that should tend to coagulate sulphides more readily. On the other hand, the addition of a substance furnishing a readily adsorbed anion, or furnishing a colloid which may be readily adsorbed and so act as a protecting colloid, would give more finely divided particles, which would be expected to be of a lighter color. Higher temperature of reaction will also tend to agglomerate the particles.

The golden trisulphides offer a rather limited range of colors, so the crimson sulphides were chosen at the first series of tests.

Crimsons were made for this first series by precipitation of the sulphides from a solution of potassium antimonyl tartrate mixed with sodium thiosulphate. The strengths of these solutions were fixed at twenty grams of antimony per liter of the tartrate solution, and five hundred grams of the anhydrous sodium thiosulphate per liter of solution. The gelatin contained fifty grams of gelatin per liter.

Five cc samples of the tartrate solution (equivalent to 100 mg. of antimony) were placed in test tubes. The desired amount of gelatin was then added to each tube, and the total volume brought up to ten cc, using distilled water. Five cc of the thiosulphate solution were then added to each tube, all the tubes stoppered, heated to the desired temperatures, and the results observed.

The results of these tests were striking. At room temperature, samples to which little or no gelatin had been added gave a light red suspension, which settled slowly. After two days these suspensions had settled out as red precipitates, giving clear, water-white supernatant liquids, which were found to be free from antimony. This indicated that the precipitation of the antimony was complete.

The addition of as much as one milligram of gelatin showed an appreciable effect. Further additions of gelatin showed three effects: (1) the colors of the suspensions and precipitates became lighter in color; (2) the amounts of precipitates were decreased, and the removal of the antimony incomplete; and (3) the liquid became more cloudy. When the point was reached at which about six milligrams of the gelatin had been added to the samples, the suspensions became much more clear; when as much as twelve milligrams of the gelatin had been added, the entire suspension was perfectly clear, brightly golden in color. The amounts of precipitates had become practically zero. Even after standing three months, the pigments were still in colloidal suspension.

The addition of larger amounts of gelatin showed little or no effects on the colors of the suspensions or precipitates. At very high concentrations of the gelatin, the thiosulphate solution caused some of the gelatin to coagulate, again giving a cloudy suspension.

At higher temperatures the effects of the gelatin were similar to those at room temperature, but much more pronounced. The colors of the samples

[1] Picton: J. Chem. Soc., **61**, 116 (1892).

were in every case darker than in the corresponding samples of the series at room temperature. The amounts of precipitate were increased.

The addition of acid to sample tubes gave the results expected. Very dilute hydrochloric acid solutions were used. These caused more immediate and complete precipitation of a darker colored sulphide, than the corresponding sample in the neutral series.

The addition of the alkali had an opposite effect, lightening the colors of the precipitated sulphides, and decreasing the amounts of precipitates. The upper limit for the addition of alkali was reached when the antimony began to precipitate as the hydroxide or a basic salt.

Using a slit ultramicroscope (Zsigmondy) the sizes of the particles from different samples, prepared as above, were measured. The particle sizes ranged from 0.25-0.4$\mu$ up to much larger sizes. The larger sizes had agglomerated so badly that a correct estimate of particle size was impossible. Counting the number of particles per field of the ultramicroscope, showed that the colors of the samples steadily darkened as the particle size increased. Series of samples arranged in colors grading from light to darker shades were found to contain particles of regularly increasing size. This agreed exactly with the results predicted.

From the preceding experiments it was thought likely that the colors of samples of antimony trisulphide might be appreciably lightened by grinding or in any other way reducing the particle sizes[1]. Unfortunately, grinding artificial antimony sulphides causes the formation of the black variety[2]; this effect is probably due to the heat developed by the grinding. The effect of heat on the dry powder was taken up in a later part of the study. It is sufficient here to state that the effect of heat developed in grinding the dry trisulphide in a mortar is more than sufficient to off-set any change in color due to reduction in particle size.

Grinding under water was then attempted, with little noticeable results. In order to prevent agglomeration of particles which might be reduced to very small sizes, some gelatin was added to the water.

A fresh sample of stibnite was ground to a fine powder. A dilute gelatin sol was added to the mortar and the mixture well stirred. It was then divided into equal parts, one part poured into a test tube. The other half was left in the mortar, and the mixture thoroughly ground with the pestle. After long grinding the mixture from the mortar was poured into a second tube and allowed to set to a jelly. The first sample had set solidly, the heavier particles going to the bottom of the tube and concentrating before the gelatin had begun to set. The upper portions of the tube showed lower concentrations of black particles, while an almost clear layer of jelly was formed at the top. The second sample, which had been ground in the presence of the gelatin, showed similar effects. In this latter case, however, the top layer of the gel, although

[1] Bancroft: "Applied Colloid Chemistry", 148, 205 (1921).

[2] Von Bacho: Ann. chim. applicata, 12, 143-152 (1919).

clear, showed traces of a reddish color. This effect was so slight that the experiment was repeated—with the same results.

This experiment showed that reduction of particle size of the stibnite, known to be crystalline, tended to change the color from gray-black to reddish. The experiment was encouraging but not conclusive.

Bredig[1] and Svedberg[2] have prepared colloidal solutions of practically all the metals. They made use of electrical dispersion methods. It was thought worthwhile to attempt the preparation of finely divided sulphide by electrically dispersing stibnite. This method should, it was thought, give a lighter colored—(at least a colored)—sulphide.

A set-up was arranged by means of which a high voltage arc could be formed between stibnite electrodes immersed in cold distilled water[2]. With 4,000 volts the reaction was almost explosive. Some of the electrodes was disintegrated and settled to the bottom of the cell, as a bright yellow sludge. As the time for the current increased the temperature of the water increased rapidly, and the color of the sludge became darker. When the temperature of the water had reached approximately 75°C., the formation of the yellow particles ceased.

The colored substance formed by this electrical disintegration was analyzed and proved to be antimony trisulphide. The filtrate after removal of this trisulphide showed the presence of sulphate and sulphite ions. These substances were due, no doubt, to oxidation of a small part of the stibnite to antimony sulphate, or oxide. When sufficient electrolyte was formed, the solution carried most of the current and no stibnite was arced.

Experiments were made using higher and lower voltages, with inductance in circuit, and condensers in series or shunt with the cell. The differences in effects were not very marked. In general, the higher voltages gave more finely divided particles, while the use of a condenser apparently gave slightly coarser particles. The changes due to the differences in the electrical circuits, were more than off-set by the differences caused by the rise in temperature of the cell.

The effect of temperature of the cell was in every case in agreement with the effect on precipitated sulphides. Rising temperatures increased the particle size and darkened the color of the precipitate or disintegrated sulphide. The additions of small amounts of gelatin to the distilled water in the cell gave exactly the effects expected,—namely, a more finely divided and lighter colored sulphide. If sufficient gelatin were added, a suspension of the yellow trisulphide could be formed. This suspension was stable after three months standing. Here again, the gelatin acts as a protecting colloid, preventing the agglomeration of the finely divided particles, and so forming a clear colloidal suspension. The gelatin in this way tends to counterbalance the effect of the rising temperature.

---

[1] Z. Elecktrochem., 4, 514 (1898); Z. physik. Chem., 31, 258 (1899).

[2] "Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe", 424 (1909).

Having succeeded in preparing very finely divided trisulphides and shown that these were generally lighter in color, it was next thought possible to form large particles or crystals which would be of a darker color.

Methods were employed which are known to favor slow reactions and give opportunity for the growth of large crystals. Interaction of very dilute solutions, slow diffusion of solutions through diaphragms, and formation of the precipitates in gels, were all tried. Particular efforts were made to grow large crystals by diffusion through gels. Silica gel, gelatin, and agar agar were used[1].

The results agreed very well with each other but were not those hoped for or expected. Silica gels were made as directed by Holmes. When solutions of sodium thioantimonate were poured in on top of these gels and allowed to diffuse down, orange and brownish antimony sulphides were formed. The colors appeared little different from those of sulphides precipitated in the usual way,—except for one noticeable effect. All tubes showed pronounced Liesegang rings or rhythmic banding effects. These were particularly clear in cases where the surface of the gel was first washed with a solution of sodium carbonate, and a small amount of carbonate added to the thioantimonate solution. The carbonate prevented the rapid reaction at the surface of the gel.

Other samples of gel were prepared and antimony sulphides precipitated. The following methods of precipitation were used.

| | Gel | Solution added. |
|---|---|---|
| (1) | Silica gel (Acid) | and sodium thioantimonate. |
| (2) | Sodium thiosulphate in gelatin gel | and $SbCl_3$ solution. |
| (3) | Antimony chloride in gelatin gel | and sodium thiosulphate. |
| (4) | Same as (2) and (3) using agar agar in place of gelatin. | |

(5) Using a gel in the bottom of a U-tube, allowing the two solutions in the two arms of the tube to diffuse together.

Antimony sulphides were precipitated in every case. In most cases the rhythmic banding was noticeable. In no case was there any evidence of any noticeable increase in particle size. In cases wherever possible, the gel containing the sulphides was removed and the size of sulphide particles measured with the ultramicroscope.

In general, the size of antimony sulphide particles precipitated in gels by above methods does not differ from those precipitated in the usual manner. This matter was not carried further along these lines.

The experiments described above make the following conclusions obvious:

(1) Particle size is an important factor in affecting the colors of antimony trisulphides.

(2) Precipitated antimony trisulphides may tend to remain in suspension as negatively charged particles.

(3) Addition of acid tends to flocculate suspended trisulphide. Addition of alkali tends to peptize it.

[1] Cf. Holmes: "Laboratory Manual of Colloid Chemistry", 91 (1922).

(4) Heating suspensions tends to flocculate the sulphide and, if already precipitated, tends to darken the color of the precipitate.

(5) Addition of gelatin furnishes a colloid which is apparently easily adsorbed. This prevents agglomeration and causes the formation of a more finely divided pigment.

(6) Increasing temperature of reaction, addition of acids will give sulphides with a darker color.

(7) Addition of gelatin or alkalies to solutions, or mechanical reduction of particle size, tend to form lighter colored sulphides.

(8) Using a method similar to that described by Svedberg, natural black antimony trisulphide may be electrically disintegrated, giving a finely divided sulphide which is similar to the ordinary precipitated antimony sulphide.

(9) The methods used to grow large crystals of antimony sulphide were not successful. Precipitation of the sulphides in gels showed Liesegang ring effects.

The effect of increasing temperature on the colors of suspensions or precipitates of antimony trisulphides has already been discussed, p. 222. The effect of heat on dry antimony sulphides was also studied. It was found that in this case, too, heating dry antimony trisulphides caused noticeable changes in color. Continued heating at relatively high temperatures caused all the antimony sulphides to become entirely black. The object of this study was to account for these color changes.

These changes in color have already been the subjects of considerable study[1]. Von Bacho[2] made a careful study of the effect of heat on the color changes of the sulphides of antimony. His work dealt, for the most part, with the change to the black modification, and the effect of impurities on the rate of this change. Von Bacho concluded that the black modification contains "traces of colloidal antimony, in consequence of an almost imperceptible decomposition due to chemical or mechanical causes." This conclusion can not be checked easily. The effects of impurities as listed by von Bacho have, in most cases, been checked by Williams. The presence of salts, particularly the chlorides, and of acids, was found to lower the temperature at which the change to the black modification was complete. Sodium chloride, antimony oxy-chloride (or chloride) and hydrochloric acid were found to be very sufficient in promoting the change to the black crystalline form. Hautefeuille and Perrey[3] found that under certain conditions hydrochloric acid gas causes amorphous oxides of aluminum, titanium, and zirconium to change to the corresponding crystalline oxides.

Von Zani[4] also states that one cause for the formation of the black trisulphide is the coating over of the individual particles with a film of metallic

[1] Gmelin-Kraut: "Handbuch anorg. Chem.", 311, 699-705; Guinchant and Chrétien: Compt. rend., 138, 1269 (1904); 139, 51, 288 (1904); 142, 709 (1906).

[2] Ann. chim. applicata, 12, 143 (1909).

[3] Compt. rend., 110, 1028 (1890).

[4] Chem. Abs., 4, 2758 (1908).

antimony. The formation of the metallic antimony is said to take place as follows: the amorphous trisulphide readily absorbs oxygen, then loses sulphur dioxide, leaving small particles of metallic antimony. This theory could not be checked analytically. Furthermore, the colored trisulphides change to the black modification quite readily when heated in the absence of oxygen. Heating the sulphides in an atmosphere of hydrogen sulphide gives a rapid change[1], while heating in carbon dioxide or in sulphur dioxide also gives the black modification.

It is a well-known fact that the degree of fineness of powdered materials may have a decided effect on their colors. Red mercuric oxide may be ground to such a fine powder that the color is no longer red, but yellow. Potassium ferricyanide is brown-red in coarse crystals, and yellow when powdered. Ferric oxide has been prepared in both red and yellow forms, the yellow being the finer powder. Thin plates of hematite are yellow by transmitted light, the color varying with increased thickness through reddish brown to deep brown red or blood red[2]. The massive hematite may be almost black, although its streak is always reddish. Size of particle also has an important bearing on the colors of antimony sulphides. This will be shown below.

To explain the color changes observed when dry antimony trisulphide is heated, the following hypotheses are made: (1) Antimony trisulphide exists in both the crystalline and the amorphous states. (2) Very finely divided crystalline trisulphide is yellow, while the slightly larger crystals are black. (3) Finely divided amorphous trisulphide is also yellow; coarser amorphous antimony trisulphide is crimson. (4) The black crystalline modification is the stable one at high temperatures.

An effort is here made to justify these assumptions and with them to explain the color changes of the antimony trisulphides.

By means of X-ray diffraction patterns, the existence of both amorphous and crystalline states of antimony trisulphide may be proved. (This work is described on pages 236-237 of this paper.) This method gives definite proof of the existence or non-existence of a crystal structure in a material. Antimony trisulphides may be prepared in either the amorphous or the crystalline form.

It has already been shown that black crystalline stibnite may be electrically disintegrated to give a yellow trisulphide. (Page 227.) Ultramicroscopic measurements show that the yellow particles are very finely divided—much more so than could be accomplished by mechanical methods of size reduction. Chemically, the yellow sulphide is identical with the original stibnite. By X-ray methods the crystal structures of the two are shown to be identical. It is therefore considered that the reduction in particle size is the only cause of the difference in color between the yellow and the black crystalline forms.

The interaction of solutions of sodium thiosulphate and antimony chloride will, at room temperatures, give a light yellow precipitate. This may be filtered off, washed thoroughly and dried in a vacuum desiccator over sul-

[1] Mourlot: Compt. rend., 123, 54 (1896); Ann. Chim. Phys., 7, 17 (1899).

[2] Bancroft: "Applied Colloid Chemistry", 205 (1921).

phuric acid. The resulting product is a fine yellow powder, which may be easily passed through a 100-mesh sieve, no crushing or grinding being required. If this fine powder is placed in an air oven at 105°-110°C., a marked difference in color will soon appear. The color will change steadily, passing through orange shades, finally reaching a point at which all of the yellow color will have disappeared and the powder is uniformly red. Further heating at this temperature forms a rich crimson colored powder. If the oven temperature is next raised to 150-170°C., and the heating continued at this temperature, the color of the sulphide changes slowly, passing through a series of shades of crimson and maroon[1], finally becoming uniformly black.

Measurements with the ultramicroscope show that the yellow sulphide is more finely divided than the various orange shades, while the latter are finer than the crimson particles. The increase in particle size follows in the same order as the changes from yellow through to red and crimson. Beyond the crimson stage, the change (if any) is too slight to be measured.

Both the yellow and crimson sulphides as prepared above may be proved amorphous. The final black form is crystalline, (see pages 237).

The precipitation of the trisulphides of antimony, as described above, may be varied within limits and the resulting sulphides will tend to vary in color, depending on the exact conditions. In every case, it will be found that the same set of conditions that tends to give a more finely divided precipitate will always give an antimony sulphide with a lighter yellow color, (see page 225).

These experiments show that our assumption, of a fine yellow and a coarser crimson amorphous antimony trisulphide, was justified.

The tendency of all antimony sulphides to change at high temperatures to the black crystalline trisulphide has long been recognized. The temperature at which the change to the black form begins, and that at which the change is complete, varies with the purity of the sulphide and the method used in preparing it[2].

The maroon shades may be considered as mixtures of red with a certain amount of black. The maroon shades of antimony sulphides are very little, if any, larger than the crimson material. The formation of the various maroon shades is considered as resulting from the formation of increasing amounts of the black modification of the trisulphide. This black material when mixed in with the crimson powder, gives the maroon shades. Under the microscope the maroon sulphides appear homogeneous, so it is evident that the black modi-

[1] The names "crimson" and "maroon" as here given to the colors of the antimony sulphides, are the names used in the industry manufacturing these sulphides for use as pigments. *Webster's New International Dictionary* defines these words as "maroon—sometimes a dark brown chestnut color; ordinarily, any red of dull luminosity, a dull red". "Crimson—a deep red color tinged with blue, one of the primary pigment colors; also red color in general". The pigment color here called crimson is a rich red, but does not appear to contain any blue tinge. The maroon color does not appear to contain any brown color. Both the crimson and the maroon are dark reds, the maroon shades appearing much darker. They are later shown to be mixtures of the crimson and black.

[2] Abegg: "Handbuch anorg. Chem.", 3 III, 598 (19 7); Moissan: "Traité de Chimie minerale, 2, 10, 47 (1905); Unger: J. Chem. Soc., 25. 41 (1872).

fication forms in small amounts in the crimson particles themselves. What probably happens is that some of the crimson particles in a particular aggregation change to the black, but being so small, the black particles can not be distinguished from the red particles around them. The same shades of maroon pigment may be duplicated by mixing the correct proportions of the crimson and black modifications. Here, however, the two phases may be distinguished under the microscope.

Further corroboration, of the statements made above, may be found in the fact that the densities of the sulphides are found to change in exactly the same order as do the colors: the yellow pigments have a density of approximately 4.10-4.12, the crimson 4.12-4.38, while the black form has a density[1] of 4.6-4.8. The density of the maroon shades is usually about 4.4-4.5: the approximate density may be calculated if the color of the pigment is matched with a mixture of known amounts of crimson and black sulphides of known densities.

It may thus be seen that the existence of yellow and crimson amorphous trisulphide and a black crystalline modification will explain the color changes observed when a certain antimony sulphide is heated. The formation of the maroon-colored sulphides offers no particular difficulty. The finely divided crystalline yellow sulphide is not ordinarily formed and does not occur in most sulphides.

There yet remains one class of antimony trisulphides that requires some consideration and explanation.

Williams has noted that no crimson-colored pigment is formed if the sulphide is precipitated in the presence of hydrogen sulphide. Antimony sulphides as ordinarily precipitated by hydrogen sulphide from solutions of trivalent antimony, at room temperature are light golden yellow. On standing at room temperature, the precipitate settles slowly and darkens slightly. If it is next filtered off, washed thoroughly, and dried over sulphuric acid in a vacuum desiccator, the resulting pigment will be a rich golden. Heating this golden pigment at 105°-110°C. causes little or no color change, except perhaps, a slight dulling of the color. Further heating at higher temperatures (150°-170°C.) causes the pigment to change through varying shades of brown to the black modification.

The brown pigments are considered mixtures of varying proportions of yellow (golden) and black trisulphides. The brown colors may be duplicated by mixing the proper proportions of black trisulphide with the golden pigment. As in the case of the maroon shades, the densities of the brown pigments lie between the densities of the light colored and the black modifications. Under the microscope, both brown and maroon pigments made by mixing black with the colored pigments may be distinguished as mixtures. The corresponding colors made by heating the golden and crimson sulphides do not appear as mixtures, but are quite homogeneous to the limit of magnification. This

[1] Kirschoff: Z. anorg. Chem. **114**, 266 (1920); Guinchant and Chrétien: Compt. rend., **138**, 1269 (1904); **139**, 51, 288 (1904); **142**, 709 (1906); Fehling: "Neues Handwörterbuch Chem." 1, 698 (1874); Roscoe and Schorlemmer: "Treatise on Chemistry", 970 (1895).

shows that the formation of the black modification takes place very uniformly throughout the pigment, and forms in very small particles or crystals.

None of the above offers any explanation of the fact that golden sulphides, precipitated in the presence of hydrogen sulphide, will not darken through the crimson stage.

It is supposed that some factor prevents the growth of the particles of the amorphous golden to the size of the crimson particles. Before the conditions required to form the crimson are reached the golden begins to change to the black modification, and we have the series of shades of brown to black, instead of the crimson and maroon shades.

The formation of a protecting film around each particle of golden pigment would prevent intimate contact and the formation of the crimson particles. The color of the powder would, under these conditions, tend to remain the same as that of the individual particles which are originally yellow or golden. If this film could be removed agglomeration would take place unretarded, forming first the crimson pigment, then the maroon shades, and finally the black form.

It is not difficult to prove that such a film may cause the effect observed in the case of antimony goldens. If a sample of the dry pigment prepared from sodium thiosulphate and antimony trichloride, as above, dried over sulphuric acid is moistened, with a gelatin sol, the color changes on subsequent heating at 105°C. will be much like those observed for golden antimony. The effect is further increased if some gelatin sol is present in the solution when the sulphide is precipitated.

The effects always caused by hydrogen sulphide lead one to believe that it is this substance that forms the film over the particles of antimony sulphide. This idea was checked up in the following experiments.

The addition of a very small amount of sodium sulphide to the sodium thiosulphate solution used in precipitating sulphides of antimony will tend to give a precipitate that is much lighter in color than that formed in the absence of the sodium sulphide. When this precipitate is filtered off, washed dried and heated as above it behaves like the antimony goldens and not like the crimson sulphides, as might be expected. In other words, its color changes are like those of sulphides entirely precipitated by hydrogen sulphide. As little as one-half of one percent of sodium sulphide will cause this effect.

In order to prepare a sulphide of antimony in the absence of hydrogen sulphide, excess salts or acids, an electrolytic method was decided upon. (Compare LeBlanc and Schick: Z. physik. Chem., 46, 213 (1903) White: Trans. Am. Electrochem. Soc., 9, 305 (1906).)

In order to carry out this method an electrolytic cell was arranged using electrodes of pure antimony metal. These were immersed in a solution of sodium thiosulphate and a current passed through. Different strengths of solution and varying currents were used. Alternating current electrolysis was tried, and found to give fair results. Due, however, to a tendency of the sulphide formed to stick to the electrodes necessitating continual scraping, it was decided that for most of this work direct current would be preferable.

In a cold solution of concentrated thiosulphide the passage of the current carried antimony into solution as ions. These immediately reacted with the thiosulphate ions present, and then decomposed to form antimony trisulphide, which precipitated. This precipitate was light yellow in color. At higher temperatures, the formation of the precipitate was much more rapid, and the color of the sulphide slightly more golden in color.

This electrolytic pigment was filtered, washed and dried. On heating the colors did not pass through the maroon and crimson stages, but were found to change through the brown and black. This was hardly as expected, so an explanation was sought. It was easily found when it was observed that at the cathode of the cell, some stibine and some hydrogen sulphide was liberated. This, of course, was equivalent to precipitating the sulphide from thiosulphate solution in the presence of hydrogen sulphide, and this has already been described as giving the golden modification. This difficulty was easily eliminated by using a porous diaphragm around the cathode, and thus keeping the hydrogen sulphide solution from mixing with the solution containing the thiosulphate and precipitated sulphide. The precipitate as formed in the anode compartment was then found to act exactly as the samples of crimson prepared in the usual way.

As would be expected from the first part of this work (see page 229) the formation of electrolytic antimony sulphides in more concentrated solutions at low temperatures, or with the addition of a small amount of gelatin sol, was found to give a precipitate of smaller particle size, and of a lighter color.

The following method was suggested to definitely establish the fact that golden antimony sulphides actually contain hydrogen sulphide, probably as an adsorbed film. A sample of pure trisulphide was washed, dried, extracted with carbon tetrachloride, and then thoroughly dried at 105°C. for two months. The resulting trisulphide was a light golden color. Samples of this pigment were then placed in small glass tubes of thick-walled Pyrex glass, evacuated to a pressure of less than one millimeter, and sealed off. The tubes were then placed in an electric furnace and heated at temperatures of 200-225°C for six hours. They were then removed and slowly cooled.

The pigment in the tubes was all converted to the black crystalline variety—as was expected. When the tubes were scratched and broken, a pronounced odor of hydrogen sulphide was noticed.

Adsorption of the hydrogen sulphide by the antimony sulphide is a surface effect. Any hydrogen sulphide not adsorbed would be removed by the treatment given the pigment before sealing in the tubes. Heating the pigment at the high temperature caused the adsorbed gas to be driven off into the evacuated tube. When the pigment crystallized, with much larger particles, and hence much less surface, the gas was not re-adsorbed on cooling.

Antimony crimson samples, similarly treated, gave no indication of liberated hydrogen sulphide. This seemed to prove definitely that hydrogen sulphide is adsorbed by the antimony sulphide whenever the gas is brought into contact with the pigment. This was proved in a similar manner, by exposing

crimson antimony to hydrogen sulphide, again washing, drying, extracting and drying, evacuating and sealing the tube. When this tube was heated, cooled and broken, a trace of hydrogen sulphide was noted, although much less than in the case of the golden where the gas was adsorbed at the time of precipitating.

The preceding experiments definitely prove that antimony sulphides precipitated in the presence of hydrogen sulphide constitute an entirely different class from those precipitated in the absence of this substance. The essential difference between these two classes lies in the color changes resulting when the two kinds are heated. One class may form a brown material, the second class under the same conditions giving a maroon material. The cause for this difference is the formation of an adsorbed film of hydrogen sulphide on particles of antimony sulphide precipitated in the presence of this compound.

In carrying out several of the preceding experiments, it was noticed that antimony sulphides often tended to show pretty series of film colors. Several tests were made to form these films.

It was found that coating a glass plate with a dilute solution of an antimony salt, allowing the solution to evaporate almost completely, and then exposing to hydrogen sulphide fumes formed a thin film of the antimony trisulphide which showed many of the effects of Newton's rings[1]. On carefully heating the center of the glass plate, the sulphide in the center will change to orange and then to black, leaving more or less concentric rings of vari-colored sulphides.

If graphite electrodes are placed in a suspension containing very finely divided antimony sulphides, and a low voltage applied, the electrodes will be coated with a thin film of the sulphide. This film may vary in color, depending on thickness, etc.; but in general will show blue, green and yellow.

The same-colored film effect may be secured by subjecting electrodes of stibnite held a few centimeters apart in an evacuated system, to very high voltages. The cathode becomes coated with the colored film, probably metallic antimony, for a trace of sulphur may be driven out of the stibnite.

These film colors of the sulphides are striking and quite interesting but they should not in any way be confused with the actual pigment colors.

The effect of heat on the colors of the antimony penta- and tetrasulphides was mentioned on page 222 of this paper. In general, the effect of color is but slight, a general darkening being the most noticeable effect. After the decomposition to the trisulphide is complete, the color changes are then like those of all the trisulphides precipitated in the presence of hydrogen sulphide. Heating at moderate temperatures (150°C.) may cause appreciable darkening of the higher sulphides before all the higher sulphide is decomposed to the trisulphide. This darkening may be explained as the result of the formation of black trisulphide throughout the mass of pigment, causing any unchanged higher sulphide or trisulphide to appear brown.

[1] Tyndall: "Electricity and Light", 97 (1895)

It was considered worth-while to make a study of the crystal structure of the different antimony sulphides. For this work, X-ray powder photographs of the sulphides were made. The apparatus used was that described by Davey[1]; a complete description of this apparatus will be omitted here. It is based on the principles discovered and worked out by Laue[2] and the Braggs[3] and later modified by Hull[4].

The samples of sulphides to be studied were finely powdered, placed in thin-walled glass tubes of about 1/32 inch inside diameter, and placed in position in the apparatus. A monochromatic beam of X-rays (the Molybdenum K-alpha doublet) reduced to a suitable slit system (see Davey page 566) was then passed through the sample tube. The X-ray diffraction pattern was recorded on a strip of photographic film placed in a cassette which automatically held the film on the arc of a circle of 8-inch radius, having at its center the sample of powdered sulphide.

The photographs of X-ray diffraction patterns look very much like the pictures of line spectra. A full account of the mathematical theory of the pattern is given by Hull.

For this work on antimony sulphides the following samples were prepared and their X-ray diffraction patterns taken:

(1) Metallic antimony.
(2) Sulphur, both precipitated and "flowers."
(3) Antimony pentasulphide.
(4) Antimony tetrasulphide.
(5) Antimony trisulphides:
    (a) Precipitated golden trisulphide.
    (b) Precipitated crimson trisulphide.
    (c) Electrolytic trisulphide (see page 233 of this paper).
    (d) Natural stibnite.
    (e) Stibnite disintegrated by the Svedberg arc.
    (f) Artificial black trisulphides.

Patterns of these samples were taken separately, or simultaneously with that of NaCl, in order to give a comparison scale. The time required for exposure in order to give clear patterns varied with the nature of the samples. NaCl gave a clear pattern in five hours. For the other samples, approximately twenty hours was found to be the most satisfactory length of exposure.

It was hoped that this method would show different crystal structures for the tri-, tetra-, and pentasulphides of antimony, and so furnish a convenient method of distinguishing between them. The results of these efforts were rather surprising. Instead of giving different patterns for each sulphide, all of the precipitated sulphides of antimony were alike in that none gave X-ray

[1] Gen. Elec. Rev., 25, 565 (1922).
[2] Sitzungsber. bayr. Akad. Wiss., (1912).
[3] W. H. and W. L. Bragg: "X-rays and Crystal Structure", (1915).
[4] Phys. Rev., 10, 661 (1917); Proc. Am. Inst. Elec. Eng., 38, 1171 (1919).

diffraction patterns or any indications of definite crystal structure. They are evidently amorphous substances[1].

This conclusion was at first doubted, but further work on the subject leaves little doubt that the precipitated sulphides of antimony—including the tri-, tetra-, and pentasulphides are really amorphous precipitates. All efforts to obtain patterns showing a crystalline formation have failed. Prof. Debye and Dr. Davey both agree that the indications are very strong that we have truly amorphous substances.

The cases of sulphur and antimony were much more simple. Both gave the diffraction patterns expected[2].

Precipitated golden and crimson trisulphides, and the "electrolytic trisulphide" are evidently amorphous.

The natural stibnite, artificial black trisulphides, and the trisulphide disintegrated by the Svedberg arc, all are crystalline and show the same diffraction pattern. This is particularly interesting if one remembers that the disintegrated material is golden in color, and very similar to the precipitated amorphous material. This is the only case in which a colored antimony sulphide was found to have a definite crystal structure. The method of preparation of the artificial black trisulphides seemed to have no effect on the crystal structure of the resulting product.

## Conclusions

(1) Precipitated antimony sulphides are all amorphous solids. These include antimony pentasulphide, antimony tetrasulphide, and both golden and crimson antimony trisulphides. All these sulphides are colored.

(2) All amorphous sulphides of antimony may be converted into the black crystalline modification of the trisulphide by long heating at high temperatures—around 200°C. The resulting black modification is the same regardless of the sulphide used as the starting material.

(3) The amorphous antimony trisulphide in a very fine state of subdivision is yellow. Larger amorphous particles are crimson in color. Intermediate colors are also of intermediate size or mixtures of the yellow and crimson.

(4) Maroon shades of antimony trisulphide are mixtures of crimson and black sulphides.

(5) A crystalline yellow antimony trisulphide may be prepared by means of electrical disintegration of stibnite under water. This colored crystalline material shows exactly the same crystal structure as do all the artificially prepared crystalline sulphides of antimony. The yellow crystalline form is the very finely divided crystalline form. All the artificially prepared crystalline sulphides of antimony show a crystal structure identical with that of stibnite, the natural crystalline variety.

---

[1] Haber: Ber. **55B**, 1717-1733 (1922)

[2] Wyckoff: "The Structure of Crystals" (1924).

(6) Antimony pigments precipitated in the presence of $S''$ or $HS'$ ions will not darken through crimson and maroon shades, but instead darken through varying shades of golden to brown and then to the black modification. The difference between the brown and the maroon pigments is due to the adsorption of a film of hydrogen sulphide by the former. This adsorbed film prevents the intimate contact of the particles, and so prevents the growth of larger particles forming the crimson variety. The varying shades of brown may be explained as resulting from mixing the golden pigment with varying quantities of the black modification.

(7) Crystalline crimson pigment can not be prepared by any of the methods studied. The golden variety may be prepared amorphous by precipitation, crystalline by disintegration of stibnite. The larger particles of amorphous trisulphide alone give the crimson variety.

I welcome this opportunity to acknowledge my indebtedness to Professor Wilder D. Bancroft, and to express my gratitude to him for the many helpful suggestions and valuable criticisms offered during the progress of this work.

I also wish to express my thanks to Professor F. K. Richtmyer and Mr. H. W. Russell for their co-operation and suggestions in carrying out parts of this work.

*Cornell University*

# THE APPARENT VISCOSITY OF COLLOIDAL SOLUTIONS AND A THEORY OF NEUTRAL COLLOIDS AS SOLVATED MICELLES CAPABLE OF AGGREGATION*

259

BY JAMES WILLIAM McBAIN

Our work on nitro cotton led several years ago to a hypothesis which has proved useful throughout subsequent experiment. It attempts to explain viscosity relationships and their changes with time and conditions, the structure of jellies and their reversible changes; and it emphasizes the relation between solvent and colloid ascribing to solvation a role which we believe to be of far more general importance than the more familiar electrical charges.

*A. The mechanical explanation of viscosity.*

There are four ways of explaining the high viscosity of colloidal solutions, suspensions and emulsions as compared with the viscosity of the solvent:—

a) The increased shear imposed upon the solvent for a given amount of flow when small particles, droplets, or micelles are suspended in the solvent. This is the conception of Einstein as applied impartially by him to suspensions and true solutions of large molecules such as sucrose.

b) The increased shear imposed upon the solvent, (or rather, solution) for a given amount of flow by droplets of an emulsified liquid that contains a relatively smaller proportion of solvent. This is the usual emulsoid conception, associated with the teaching of Wo. Ostwald, which assumes partial miscibility of the two liquids.

c) The increased shear imposed upon the solvent for a given amount of flow when small rigid colloidal particles or micelles cohere to form loose or open aggregates suspended in the solvent. These larger structures practically immobilise the solvent which they embrace. This is the view held by the writer and by Loeb.

d) An additional effect, only occurring in concentrated suspensions or emulsions, or where the aggregates ramify throughout a large part of the solution, is the deformation of the droplets or aggregates caused by the mutual interference of the particles which are necessarily brought into contact during shear. Much of the work of E. C. Bingham on viscosity and plasticity has lain in this field. Hatschek has developed an elegant treatment of the case of the deformation of liquid droplets in concentrated emulsions during shear.

He deduced the formula $\frac{\eta}{\eta_0} = \frac{\sqrt[3]{A}}{\sqrt[3]{A-1}}$, where A is the ratio between the total volume of the emulsion and the volume of the dispersed droplets, the formula being applicable to cases where A is less than 2. Incidentally he showed that the formation and behaviour of an elastic solid such as a jelly cannot be explained on the basis of a liquid-liquid model. There appears to

*Compare preliminary notice in Trans. Faraday Soc., 20, 22-24 (1924).

be no evidence for regarding the particles of nitro cotton as being liquid either in sol, jelly or gel; they may rather be considered as composed of non-deformable micelles which form aggregates, change in whose structure or orientation will require work to be done.

In the case of a dilute suspension (see explanation (a) above), Einstein[1] and Hatschek[2] have independently deduced formulae which ascribe the enhanced viscosity entirely to the extra movement required of the solvent. Their formulae are $\eta = \eta_0(1+kv)$ where $v$ is the fraction of solid present by volume and $k$ is a constant which Hatschek thought would be 4.5; Einstein found it as 1 and afterwards altered it to 2.5. The formulae agree in relating the enhanced viscosity to the total bulk of the particles independent of their degree of subdivision. This formula holds to a certain extent, but it is usually necessary to postulate a larger bulk of particles than that which corresponds to their pure dry condition. This is ascribed to solvation of the particles and the conception of solvation and enhanced viscosity arising therefrom has taken a firm hold on present-day chemists.

Hatschek's interpretation of viscosity has not in practice discriminated[3] between (a), (b) and (c). In discussing the high viscosity of very dilute solutions of reversible colloids such as proteins and nitro cotton, where according to his formula the viscosity far exceeds that ascribable to the volume of the dry colloid, this is ascribed to "solvation" although it would involve the greater part of the liquid present. This is however not true solvation.

It does not appear to the writer to be legitimate to treat as solvation solvent that is included in liquid droplets of an emulsion, as in (b), or merely entangled in a ramifying aggregate, as in (c). The effects observed under (a) and (c) are of different orders of magnitude. In the present case we know for example, from our experiments on sorption, that the true solvation of nitro cotton does not exceed an amount of solvent equal to the weight of nitro cotton itself, and the excess viscosity due to the increase in volume of the nitro cotton caused by this true solvation is negligible in comparison with the actual viscosities observed. For example, if the nitro cotton in 1% solution in any solvent of approximately unit density is anhydrous and is of density[4] 1.67 the viscosity slope would be 0.012; if hydrated to unit density it would still be only 0.02.

In place of such low viscosity slopes as 0.01 or 0.02 we get values up to several hundred fold greater. In other words, the apparent viscosity of such solutions as nitro cotton is of a different order of magnitude from that ascribable to simple massive particles according to the principles developed by Einstein and Hatschek; even solvation or the assumption of a film of solvent enveloping and clinging to each particle is wholly inadequate as an explanation.

If Einstein's and Hatschek's formulae are strained beyond the limits in order to explain the high apparent viscosity of these dilute solutions, it is im-

[1] Ann. Physik, (4) **19**, 289 (1906).
[2] Kolloid-Z., **7**, 301 (1910); **8**, 34 (1911); Trans Faraday Soc., **9**, 80 (1913).
[3] See for example Biochem. J., **10**, 330 (1916).
[4] J. Soc. Chem. Ind., **26**, 449 (1907).

possible to go further than to assume that the fractional volume $v$ is equal to unity; that is, that the whole volume of the solution is ascribed to the particles themselves: and yet this impossible extreme does not suffice. The formulae thus give at the utmost a viscosity slope of 0.54 (Einstein) or 0.74 (Hatschek), whereas the observed slopes are often very many times greater.

Of course Hatschek would at once apply his cube root formula if the disperse phase were assumed to occupy over 50% of the total space and this would account under such conditions, for any required viscosity slope up to infinity. However, we have the experimental fact that these enormous viscosity slopes are observed in very dilute solution and that they are, if anything, still higher in extreme dilution; so that, if this way out were to be accepted it would be necessary to assume that in each of these successive low dilutions the greater part of the solvent must be dissolved in the disperse phase. In other words, it would be necessary to assume that in extreme dilution the composition of the two phases was almost indistinguishable and yet that they did not mix but formed a concentrated emulsion.

Hence, we can with confidence conclude that the structure of these dilute emulsoid sols is not at all that contemplated in the deduction of the Einstein and Hatschek formulae. The argument here developed appears to involve further conclusion that viscous sols such as nitro cotton do not exhibit true viscous flow.

Hatschek's formula is however beautifully confirmed for the case of true emulsions. A striking illustration of this is the viscosity exhibited by suspensions of blood corpuscles in which each corpuscle is separate although in the most concentrated suspension the corpuscles occupy 90% of the total volume of the system[1]. The relative viscosity observed 30.5 is precisely that predicted by the Hatschek cube root formula. Although this relative viscosity appears high, it is incomparably lower than that which would be exhibited in any corresponding solution of nitro cotton where we believe that the colloidal particles are not separate but are linked together to form ramifying aggregates, which produce an apparent viscosity far greater than that accounted for by their real volume. If the relative viscosity of a dilute solution (say 3%) of nitro cotton, is 1000 and the attempt were made to interpret this as an emulsion according to the Hatschek formula it would have to be assumed that the nitro cotton occupied 99.8% of the total volume leaving only 0.2% for the solvent as continuous medium. For a solution of nitro cotton only a little more concentrated the total volume of the "continuous medium" becomes infinitesimal. However, we know from direct sorption experiments that nitro cotton does not take up more than its own weight of solvent and that therefore this extraordinary emulsoid explanation is inadmissible.

Hypothesis (c) is advocated by the writer to explain these enormous viscosities which are evidently so far beyond the effects of solvation or immobilised solvent films; (although both probably occur, they are of minor importance). The explanation is that given in paragraph (c) and (d) at the

[1] Kolloid-Z., 27, 164 (1920).

beginning of this section; that is, that ramifying colloidal aggregates embrace and practically immobilise large portions of the solution. This necessarily involves interference between these particles and deformation of these structures when the solution is made to flow. It is equally evident that if each of the regions of the solvent which is immobilised by the presence in it of one or more ramifying aggregates behaves, to a certain extent, as an entity, that the apparent viscosity of the whole system must have some such form as that provided in the empirical Arrhenius formula and explained on mechanical and geometrical grounds in the Hatschek cube root formula.

It is clear therefore that the chief source of viscosity is ascribable to the formation of ramifying aggregates, and that the best solvent is that which most efficiently dismembers them. The highest viscosity slopes do not reflect high solvation, but probably the contrary; that is, insufficient solvation to disintegrate the particles.

Before proceeding to discuss the hypothesis of neutral colloids it should be pointed out that the preceding discussion has largely justified the use of relative viscosity ($\eta/\eta_o$) compared with that of the solvent as a correct formulation of results of viscosity measurements in various solvents since in all cases enhanced flow is required of the solvent itself.

We have studied the viscosity of nitro cotton only in diluted solution and at temperatures usually above gelatinising temperature. Nevertheless, we are justified, if our conception of viscosity as due to ramifying aggregates is correct, in deducing therefrom the behaviour of nitro cotton at concentrations and temperatures where it does form hard gels.

Further corroborative evidence is to be found in the parallelism between the mechanical strength of cotton hairs on the one hand and the viscosities of solutions of the same cotton in cuprammonium[1]. This parallelism is well known to apply extensively between various solutions derived from different samples of cellulose when compared in a series of different solvents, even after the samples of cellulose have been submitted to drastic treatment and esterified.

*B. Further evidence that the apparent viscosity is not the true viscosity even when fully reproducible.*

Different specimens of nitro cotton of similar composition give different viscosities and the temperature coefficient of viscosity is extremely large. We have to enquire whether the viscosity we have measured at 55° is a true viscosity independent of the rate of shear and method of measurement. We know of no single solution of any cellulose ester for which it has been actually demonstrated by experiment that true viscosity exists. Wherever in our own work or in the recorded literature (as far as we know) any direct test has been applied, the flow was found to be dependent on the type of viscometer and the apparent viscosity was not a constant independent of the rate of shear. In Mardles' work on cellulose acetate the Poiseuille tube, the falling ball, and

[1] Farrow and Neale: Shirley Inst. Mem. 3, 67 (1924); J. Text. Inst. 15, 157 (1924).

the Störmer rotating cylinder not only gave different numerical values, but the viscosity-concentration curves differed even in form.

Bingham and Hyden[1] studied nitro cotton (12.1% nitrogen) in acetone and by extrapolation of results with 7.708% solution in acetone at only 5°, 20° and 35° concluded that the deviation from proportionality between actual flow and shearing stress would probably disappear at 43° and he states that there is nothing in his experiments "inconsistent with the view that this 'transition point' is independent of the concentration." His actual data however for 4.966% at 20° and 35° similarly extrapolated point to 60°. His data for 3.98% at 10°, 20°, 30° and 40° point to 70°. In other words all actual measurements gave a distinct deviation from Poiseuille's law and thus do not show a true viscosity as defined by all physicists since 1860. Bingham and Hyden found it possible within their experimental error to obtain a proportionality between flow and shearing stress if for each concentration at each temperature a small arbitrary amount (different for each series) was subtracted from the actual shearing stresses. These corrections he called friction or yield value and it is to be noted that their evaluation involved fairly big extrapolations. The significance ascribed to the yield values was to the effect that at lower shearing stresses no flow at all would occur. However, it must be remembered that no such phenomenon has ever been observed with sols of cellulose ester and there seems to be no cogent theoretical necessity for the existence of such yield values. Bingham[2], in a later paper now finds that even the apparent yield values for a given solution as obtained by extrapolation vary widely with the dimensions of the viscometer.

Hatschek[3] reiterates the result of his work with Miss Humphrey[4] in which they used a suspension of granules of starch in a mixture of toluene and carbon tetrachloride. Here there is no question of gelatinising particles but the viscosity as measured diminishes with increasing rate of shear and the highest concentrations show this most clearly. Hatschek regards the behaviour of his suspensions as a part of the typical behaviour of all sols including the so-called emulsoid sols such as for example our solutions of nitro cotton. He does not ascribe it like Bingham to plasticity nor to elasticity but considers that each particle is covered with a thin layer of clinging liquid which is diminished in thickness as the shear increases. He is inclined to extend this explanation of variable viscosity to all colloidal systems; but compare the preceding discussion.

L. E. Smith has carried out the following experiments (Table I) to investigate the relation between rate of flow in the viscometer and the head of pressure employed. It is seen that in every case there is a lack of strict proportionality between efflux and shearing stress, and that the apparent viscosity is not a true viscosity.

[1] Franklin Inst. **194**, 731 (1922).
[2] "Colloid Symposium Monograph," **2**, 210 (1925).
[3] Kolloid-Z., **37**, 25 (1925).
[4] Proc. Phys. Soc. London, **28**, 274 (1916).

TABLE I

Relation between head of pressure and rate of flow in the viscometer for solutions of nitro cotton. L. E. Smith.

| Time (secs) | Pressure cms Hg | $\frac{p.t}{1000}$ | $\frac{1}{10{,}000t}$ |
|---|---|---|---|
| | *Benzyl formanilide at 25.0°C* | | |
| 897 | 79.4 | 71.2 | 11.15 |
| 1425 | 52.0 | 74.1 | 7.02 |
| | Therefore friction $= 5 \times 10^3$ cms. Hg | | |
| | *Ethyl formanilide at 55.0°C* | | |
| 326.4 | 84.7 | 27.65 | 30.65 |
| 381.2 | 72.6 | 27.67 | 26.24 |
| 496.4 | 56.45 | 28.03 | 20.14 |
| 648.4 | 43.6 | 28.28 | 15.41 |
| 1008.0 | 28.65 | 28.87 | 9.93 |
| 2357.0 | 12.2 | 28.77 | 4.24 |
| | Therefore friction or yield value $= 2.5 \times 10^3$ cm. Hg. | | |
| | *Benzyl phenyl urethane and phenyl urethane mixture at 55.0°* | | |
| 33.2 | 78.3 | 2.60 | 3.00 |
| 36.8 | 72.75 | 2.68 | 2.72 |
| 38 | 69.2 | 2.63 | 2.63 |
| 43.8 | 61.75 | 2.71 | 2.28 |
| 50.4 | 58.05 | 2.77 | 1.98 |
| 54.0 | 51.6 | 2.78 | 1.85 |
| 63.4 | 44.6 | 2.83 | 1.54 |
| 65.0 | 43.7 | 2.84 | 1.54 |
| 68.8 | 40.85 | 2.81 | 1.45 |
| 81.6 | 35.75 | 2.92 | 1.23 |
| | Therefore friction or yield value $= 5 \times 10^3$ cms. Hg. | | |

Even if the yield value were found to be negligibly small or within the limits of experimental error, this would not invalidate the suggestion here advanced that the chief source of viscosity is the mutual interference of the loose aggregates of the primary micelles; it would merely show that they were readily deformed and could slip past each other easily.

*C. Theory of neutral colloids or solvated micelles capable of aggregation.*

The study of soap solutions in this laboratory has established the fact of aggregation of molecules to form a colloidal unit or micelle. These micelles may be of various kinds. In the past great attention has been given to the role that electrical charges play in the stabilistaion of such particles and this is the usual standpoint from which the so-called suspensoid colloids are discussed. The extreme and most interesting case is the ionic micelle which is essentially an aggregation of fully charged ions. The writer is however convinced that the most important micelles are those in which electrical charge

plays but an insignificant role. These are the neutral micelles or neutral colloids exemplified by undissociated soap and sols of nitro cellulose, and which according to Laing and McBain[1] are the particles from which the gel structure of soap solutions are made up.

The stabilising agent in neutral micelles is solvation which gives the surface of each micelle sufficient degree of similarity to the solvent medium. It is common knowledge that compounds of similar character such as hydrocarbons are mutually soluble. Giles and Salmon[2] in a significant study of sols of silver in stearic acid have shown that stabilisation in this non-ionising solvent is due to a coating of each silver particle with silver stearate, the stearate end of each molecule being directed outwards.

A nearly perfect solvent would be one in which the complicated structure of fibres of nitro cotton would be completely reduced to its constituent units; that is, into separate solvated colloidal particles or neutral micelles all existing independently of each other and for such a solvent the viscosity slope would be between 0.01 and 0.02 (of course a still more perfect solvent might be found in which the nitro cotton dissolved as separate molecules, i.e., a crystalloid but no such solvent is known).

The conception here put forward is that the nitro cotton fibres are made up of micelles which are linked together at various points by bonds of residual affinity or chemical valency, these bonds vary greatly in nature and strength. Disjunction of these bonds is brought about by combination with solvent molecules which by adding on satisfy the residual affinities. The action is the same as the loosening of a glass stopper by the penetration of a film of oil which separates the two glass surfaces by uniting with each of them. An exact parallel is also found in the action of a soap solution in separating dirt from a fabric through the soap combining with the fabric and with the dirt according to the equation suggested by the writer in 1920:[3]

$$\text{Fabric} : \text{dirt} + \text{soap} = \text{fabric} : \text{soap} + \text{dirt} : \text{soap}$$

Definite chemical groups are required for combination with definite portions of the molecules on the exposed surfaces of the micelles. The best practical solvents are those which are most effective in disuniting the bonds between the micelles. The disjunction fails in the case of non-solvents although they may combine to a certain extent and disunite a few bonds without releasing the whole aggregation. Poor solvents effect it slowly and not to so great an extent as good solvents. The so-called degradation or ageing of nitro cotton discussed in the previous paper must be largely progressive dismemberment.

This conception shows clearly how apparent viscosity of various solutions of nitro cotton is to be explained. It is due to the presence of loose ramifying aggregates of micelles. The best solvents are those in which dismemberment proceeds furthest through solvation of the various points of affinity.

[1] J. Chem. Soc., **117**, 1507 (1920).
[2] J. Chem. Soc., **123**, 1597 (1923).
[3] "Third Colloid Report of the British Association," 26 (1920).

Poorer solvents are those in which dismemberment is less complete and the apparent viscosity therefore much higher. Similarly there is a complete series of gradations among non-solvents from substances which are completely indifferent to nitro cotton, if any such exist, through those which combine more up to those where just sufficient bonds are loosed to form colloidal sol, and the non-solvent just becomes a solvent.

It is also clear why mixtures are so very frequently much better solvents than pure substances, because a variety of chemical groupings is offered for union with the corresponding bonds.

There is not the least uncertainty about the existence of combination between nitro cotton and various substances, more especially the good solvents. Reid in an unpublished ebullioscopic study has proven the fact of combination and all our evidence from the sorption of vapours of solvents and non-solvents by nitro cotton and from sorption by nitro cotton of solvents from solution in diluents shows a graduation in the strength of the various bonds. The affinities are very different, some strong, others remarkably weak. Hence, anything which lowers the availability of the solvent markedly decreases the combination. Very slight alternations are necessary to effect important changes. Thus a small amount of diluent would remove the solvent from the localities of weakest affinity, owing to the slight lowering of the chemical potential of the solvent.

The bonds between the particles are restored if the suitable localities of those particles are deprived of their chemical complements (not necessarily molecules of the solvent) whether by change of temperature addition of diluents, lowering of vapour pressure, change of concentration or direct chemical action.

The formation of a jelly from a sol need not involve any extensive alteration in the micelles existing in the sol, even if in the sol they exist quite independently of each other. Only a few points have to be deprived of their chemical complement for a loose union between adjacent micelles to occur and a jelly structure to result. In the case of soap it has been shown that the micelles in sol and jelly are practically identical and the conductivity of sols of gelatine containing salt or of agar containing salt has been shown by Arrhenius and Hatschek respectively to be practically unchanged on formation of a jelly. In a definite sense the degree of dispersion may be equally great in a sol and in a jelly. Unpublished work by Salmon and Manning explains the action of urea in depriving gelatin of its power to set to a jelly, combination of the urea with the gelatin replacing the usual linking up of the terminal amino and carboxyl groups. I venture to suggest that the presence of elasticity in a colloidal solution is a specific positive test for the presence of ramifying aggregates.

The standpoint here advocated lends a fuller significance to lyophile and lyophobe colloids respectively; namely, those in which the disperse phase has such an affinity for solvent that sols can and cannot be formed spontaneously.

To sum up, the linking together of colloidal particles or micelles to form larger structures is caused by bonds of union which are at least as local and specific as the processes operative in adsorption or residual affinity. These bonds are loosed by the substitution in them of various chemicals. This generalised form of solvation is the essential factor in gelatinising and dissolving nitro cotton and in explaining the apparent viscosity of the resulting systems. Only when aggregation is on an excessively coarse scale can mechanical means be effectually employed towards breaking it up. Otherwise, the one great operative force to be taken into account is the solvation, physical or chemical or both, of the molecules in the colloidal micelle.

*Department of Physical Chemistry,*
*The University,*
*Bristol, England.*
*September, 1925.*

# EQUILIBRIUM IN THE SYSTEM ARSENIC PENTOXIDE, BARIUM OXIDE, WATER. (ACID SECTION)*

BY STERLING B. HENDRICKS

The increasing use of alkaline arsenates as insecticides necessitates a more complete knowledge of the chemical properties of these substances. The following research describes the results obtained from a study of the acid section of the system BaO, $As_2O_5$, $H_2O$. Since equilibrium conditions are not rapidly established in basic solutions the basic section of this system will be reported later.

*Preparation of Materials.*—$Ba(OH)_2 . 8H_2O$ was prepared by recrystallizing "C.P." reagent from $CO_2$—free distilled water. It gave a negative test for $Cl^-$, $CO_3^{--}$, and $NO_3^-$. $As_2O_5 . 4H_2O$ was prepared by the method previously described by C. M. Smith[1].

*Experimental Procedure.*—100 cc. paraffined cork stoppered oil sample bottles were used for experimental vessels. Solutions of known concentration, containing some of the solid phase, were placed in these and were then immersed in a thermostat regulated at $30° \pm .1°$. Equilibrium conditions were determined by analysis of the solutions at intervals of one week. Analyses were made in the manner given below.

*Analysis.*—The densities of the solution were determined by means of a pycnometer, the temperature being 20°. The barium was determined by the sulfate method, the ignited $BaSO_4$ being moistened with conc. $H_2SO_4$ and reignited in order to remove chloride impurities. The arsenic was determined by titrating the $I_2$ liberated from an iodide in conc. HCl solution, accurately standardized $Na_2S_2O_3$ solution being used.

Since any attempt to dry or wash the solid phase would probably have resulted in hydrolysis or dehydration, it was necessary to use the method of analysis of wet precipitates[2] in order to determine the compositions of the solid phases. Since there were slight experimental errors involved in the analysis, the exact point of intersection of several lines determining the composition of a solid phase could not be determined by graphical means. The most probable point of intersection of several lines was assumed to be that point at which the sum of the squares of the perpendicular distances to the lines was a minimum. Since the two points determining a line were very close together in the case of the more acid solutions, it was necessary to identify the solid phases present by microscopic means. The results of the analyses are given on pages 250-251.

The stable phases and the solutions in equilibrium with two of them are: $BaHAsO_4 . H_2O$ and $BaH_4(AsO_4)_2 . 2H_2O$, solution, 16.65% BaO and 28.01% $As_2O_5$; $BaH_4(AsO_4)_2 . 2H_2O$ and $3As_2O_5 . 5H_2O$, solution 72.04% $As_2O_5$ and

*Contribution from the Kansas State Agricultural College.

[1] J. Am. Chem. Soc., 42, 259 (1920).

[2] Bancroft: J. Phys. Chem., 6, 178; Browne: 287 (1902).

a trace of BaO; $BaHAsO_4 . H_2O$ and some more basic arsenate, probably $Ba_3(AsO_4)_2 . x H_2O$, solution, .025% BaO and .03% $As_2O_5$. $3As_2O_5 . 5H_2O$ was assumed to be the solid phase present in the most acid solution, since the analysis of the wet solid gave proof that $As_2O_3 . 4H_2O$ was not present. Menzies and Potter[1] reported these oxides, $3As_2O_5 . 5H_2O$ being stable above 29°, thus explaining the conversion in this experiment. The constant solution

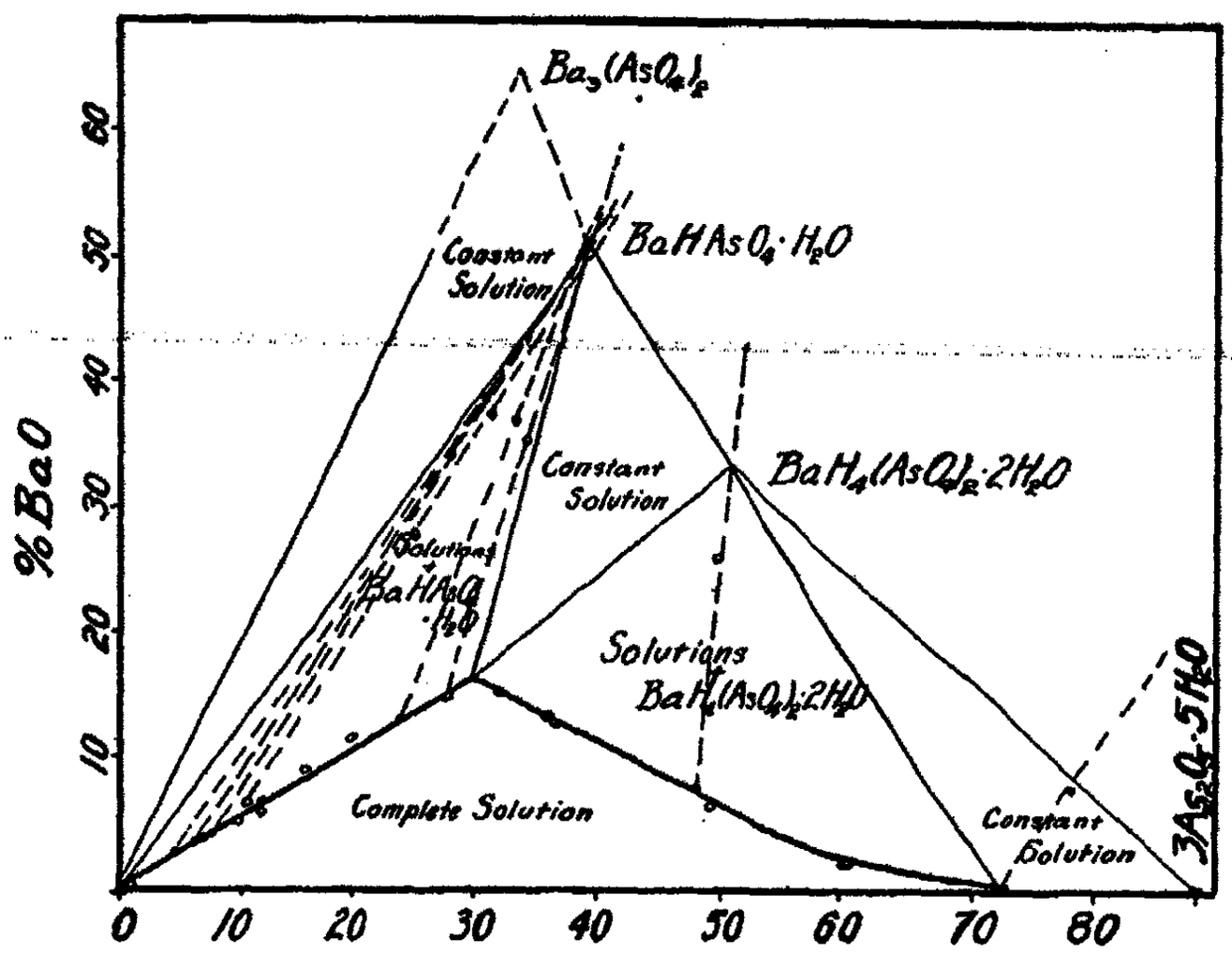



FIG. 1

containing .025% BaO and .03% $As_2O_5$ with $BaHAsO_4 . H_2O$ and $Ba_3(AsO_4)_2 . x H_2O$ as a solid phase gave no evidence of existing in equilibrium with $Ba_5H_2(AsO_4)_4 . x H_2O$, the analogous calcium compound has been recently prepared. These compounds with the exception of the latter have been previously described[2].

*Preparation of Barium Arsenates.*—Since most of the methods of preparation of barium arsenates previously described were found to be unsatisfactory, the older methods have been tested and new methods devised. Mono barium arsenate has previously been described by Mitscherlich[3] by adding $Ba(OH)_2$ to conc. $H_3AsO_4$, which is essentially precipitation beyond the invariant point in the previous diagram, Fig. 1. The following method gave satisfactory

[1] J. Am. Chem. Soc., 34, 1469 (1912).

[2] Gmelin Kraut: "Handbuch anorg. Chem.", 3 II, 584.

[3] Gmelin Kraut: *loc. cit.*

TABLE I

Analysis of equilibrium experiments in the system BaO, $As_2O_5$, and $H_2O$

| | Solutions. | | | | | | Solids | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Exp. No. | Density | %BaO | %$As_2O_5$ | Mol ratio | Grs. BaO per L. | Grs. $As_2O_5$ per L. | %BaO | %$As_2O_5$ | Mol ratio | Comments |
| 1 | 1.003 | .22 | .002 | 136.8 | 2.22 | .03 | 51.64 | 23.10 | 3.55 | "Solid solution" probably. |
| 2 | 1.002 | .11 | .003 | 57.3 | 1.07 | .03 | 44.45 | 21.75 | 3.07 | |
| 3 | 1.001 | .03 | .034 | 1.02 | .23 | .34 | 45.89 | 22.73 | 3.01 | Solid phases $BaHAsO_4$. $H_2O$ and $Ba_3(AsO_4)_2$. Two months required to establish equilibrium. |
| 4 | 1.001 | .03 | .034 | 1.20 | .27 | .34 | 45.24 | 23.77 | 2.86 | |
| 5 | 1.001 | .03 | .031 | 1.20 | .25 | .31 | 46.41 | 25.62 | 2.73 | |
| 6 | 1.001 | .03 | .032 | 1.16 | .25 | .32 | 35.34 | 20.27 | 2.61 | |
| 7 | 1.002 | .02 | .032 | 1.37 | .20 | .32 | 42.11 | 26.02 | 2.43 | |
| 8 | 1.002 | .03 | .029 | .93 | .27 | .29 | 42.13 | 28.77 | 2.21 | |
| 9 | 1.067 | 2.63 | 3.98 | .99 | 28.06 | 42.46 | 38.34 | 29.60 | | Solid phase—$BaHAsO_4$. $H_2O$ |
| 10 | 1.094 | 3.60 | 5.86 | .92 | 39.38 | 64.10 | 34.10 | 27.24 | | |
| 11 | 1.105 | 4.44 | 7.19 | .92 | 49.01 | 79.50 | 37.31 | 29.48 | | |
| 12 | 1.108 | 4.04 | 6.72 | .90 | 44.76 | 74.45 | 31.94 | 25.50 | | |
| 13 | 1.117 | 4.36 | 7.26 | .90 | 48.59 | 81.09 | 38.01 | 30.22 | | |
| 14 | 1.151 | 5.49 | 9.28 | .89 | 63.15 | 106.71 | | | | |
| 15 | 1.176 | 6.25 | 10.56 | .89 | 73.49 | 124.2 | 27.83 | 24.13 | | |
| 16 | 1.188 | 6.62 | 11.27 | .88 | 78.64 | 133.9 | | | | |

TABLE I (continued)

Analysis of equilibrium experiments in the system BaO, $As_2O_5$, and $H_2O$

| | Solutions | | | | | | Solids | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Exp. No. | Density | %BaO | %$As_2O_5$ | Mol ratio | Grs. BaO per L. | Grs. $As_2O_5$ per L. | %BaO | %$As_2O_5$ | Mal ratio | Comments |
| 17 | 1.281 | 6.98 | 11.12 | .94 | 82.50 | 131.5 | Three weeks required to produce equilibrium. | | | |
| 18 | 1.271 | 9.46 | 14.92 | .95 | 120.2 | 189.8 | Solid phases examined microscopically, proved | | | |
| 19 | 1.357 | 11.67 | 18.52 | .94 | 158.1 | 251.4 | to be $BaHAsO_4 . H_2O$. | | | |
| 20 | 1.474 | 13.59 | 22.95 | .90 | 200.1 | 338.0 | 36.95 | 32.52 | | |
| 21 | 1.592 | 15.37 | 27.26 | .85 | 244.8 | 434.5 | 35.01 | 33.62 | | |
| 22 | 1.694 | 15.65 | 31.17 | .75 | 265.2 | 528.0 | Two weeks required to establish equilibrium. | | | |
| 23 | 1.704 | 13.70 | 35.10 | .58 | 233.7 | 597.8 | Solid phases $BaH_4(AsO_4)_2 . 2H_2O$. | | | |
| 24 | 1.719 | 13.35 | 35.87 | .56 | 229.3 | 616.2 | | | | |
| 25 | 1.809 | 7.53 | 47.27 | .24 | 136.2 | 855.1 | 26.83 | 40.25 | | |
| 26 | 1.817 | 6.56 | 48.48 | .20 | 119.1 | 880.0 | | | | |
| 27 | 2.150 | trace | 68.40 | — | trace | 1471.0 | | | | |
| 28 | 2.280 | trace | 72.04 | — | trace | 1644.0 | 8.91 | 77.60 | | $3As_2O_5 . 5H_2O$ and $BaH_4(AsO_4)_2 . H_2O$ are the solid phases. Solid phase is $BaH_4(AsO_4)_2 . 2H_2O$. |
| 29 | 1.869 | trace | 59.44 | — | trace | 1110.0 | | | | |

results; melted $Ba(OH)_2 . 8H_2O$ was poured into an excess of 45% $H_3AsO_4$, the hard, well-crystallized solid, was removed, dired at 130°, and analysed. The analysis gave 36.30% BaO, 55.45% $As_2O_5$, 8.25% $H_2O$; calculated for $BaH_4(AsO_4)_2$ 36.58% BaO, 54.83% $As_2O_5$, 8.57% $H_2O$.

The following table summarizes the results obtained in the investigation of $BaHAsO_4 . H_2O$.

TABLE II

| Method used | %BaO | $\%As_2O_5$ | Ratio $BaO/As_2O_5$. |
|---|---|---|---|
| Excess $H_3AsO_4$.$Ba(OH)_2$ added drop by drop. | 41.73 | 32.89 | 1.90 |
| Excess $Ba(OH)_2 . H_3AsO_4$ solution added drop by drop. | 51.09 | 37.56 | 2.03 |
| $H_3AsO_4 . Ba(OH)_2$ solution added drop by drop until the solution was neutral to phenolphthalein. Refluxed for four hours. | 51.43 | 37.71 | 2.04 |
| Excess $BaCl_2$ disodium arsenate solution added to boiling solution. | 51.82 | 36.68 | 2.12 |
| Impure dibarium arsenate dissolved in dilute HCl and reprecipitated by the slow addition of dilute ammonium hydroxide. | 51.32 | 38.20 | 2.01 |
| Disodium arsenate, dilute solution, saturated with dibarium arsenate in the cold, heated to boiling and filtered. | 51.71 | 38.68 | 2.00 |
| Calc. for $BaHAsO_4 . H_2O$. | 51.93 | 38.93 | 2.00 |

The last method was devised on the basis of the decrease in the solubility of $BaHAsO_4 . H_2O$ with an increase in temperature. The filtrate from the first solution deposited large crystals, .5 cm. long, having a common index of refraction = 1.635. This table illustrates the necessity of preventing the more basic compounds from precipitating from the solutions.

The methods previously described for the preparation of $Ba_3(AsO_4)_2$ proved to be unsatisfactory. Alkaline hydrolysis of $BaHAsO_4 . H_2O$, with $NH_4OH$, gave $BaNH_4AsO_4$ in some cases and but rarely gave $Ba_3(AsO_4)_2$[1]. It was hoped that this system would prove to be similar to a similar system of lead[2], but it proved to be quite different.

Dibarium arsenate, prepared by the sixth method given in Table II and containing 38.04% $As_2O_3$ and 51.60% BaO, was subjected to hydrolysis by $NH_4OH$ solutions. In order to determine whether ammonia entered the solid phases or not, preliminary hydrolytic experiments were made with solutions varying from 1 to .01 M. Examination of the solid phases, after careful washing with acetone, showed the absence of ammonia, the Nessler test was used. In the experiment as summarized in Table III one gram samples of the dibarium arsenate were treated with $CO_2$-free $NH_4OH$ (prepared by distillation in the presence of $Ba(OH)_2$), the arbitrary dilution being .0383 N.

[1] Salkowski: J. prakt. Chem., **104**, 143 (1868); Lefevre: Ann. Chim. Phys., **27**, 13 (1892).
[2] Smith and McDonnell: J. Am. Chem. Soc., **38**, 2366 (1916).

Referring to Table II one can see that the first additions of $NH_4OH$ resulted in a constant solution in equilibrium with $BaHAsO_4 . H_2O$ and $Ba_3(AsO_4)_2 . x\ H_2O$. The disappearance of the dibarium arsenate is shown by the breaks in curves; the lower curve is a rectangular hyperbola showing that hydrolysis of $Ba_3(AsO_4)_2$ does not take place. Analysis of the dried solid phases from several experiments supposed to contain the tribarium arsenate gave the following results: BaO, 66.60%; $As_2O_5$, 33.11%; calculated for $Ba_3(AsO_4)_2$; BaO, 66.67%; $As_2O_5$, 33.33%.

TABLE III

| Exp. no. | Cc. $NH_4OH$ used. | Grs. $As_2O_5$ removed. | Grs. $As_2O_5$ removed per liter. | Mol ratio in solid phase $BaO/As_2O_5$. |
|---|---|---|---|---|
| 1 | 40 | .0425 | 1.0613 | 2.25 |
| 2 | 50 | .0504 | 1.0084 | 2.30 |
| 3 | 60 | .0596 | 0.9936 | 2.37 |
| 4 | 80 | .0830 | 1.0369 | 2.55 |
| 5 | 90 | .0881 | 0.9788 | 2.59 |
| 6 | 100 | .1005 | 1.0050 | 2.71 |
| 7 | 120 | .1165 | 0.9713 | 2.86 |
| 8 | 130 | .1264 | 0.9722 | 2.98 |
| 9 | 140 | .1291 | 0.9225 | 3.01 |
| 10 | 150 | .1285 | 0.8569 | 3.00 |
| 11 | 170 | .1294 | 0.7612 | 3.01 |
| 12 | 200 | .1331 | 0.6657 | 3.04 |
| 13 | 210 | .1275 | 0.6075 | 3.00 |
| 14 | 300 | .1308 | 0.4360 | 3.02 |
| 15 | 400 | .1340 | 0.3350 | 3.03 |
| 16 | 440 | .1305 | 0.2966 | 3.00 |
| 17 | infinite | trace | trace | 3.00 |

Control field tests using commercial barium arsenate as a dust are now being carried on by the Southern Field Crops Investigation Laboratory of the Bureau of Entomology, the boll weevil (Anthonomus grandis Boh) being used as the experimental insect. Preliminary results show that its toxicity is as great as that obtained from commercial calcium arsenate, the poison used at the present time.

I wish to thank Dr. H. H. King of the college and Mr. C. M. Smith of the Bureau of Chemistry, Washington, D. C. for assistance given to me during the course of this research.

## Summary

The stable compounds in the acid division of the system BaO, $As_2O_5$, $H_2O$ at 30° are $BaH(AsO_4) . H_2O$, $BaH_4(AsO_4)_2 . 2H_2O$, and $3As_2O_5 . 5H_2O$.

Alkaline hydrolysis of $BaHAsO_4 . H_2O$ gave $Ba_3(AsO_4)_2 . x\ H_2O$. Methods for the preparation of other arsenates are described.

*Pasadena, California.*

# ANOMALOUS FLOCCULATION IN COLLOIDAL CLAYS AND SOILS

BY F. HARDY

## Introductory

Anomalous flocculation is the term applied by Comber[1] to denote the particular behavior of aqueous suspensions of colloidal clay towards lime. According to the isoelectric point theory, aqueous disperse systems of electronegative colloids should be stabilized, not flocculated, by small additions of alkali. Clay suspensions, however, are rapidly flocculated by calcium hydroxide, though markedly stabilized by hydroxides of alkali metals and ammonium. By a series of critical experiments with soils, Comber was able to demonstrate that fine silt belongs to the suspensoid class of colloids, whilst clay, though not necessarily composed entirely of emulsoid matter, consists of particles so heavily protected by emulsoid matter, that it behaves as an emulsoid colloid[2].

In order to explain anomalous flocculation, Comber has suggested that a chemical interaction takes place between the emulsoid material and its flocculant[3]. The fact that silicic acid in aqueous dispersion reacts with calcium hydroxide, or with neutral calcium salt in the presence of soluble alkali hydroxide, to form a flocculant precipitate of calcium silicate, is adduced as evidence that a similar reaction may account for the anomalous flocculation of siliceous clay by lime. Hydroxyl-ion peptizes the emulsoid protection of the clay particles; calcium-ion unites with, or is "adsorbed" by the highly dispersed silica; the emulsoid loses its intimate relationship with the dispersion medium, and the particles settle, entrained in the voluminous coagulum.

Anomalous flocculation by lime is apparently not confined to emulsoid clay suspensions. Comber's further investigations[4] have shown that aqueous suspensions of aluminium phosphate, ferric phosphate, basic slag, rock phosphate and powdered bones display similar anomality, provided they are initially free from uncombined lime. In certain instances, ignition does not impair the reactivity of the substance sufficiently to prevent its exhibiting anomalous behaviour in flocculation experiments. It therefore appears that emulsoid soil clay possesses some constitutional feature in common with many phosphatic materials.

Recently the writer has extended the scope of Comber's suggestive researches by demonstrating that certain tropical lateritic soils, examined by the methods elaborated by Comber, exhibit marked anomalous flocculation by lime. The lateritic soils studied have been fully described elsewhere[5]. They were two in number. The first is an orange-red subsoil occurring in the

[1] J. Agr. Sci. 10, 425 (1920); Trans. Faraday Soc., 17, 349 (1922).
[2] J. Agr. Sci. 10, 426-430 (1920).
[3] J. Agr. Sci. 11, 450 (1921); Trans. Faraday Soc., 17, 349 (1922).
[4] J. Agr. Sci. 12, 372 (1922).
[5] F. Hardy: J. Agr. Sci 13, 243, 340 (1923).

upland regions of Barbados. It is a residual clay derived from coral limestone containing andesitic volcanic ash. The second is a dark-red subsoil occurring in the rainy mountainous regions of Dominica, where andesite has been intensely weathered. Both soils are acidic (pH 6.7 and pH 5.9 in 1 to 3 aqueous suspension); they contain traces only of organic matter and lime, but are rich in alumina and ferric oxide. They also contain appreciable amounts of silica. Their aqueous suspensions in all concentrations settle rapidly; they are stabilized markedly, however, by the addition of relatively small but different amounts of soluble alkali, such as sodium hydroxide and sodium carbonate. In the field, the soils, in common with lateritic soils in general, occur in a highly aggregated condition, so that water percolates readily through them.

The chemical constitution of the colloidal matter of clays and soils is uncertain. Conventional chemical analysis merely expresses the fact that inorganic soil colloids are mainly composed of varying proportions of water, silica, alumina and ferric oxide. Whether these components are simply mixed, or are combined to form colloidal complexes or true compounds, cannot be decided by precise experimental methods. Nevertheless, there is sufficient evidence to prove that many highly siliceous clays and soils contain free hydrous silica, and that many laterites contain free hydrous alumina and free hydrous ferric oxide. A comparison of the physico-chemical features and constitution of these individual substances may therefore lead to a clearer understanding of the properties and behaviour of clays and soils, and in particular to a more exact elucidation of their flocculation phenomena.

## I. Hydrous Alumina

Alumina, in aqueous dispersion, behaves as a weak amphoteric electrolyte. The basic and acidic dissociation equations are usually written thus[1]:— $Al(OH)_3 \longrightarrow AlO_3''' + 3H^{\cdot}$ and $Al(OH)_3 \longrightarrow Al^{\cdots} + 3(OH)'$. The isoelectric point of alumina has been determined by von Euler and Nilsson[2], who assign to it the pH value 6.50. This implies that the basic and acidic dissociation constants are numerically equal[3] when the reaction of the aqueous dispersion medium is pH 6.50.

The aluminates are generally regarded as salts of the tribasic acid, $H_3AlO_3$. Heyrovsky[4] suggests, however, that they are more probably salts of the monobasic acid, $HAl(OH)_4$, or $Al(OH)_3.H_2O$, and that they are really "additive compounds". Sodium aluminate, for example, according to this authority, should be represented by the formula $Al(OH)_3.NaOH$.

The composition and properties of several hydrogels of alumina, prepared under different conditions, have recently been investigated by Willstätter and Kraut[5], who obtained evidence that the different dry hydrogels are true

[1] Lewis: "A System of Physical Chemistry", 1, 26 (1921).
[2] Ber. 57, 217; Chem. Abs. 18, 1254 (1924).
[3] Clark: "The Determination of Hydrogen-ions", 25 (1920).
[4] J. Chem. Soc., 117, 1013 (1920).
[5] Ber. 56, 149, 1117 (1923); 57, 58 (1924).

hydrates, containing various molecular proportions of water, and exhibiting diminishing basic and acidic properties with diminishing degree of hydration. Weiser[1] has adduced corroborative evidence of the fact that the reactivity of hydrogels of alumina depends on the degree of hydration, but states that only one true hydrate, namely the trihydrate of alumina, exists. Pascal[2], basing his conclusions on the results of certain magnetometric experiments, maintains that neither the hydrates nor the hydrogels of alumina are to be regarded as aluminium hydroxide, but as various hydrous aluminium oxides, and that, even in solutions of aluminates, aluminium occurs as colloidal oxide. This view is upheld by earlier results obtained by Chatterji and Dhar[3], who found that the electrical conductivity of a solution of sodium hydroxide is not appreciably altered when hydrous alumina is dissolved in it, proving that true chemical combination does not occur, but that the alumina is merely peptized by the alkali. The aluminates thus appear to be adsorption complexes rather than the additive compounds of Heyrovsky.

In accordance with these findings, it would perhaps be more exact to express, *in its simplest form*, the dissociation of hydrous alumina thus: $Al_2O_3 . 3H_2O \longrightarrow Al_2O_3 . 3OH' + 3H^{\cdot}$, and $Al_2O_3 . 3H_2O \longrightarrow Al_2O_3 . 3H^{\cdot} + 3(OH)' \longrightarrow 2Al^{\cdot\cdot\cdot} + 3(OH)' + 3(OH)'$. Since the chemical activity of hydrous alumina dispersed in water appears to be mainly decided by the degree of colloidal hydration, it follows that the primary cause of reactivity is the ionic dissociation of molecules of water that are held at the surface of the solid phase. The relationship between these bound water molecules and the molecules or atoms comprizing the rest of the colloid is obscure. Evidently few analyses of the structure of hydrous inorganic compounds by X-ray methods have so far been attempted[4]. It appears probable, however, that the elements of water are held by residual valency forces of atoms that form the surface layer of the crystal lattices composing the colloid particles[5]. Irregular orientation of these atoms, resulting from the action of agents of disintegration[6], which produce higher degrees of dispersion at the solid crystal surface, may conceivably increase the hydration capacity, and bring about in the particles of the dispersed phase[7], "a gradual transition from the solid nucleus through stages of gel material to the water". Conversely, alumina hydrogels are known to undergo spontaneous change on standing, becoming gradually crystalline, but not necessarily losing all their water[8]. This process, usually termed "ageing", appears to be mainly a manifestation of atomic rearrangement, whereby the

[1] J. Phys. Chem. **24**, 505 (1920).
[2] Compt. rend. **178**, 481 (1924).
[3] Discussion Rept. "Physics and Chemistry of Colloids", Dept. Sci. Indus. Res. London, 1921, 123.
[4] Bragg: "X-rays and Crystal Structure", 303 (1924).
[5] Ruff: Kolloid-Z. **30**, 356 (1922); Mukherjee: Discussion Rept. "Physics and Chemistry of Colloids", 1921, 103. Bassett: "Fourth Report on Colloid Chemistry", 8 (1922).
[6] Donnan: Presidential Address. Sect. B, British Ass. Adv. Sci., (1923); J. Soc. Chem. Ind. **42**, 900 (1923); Harrison: Discussion Rept. "Physics and Chemistry of Colloids", 1921, 116.
[7] Comber: J. Agr. Sci. **11**, 450 (1921).
[8] Fricke and Wever: Z. anorg. Chem. **136**, 321 (1924).

elements of water come to occupy a more stable spacial relationship to the other atoms of the system.

We are thus led to regard a particle of hydrous alumina, suspended in an aqueous medium, as a complex colloidal electrolyte, whose reactivity or strength depends on the degree of hydration at the boundary surface. The total area of surface, and consequently the hydration capacity, will depend on the degree of dispersion, or, if we assume that the hydrogel possesses a reticulate structure,[1] on the conformation and porousness of the hydrogel skeleton.

Recent research on emulsoid colloids such as soaps[2], proteins[3], and starches[4], has revealed the existence of complex colloidal ions (the ionic micelles of McBain), which originate through the electrolytic dissociation of neutral colloidal systems dispersed in aqueous media. Such ions, in certain instances, may apparently occur in association with un-ionized colloid. At the isoelectric point, the colloid exists as a non-ionogenic substance. When the hydrogen-ion concentration of the medium is decreased, the colloid behaves as an acid; when increased, it behaves as a base.

In the case of hydrous alumina, whose isoelectric point is pH 6.5, the colloid, when placed in pure neutral water (pH 7.0), should therefore exhibit weak acidic properties, because ionization now tends to proceed in the direction of greater production of hydrogen-ion and complex aluminate-ion. Further increase in hydroxyl-ion concentration, brought about for example, by adding a soluble hydroxide, should enhance this tendency. If the added soluble hydroxide be calcium hydroxide, calcium-ion may simultaneously combine with aluminate-ion to form a calcium-aluminate complex. The electric charges on the colloidal ion will consequently be more or less neutralized[5]; the system will be "weighted"; its stability will be reduced; its relationship to the enveloping liquid will be altered through diminished hydration, and precipitation will tend to occur. By this sequence of events is the term anomalous flocculation defined. Should the added hydroxide be the hydroxide of an alkali metal, accompanied or followed by a neutral calcium salt, calcium-ion may combine in preference to alkali metal ion, because of its lower electroaffinity.[6]

The final result nevertheless, in effect, should be the same. If neutral calcium salt be added before alkali hydroxide, the reaction may be impeded, because the first-formed calcium-aluminate complex may conceivably hinder the further and continued dissociation of the colloidal electrolyte.

---

[1] Wilsdon: Mem. Dept. Agr. India, Agr. Res. Inst. Pusa, Chem. Ser. 6 (1921); F. Hardy: J. Agr. Sci. 13, 243 (1923).

[2] McBain: J. Am. Chem. Soc., 43, 426 (1920); "Third Report on Colloid Chemistry", 2 (1920); J. Soc. Chem. Ind. 42, 615 (1923).

[3] Pauli: "Colloid Chemistry of the Proteins" (1922); Loeb: "Proteins and the Theory of Colloidal Behavior" (1922); Discussion Rept. "Physics and Chemistry of Colloids", 153 (1921).

[4] Samec: ref-Pauli: Discussion Rept. "Physics and Chemistry of Colloids", 1921, 16.

[5] Donnan has pointed out that coagulation may occur as soon as the potential difference at the interface of a suspended colloid is brought within a certain *critical zone* which may extend considerably on either side of the isoelectric point, (Presidential Address, Sect. B, British Ass. Adv. Sci. (1923); J. Soc. Chem. Ind. 42, 898 (1923).

[6] Bassett: "Fourth Report on Colloid Chemistry", 9 (1922); Mukherjee: Discussion Rept. "Physics and Chemistry of Colloids", 1921, 111.

On the acid side of the isoelectric point, complex aluminous cations may combine with acid anions to form salts. According to Pauli[1], a series of oxysalts of aluminium, such as $Al(OH)Cl_2$, $Al(OH)_2Cl$ and $2Al(OH)_3 . Al(OH)_2Cl$, is formed when hydrous alumina is peptized by acids. If the process is further continued, a hydrosol results. Pauli regards this sol as an aqueous suspension of a mixture of oxysalts, ionizing to give a complex cation, together with acid anions, as for example, $3Al(OH)_3 . Al(OH^+)_2/CH_3 . COO^-$, but so far his conclusions have not been experimentally substantiated. In the parallel case of ferric oxide sols, Smith and Giesy[2] have recently shown by the use of the oxygen electrode, that oxysalts have no real existence in such sols.

Most authorities[3] prefer to regard the sols of hydrous metallic oxides as composed of particles of oxide suspended in an aqueous phase, and adsorbing greater or lesser amounts of molecules or ions (water, metallic chloride, hydrogen chloride, hydrogen-ion, chloride-ion), depending on their nature and concentration. This view is based on the widely accepted physical theory of adsorption, which Mukherjee[4], has attempted to place on a fundamental basis by suggesting that adsorption may be an actual attachment of ions to a colloidal surface by chemical forces due to residual valences. Whilst it is highly probable that direct chemical combination often occurs at surfaces, it seems more reasonable to assume in the case of a hydrated colloidal electrolyte such as hydrous alumina, that peptization by acids is the result of the enhancement of its acidic dissociation through the effect of hydrogen-ion, which, when introduced in excess, combines with hydroxyl-ion, produced by the ionizing colloid, to form non-ionizing water molecules. The colloid is thereby removed further from its isoelectric point, the potential difference between its surface and the dispersion medium is increased, and the system becomes increasingly stable. The concurrent effect of the anion of the added acid is probably mainly decided by its specific nature and by its relative electroaffinity. Thus, in particular, if the anion be phosphate-ion, silicate-ion, or aluminosilicate-ion, insoluble complexes may result, and precipitation may occur. Each of these particular cases is entirely analogous to the anomalous flocculation of the negatively-charged colloidal aluminous-ion by calcium-ion, which has already been discussed. If the anion have other identity, its preferential combination and consequent precipitating power, may depend on its relative electroaffinity. Only in dispersions of high acidity may simple aluminium salts, such as the metallic chloride, be produced, giving aluminium-ion. Thus McGeorge[5] was able to demonstrate that free aluminium-ion is present in extracts of acid soils only when the reaction is more acidic than that represented by pH 5.8.

Finally, before the flocculation of *positively* charged ions of alumina, contained in sols or their transition systems, can be effected by the addition of

---

[1] Discussion Rept. "Physics and Chemistry of Colloids", 1921, 14; Adolf and Pauli: Kolloid-Z. 29, 281 (1921).

[2] J. Am. Pharm. Ass. 12, 855 (1923).

[3] Bancroft: J. Phys. Chem. 19, 232 (1915); Browne: J. Am. Chem. Soc., 45, 297 (1923).

[4] Discussion Rept. "Physics and Chemistry of Colloids", 1921, 103.

[5] Soil Science, 18, 1 (1924).

lime, sufficient flocculant must be added, not only to change the reaction of the dispersion medium to the pH value representing the approximate isoelectric point, but also to reverse acidic dissociation into basic dissociation. This necessitates the satisfying of a definite "lime requirement", the magnitude of which will depend mainly on the initial acidity of the system, on the presence of ions already adsorbed, and on the extent of its active surface, that is, on the degree of dispersion and hydration. That such conditions control the successful liming of soils, is well known to soil investigators.

### II. Hydrous Ferric Oxide

Like hydrous alumina, hydrous ferric oxide is an amphoteric electrolyte. Whilst its basic properties are prominent, its acidic properties are not so pronounced as those of alumina[1]. The "ferrites" are less easily prepared than their analogues, the "aluminates". As far as the writer is aware, the isoelectric point of hydrous ferric oxide has not yet been determined. The conditions for precipitation of hydrous ferric oxide and of hydrous alumina by alkali, however, are almost identical. Thus, Carr and Brewer[2] found that, in the one case, precipitation commences at pH 5.5 and is complete at pH 8.6, and in the other, at pH 5.5 and pH 7.9. This suggests that the isoelectric points of the two ampholytes are approximately the same.

The state of occurrence of water in hydrous ferric oxide appears to be similar to that in hydrous alumina[3], but only one definite hydrate of ferric oxide has so far been described[4]. This is found in crystalline form as the mineral goethite, $Fe_2O_3 . H_2O$[5], whose amorphous form is limonite[6], and whose anhydrous form is haematite. Other hydrated ferric oxide minerals, according to Weiser, are probably hydrous oxides, containing variable and indefinite amounts of water[7]. Ferric oxide hydrogels possess the characteristic property of instability, being easily dehydrated to the monohydrate, which exhibits no tendency to reabsorb water[8]. This property, which may be termed rapid ageing, finds expression in the well-known method for the quantitative separation of iron from aluminium, in which the hydrogels of the oxides are first precipitated and then boiled with excess of caustic alkali. Alumina hydrogel is thereby peptized, whereas ferric oxide hydrogel is dehydrated and remains in suspension[9].

The yellow, red, and brown colours of hydrous ferric oxide are believed to be due to diminishing degrees of hydration[10]. Weiser[11], however, was able to

[1] Caven and Lander: "Systematic Inorganic Chemistry", 316 (1921).

[2] Ind. Eng. Chem. 15, 634 (1923); Hatfield (16, 233 (1924)) gives narrower limits for the stability of the solid phase of hydrous alumina, namely pH 5.7 and pH 7.3.

[3] Weiser: J. Phys. Chem. 24, 277 (1920).

[4] Posnjak and Merwin: Am. J. Sci. 47, 311 (1917).

[5] Spencer: Min. Mag. 18, 339 (1919).

[6] Fischer: abstracted in J. Chem. Soc. 96, 241 (1909).

[7] J. Phys. Chem. 24, 277 (1920).

[8] Zsigmondy-Spear: "Chemistry of Colloids", 169 (1917).

[9] Bassett: "Fourth Report on Colloid Chemistry", 18 (1922).

[10] Fischer: loc. cit.

[11] See also Bancroft: "Applied Colloid Chemistry", 205 (1921); Bradfield: J. Am. Chem. Soc., 45, 965 (1923).

prepare transition forms of the substance, exhibiting colours ranging from yellow to red, by merely increasing the size of the particles, and Yoe[1] found that red coloured forms could be produced from finely divided yellow particles by agglomeration. There is evidently some close relationship between colour and degree of colloidality in the various types of hydrous ferric oxide, and this should be reflected in the physical and chemical properties of laterites.

Because of their amphoterism, and the close resemblance between hydrous ferric oxide and hydrous alumina as regards the state of occurrence of water in the hydrogel, the general properties and structure of disperse systems of these emulsoid colloids are markedly similar. Thus, the much-studied ferric oxide sols, in which the dispersed phase is positively charged, conform closely in character to the sols of alumina, and have recently been investigated from similar standpoints[2]. The ampholytic nature of hydrous ferric oxide has been established beyond doubt by the researches of Fischer[3], Powis[4] and Dhar and Sen[5], who have demonstrated that a reversal of sign of charge can be effected in disperse systems of this colloid by simply reversing the reaction of the dispersion medium. It therefore follows that the particular mechanism which has tentatively been propounded to explain anomalous flocculation of hydrous alumina, might equally well apply to the anomalous flocculation of hydrous ferric oxide. In actuality, the process is certainly not so simple as a consideration of the ideal cases suggests, for subsidiary factors, introduced by the presence of extraneous salts and colloidal matter, doubtless modify the sequence of changes that has been described. The precise manner in which such subsidiary factors may affect the flocculation of disperse systems of hydrous ferric oxide, (and of hydrous alumina), has received considerable attention by recent investigators[6]. Although mainly viewed from other aspects, the results obtained are susceptible of explanation in terms of ordinary ionic interaction and mass influence, regard being paid to the relative electroaffinities of the reacting units[7]. In parallel cases, certain irregular results have been shown to be due to an actual entrapping of solutions of unionized electrolytes in the intermicellar spaces of the colloid[8].

### III. Hydrous Silica

Hydrous silica differs chemically from hydrous alumina and hydrous ferric oxide in that its acidic properties are much more pronounced than theirs, whilst its basic properties, in most of its reactions, are in entire abeyance.

---

[1] J. Phys. Chem. 25, 196 (1921).

[2] Malfitano: Z. physik. Chem; 68, 232 (1909); Neidle: J. Am. Chem. Soc., 39, 2334 (1917); Pauli and Matula: Kolloid-Z. 21, 49 (1917); Pauli: 28, 49 (1921); Weiser: J. Phys. Chem. 24, 277 (1920); Browne: J. Am. Chem. Soc., 45, 297 (1923).

[3] Biochem. Z. 27, 223 (1910).

[4] J. Chem. Soc., 107, 818 (1915).

[5] J. Phys. Chem. 27, 376 (1923); Ganguly and Dhar: 28, 313 (1924).

[6] Neidle, Pauli, Dhar, Browne: loc. cit.; Weiser et al.: J. Phys. Chem. 23, 205 (1919); 24, 30, 630 (1920); 25, 399 (1921); 26, 665 (1922).

[7] Bassett: "Fourth Report on Colloid Chemistry", 9 (1922).

[8] Wintgen: Z. physik. Chem. 103, 238 (1922).

Hence hydrous silica is usually not regarded as an amphoteric electrolyte, but as a true acid. Nevertheless, the similarity that exists between compounds of silicon and corresponding compounds of germanium, tin and lead, (especially the halides[1]), suggests that silicon may be considered as a basigenic element of very low electroaffinity. Furthermore, there is some direct evidence in support of the view that hydrous silica is an ampholyte possessing an isoelectric point well on the acid side of neutrality. Thus Lösenbeck[2] has demonstrated by cataphoretic methods that the addition of hydrochloric acid to a silica sol brings about a gradual decrease in the magnitude of the negative charge on the silica particles, and that eventually a stage which appears to be coincident with the isoelectric point of the colloid, is reached. Further additions of hydrochloric acid are stated to cause the particles to assume a positive charge. The pH value of the isoelectric point is apparently not given by Lösenbeck. Schwarz[3] found no evidence, however, of the formation of a definite chemical compound between colloidal silica and hydrochloric acid, but Werner[4] noted that acids exert a powerful peptizing effect on silica hydrogel.

Recently Michaelis[5] has suggested that colloidal electrolytes might be classified into "ampholytoids", "acidoids" and "basoids". He places hydrous alumina and hydrous ferric oxide in the first category, hydrous silica in the second, but can find no examples of the third class If we regard amphoterism as a property possessed in different degree by certain colloidal electrolytes, and manifesting itself in different pH values for their isoelectric points, there would appear to be no particular advantage in this classification, at least insofar as hydrous oxides are concerned.

The state of occurrence of water in hydrous silica, as in the case of the other hydrogels considered, has been the subject of much experimentation and speculation. The characteristic changes in moisture content, vapour pressure, volume and physical properties which silica hydrogel undergoes when dried, are too well known to require repetition[6]. They may perhaps most clearly be explained on the assumption that silica hydrogel possesses a reticulate structure[7], which, when saturated, contains water in two phases, the one adsorbed at the surface of the material comprizing the gel framework; the other filling the intermicellar spaces.

It is generally conceded that no true hydrates of silica exist[8]. Nevertheless, many authorities favour the view that definite silicic acids, such as orthosilicic acid ($H_4SiO_4$), are present in silica hydrosols and hydrogels[9]. The solubility

[1] Huddleston and Bassett: J. Chem. Soc., 119, 403 (1921).
[2] Kolloidchem. Beihefte, 16, 27 (1922).
[3] Kolloid-Z. 34, 23 (1924).
[4] J. Am. Pharm. Ass. 17, 501 (1920).
[5] Kolloid-Z. 31, 256 (1922).
[6] Zsigmondy-Spear: "Chemistry of Colloids", 137-150 (1917).
[7] Van Bemmelen, Zsigmondy, Bütschli, Bachmann, Anderson and Patrick, Williams: J. Soc. Chem. Ind. 43, 97 T (1924).
[8] Hutchinson: Ann. Rept. Chem. Soc. London, 9, 259 (1922); LeChatelier: Compt. rend. 147, 660 (1908).
[9] Norton and Roth: J. Am. Chem. Soc. 19, 832 (1897); Schwartz and Sonard: Ber. 53, 1 (1920).

of silica in water has been measured[1]; the dissociation constants estimated[2]. and the reaction of a silica sol freed from electrolytes has been examined[3], and found to be acidic (pH 6.5).

Other authorities deny the existence of definite chemical compounds of silica and water, and prefer to regard all associations between them as adsorption complexes[4]. The question, however, appears to be mainly one of nomenclature. As in the case of other hydrous oxides, hydrous silica may contain water molecules united with silica in stoichiometric proportions through the agency of "chemical" adsorption forces. These complexes may exhibit acidic properties because of the ability of certain of the combined water molecules to ionize. The splitting off of small units of the adsorption complex (superficial dispersion) may account for the slight solubility of the substance in water.

The reactivity of hydrogels of silica is believed to depend mainly on the degree of hydration. Thus Tschermak, many years ago, demonstrated that the various silicic acids decolourize solutions of methylene blue to an extent varying directly with the number of hydroxyl groups present[5]. Furthermore, it has been proved that the reactivity of quartz is increased by long grinding with water[6]. On the other hand, silica hydrogels rapidly age into hydrophane[7] or into quartz[8].

These many considerations indicate that hydrous silica conforms closely to the type of emulsoid colloid exemplified by hydrous alumina and hydrous ferric oxide. It may therefore also be classified as a colloidal ampholytic hydrous oxide, differing from the others chiefly in that its isoelectric point is of very much lower pH value than theirs.

According to Comber, hydrous silica probably occurs in siliceous soils and clays as a gelatinous matrix binding together discrete mineral grains to form separate compound particles. The grains themselves may exhibit zonal differentiation as regards degree of weathering and hydration; their cores are presumably composed of anhydrous quartz or of siliceous minerals such as felspar. In aqueous suspension, the compound particles may behave as electronegative colloidal ions, because they will assume the properties of the emulsoid material that coats and protects them.

## IV. Hydrous Aluminosilicates and Ferrosilicates

During the processes of weathering, the mineral fragments of soils are hydrolysed and hydrated; the soluble bases that are liberated are simultan-

---

[1] Huddleston and Bassett: J. Chem. Soc., 19, 832 (1897); Joseph and Hancock: 123, 2022 (1923).

[2] Grünhut: Chem. Abs. 8, 3829 (1914).

[3] Bradfield: J. Am. Chem. Soc., 44, 965 (1922).

[4] Lenher: J. Am. Chem. Soc., 43, 391 (1921); Pascal: Compt. rend. 175, 814 (1922).

[5] Z. physik. Chem. 53, 349 (1905).

[6] Bancroft: "Applied Colloid Chemistry", 97, 179 (1921); Lenher: J. Am. Chem. Soc. 43, 391 (1921).

[7] Bachmann: Chem. Abs. 12, 1610 (1918); Schwarz and Stöwener: Kolloidchem. Beihefte, 19, 171 (1924).

[8] Zsigmondy-Spear: "Chemistry of Colloids", 137 (1917).

eously removed by leaching. Hydrous aluminosilicates and hydrous ferrosilicates are frequently present in the residues. A conspicuous end-product of weathering is amorphous kaolinite (clayite, lithomarge, halloysite), which has long been considered by some authorities to be an aluminosilicic acid, forming salts of zeolitic type[1]. The researches of Gedroiz[2] and others suggest, however that zeolites are adsorption compounds, rather than true salts, for they exhibit the phenomena of basic exchange in marked degree. Highly leached clays, such as laterites, contain only traces of alkali and alkaline earth metals, and in extreme cases, appear to consist almost entirely of hydrous alumina and hydrous ferric oxide in a more or less "aged" condition. The majority of lateritic clays also contain silica.

Certain investigators have recently suggested that aluminosiliceous clays are colloidal ampholytes, and, to support this view, have adduced experimental evidence, based mainly on measurements of hygroscopicity and of settling rates of clay suspensions at different hydrogen-ion concentrations[3]. From their results, values for the isoelectric points as diverse as pH 9.7 (brick clay, Arrhenius) and pH 2.78 (ball clay, Hall), have been derived. Although the validity of conclusions based on such experiments may be questioned, it is now at least generally admitted that hydrous aluminosilicates, (and hydrous ferrosilicates), react as true acids when dispersed in water, and that acidity in mineral soils is mainly due to their presence[4]. If hydrous aluminosilicates be ampholytes, possessing basigenic as well as acidic properties, their aqueous suspensions ought to be increasingly stabilized by strong acids, added in sufficient amount to lower the pH value of the system to the acid side of the isoelectric point or region. Durham's discovery (1874), recorded by Wolkoff[5], is therefore of significance in this connection; he found that "although it requires a very small amount of sulphuric acid to flocculate a suspension of white clay (? kaolin), on further additions of sulphuric acid he reached a point when the suspension did not clarify for a long time". Possibly also, certain results obtained by Bradfield, who examined the relation of hydrogen-ion concentration to the flocculation of a colloidal clay[6], may partly be interpreted in the light of these considerations. The whole question of the possible amphoterism of hydrous aluminosilicates might profitably be re-examined with the aid of physico-chemical instruments of high precision.

Certain aluminosiliceous clays are probably composed mainly of adsorption complexes of hydrous alumina and hydrous silica, rather than true hydrous aluminosilicates in which alumina and silica are present in molecular or atomic combination. It has already been pointed out that hydrous alumina, when

[1] Mellor and Holdcroft: Trans. Eng. Ceramic Soc. 10, 10 (1911); Scurti: J. Chem. Soc. 124 1, 1047 (1923).

[2] See Joffe and McLean: Soil Science, 18, 1 (1924).

[3] Arrhenius: J. Am. Chem. Soc. 44, 521 (1922); Hall: J. Am. Ceramic Soc. 6, 989 (1923).

[4] Crowther: Trans. Faraday Soc., 17, 317 (1922); Page: Ann. Rept. Chem. Soc. London, 9, 19 (1922); 10, 20 (1923); Bradfield: J. Am. Chem. Soc. 45, 2667 (1923).

[5] Soil Science, 1, 585 (1916).

[6] J. Am. Chem. Soc. 45, 1243 (1923).

dispersed in an aqueous medium of pH value less than that representing the isoelectric point of the colloid, may suffer "anomalous flocculation" by silicate-ion. Mutual precipitation of hydrous alumina and hydrous silica ought therefore, in theory, to occur in an acid medium of pH value lying somewhere between the pH values representing their isoelectric points, and would be complete if the colloids were present in equivalent amount [1]. Under such circumstances, the one colloid occurs as a complex cation, the other, as a complex anion. Similarly, mutual precipitation may occur, under appropriate reaction conditions, in dispersions containing hydrous ferric oxide and hydrous silica, and, indeed, in dispersions containing any assortment of these various hydrous oxides and hydrous aluminosilicates and ferrosilicates, granting that each of these colloidal substances possesses amphoteric properties. The facts that most lateritic clays and soils containing alumina, ferric oxide and silica occur in a highly aggregated condition in the field, and yield aqueous dispersions that rapidly settle, even in the presence of acid in excess, lend support to these conclusions.

It ought to be possible to test the various suggestions made in the foregoing discussions by a detailed examination of selected soil and clay samples. In particular, laterites seem to offer peculiar advantages for study, and their flocculation phenomena are worthy of further investigation.

## Note on Phosphatic Compounds

Comber's discovery that certain phosphatic materials exhibit anomalous flocculation in aqueous suspension, indicates that phosphates may exist as colloidal electrolytes, and may perhaps be amphoteric. The researches of Bassett[2] demonstrate that rock phosphate and bone consist mainly of either true compounds or adsorption complexes of tricalcium phosphate, calcium hydroxide and water. The water, at least, appears to be adsorbed, and this suggests that the phosphatic compounds may be of the hydrous oxide type, although some other relationship may account for their peculiar properties. Meig's observation that calcium phosphate can form a semi-permeable membrane, is ascribed to its hydrated colloidal nature[3].

Phosphates present peculiar features as components of soil and as soil amendments. They appear to be particularly strongly adsorbed, and to occur in a state of low availability in soils of lateritic type[4]. This is probably due to the formation of insoluble complexes between phosphate-ion (whether crystalloidal or colloidal), and the cations of hydrous alumina and ferric oxide, under suitable conditions of acidity. The recent researches of Gordon and Starkey[5], who found that colloidal alumina and ferric oxide possess a very much greater adsorptive power than colloidal silica for phosphate, furnish

[1] Splichal: Chem. Abs. 15, 3012 (1921); Smith: J. Am. Chem. Soc. 42, 460 (1920).
[2] J. Chem. Soc. 111, 620 (1917).
[3] Am. J. Physiol. 38, 465 (1915).
[4] McGeorge: Agr. Exp. Sta. Hawaii, Bull. No. 41 (1916).
[5] Soil Science, 14, 1, 449 (1922); Lichtenwalner, Flenner and Gordon: 16, 157 (1923).

direct evidence of this. In many instances, the beneficial effect of phosphatic manures may actually be due to their flocculating action on those colloids, and may be of considerable significance in the amelioration of tropical laterites[1].

## Summary

1. The flocculation phenomena of lateritic clays and soils are discussed on the basis of Comber's theory, which ascribes the anomalous flocculation of clay by lime to the formation of insoluble colloidal complexes.

2. Reasons are presented in support of the view that hydrous alumina and hydrous ferric oxide, which probably occur in laterites, are colloidal ampholytes, possessing isoelectric points not far removed from neutrality. On this assumption, the mechanism of their anomalous flocculation by lime, and by certain anions, such as silicate-ion and phosphate-ion, may satisfactorily be explained.

3. An attempt is made to extend the theory so as to embrace hydrous silica and hydrous aluminosilicates and hydrous ferrosilicates, and it is submitted that these colloids also may be regarded as ampholytes.

4. Mutual precipitation of colloidal ions is discussed in its relation to flocculation in certain soils.

The writer wishes to express indebtedness to his colleague, Mr. P. E. Turner, for many helpful suggestions.

*Imperial College of Tropical Agriculture*
*Trinidad, B. W. I*
*December 24, 1924.*

[1] Howard and Howard: J. Agr. India, 18 II, 148 (1923); Iyengar: J. Mysore Agr. Exp. Union, Bangalore, 4, No. 3 (1923).

# THE ULTRAVIOLET ABSORPTION SPECTRA OF AQUEOUS SOLUTIONS OF SULPHUR DIOXIDE AND SOME OF ITS DERIVATIVES

BY FREDERICK H. GETMAN

In a paper treating of the relation between the absorption spectra of acids and their salts, Wright[1] was the first to direct attention to the fact that aqueous solutions of sulphur dioxide exhibit a well-defined absorption band in the neighborhood of $\lambda = 276\,\mu\mu$. Notwithstanding the marked absorption shown by solutions of sulphurous acid, the neutral salt, $Na_2SO_3$, was found to be diactinic. In commenting on this fact, Wright suggested that, in view of the doubtful constitution of sulphurous acid, further investigation of the behavior of these substances toward ultraviolet radiation would doubtless prove of interest.

At the time of publication of Wright's paper, the subject of the ultraviolet absorption of solutions of sulphur dioxide and various sulphites was being studied by Garrett[2] and also by Schaeffer, Niggemann and Koehler[3]. Garrett measured the extinction coefficients of $H_2SO_3$, $RbHSO_3$, $KHSO_3$, $NaHSO_3$, $(NH_4)_2SO_3$, $K_2S_2O_5$, $Na_2S_2O_5$, $CH_3 \cdot C(OH)(SO_3Na) \cdot CH_3$, $NaKSO_3$, $Na_2SO_3$, $C_2H_5 \cdot SO_2 \cdot O \cdot C_2H_5$, and $SO(OC_2H_5)_2$, employing a large Hilger quartz spectrograph in conjunction with a rotating sector photometer. The extinction curve for the acid was well-defined and easily reproducible, whereas with the acid sulphites the absorption was found to increase with time, attaining a maximum value in four or five weeks. This behavior was ascribed to the influence of light, since freshly prepared solutions, and solutions which had been kept in the dark, failed to show selective absorption. Metabisulphites were found to behave similarly to the acid sulphites. The normal sulphites of sodium and potassium, as well as the mixed sulphites of these metals, the symmetrical and unsymmetrical diethyl sulphites and acetone sodium hydrogen sulphite failed to exhibit selective absorption. From these facts the author decided that no conclusive evidence as to the constitution of the sulphites can be derived from the study of their absorption spectra. He attributed the absorbing power of sulphurous acid to hydrated sulphur dioxide, $SO_2 . nH_2O$, where $n$ is indeterminate. Garrett summarized his conclusions by means of the following equations:—

(1) $Na_2S_2O_5 + H_2O = 2NaHSO_3$, (reaction in solution)

(2) $NaHSO_3 + NaHSO_3 = Na_2SO_3 + H_2SO_3$, (light reaction)

(3) $H_2SO_3 = SO_2 \cdot nH_2O$, (reaction in solution)

The relative amounts of hydrated sulphur dioxide present in equally concentrated solutions of the various acid sulphites were calculated and these quantities were shown to increase with increasing strength of the base, or, in

[1] Wright: J. Chem. Soc., 105, 669 (1914).
[2] Garrett: J. Chem. Soc., 107, 1324 (1915).
[3] Schaeffer, Niggemann and Koehler: Z. Elektrochem., 21, 181 (1915).

other words, the equilibrium represented by equation (2) shifts toward the right as the strength of the base increases.

Schaeffer and his associates studied the ultraviolet absorption of sulphur dioxide, sulphurous acid and several salts and esters of the latter by means of the familiar Hartley-Baly method. A comparison of the spectrum of a solution of sulphur dioxide in water with that of sodium sulphite indicated that the equilibrium in the reaction, $SO_2 + H_2O \rightleftarrows H_2SO_3$, lies toward the left side of the equation. On neutralizing a solution of sulphur dioxide with sodium hydroxide, the character of the spectrum was found to change from selective to total absorption in the ultraviolet. An excess of sodium hydroxide was found to exert little or no effect on the degree of absorption, which fact led the authors to conclude that sodium sulphite and its ions possess the same absorptive properties. Sodium bisulphite, prepared by adding the theoretical amount of sodium hydroxide to sulphurous acid, was found to exhibit a weak absorption in the ultraviolet resembling that of sulphurous acid. On the other hand, when sodium bisulphite was prepared by adding the correct quantity of sulphuric acid to the normal sulphite, an entirely different absorption spectrum was obtained which, after the lapse of twenty-four hours, became identical with the spectrum observed with bisulphite prepared by the former method.

Solutions of potassium metabisulphite, when freshly prepared, were found to give stronger absorption than sulphurous acid, but after forty-eight hours, the two spectra became identical.

In a later communication, Schaeffer and Koehler[1], continuing their studies on the ultraviolet absorption of aqueous solutions of sulphur dioxide, arrived at the conclusion that the true absorbent in solutions of sulphurous acid is a hydrate of sulphur dioxide which appears to be more active than sulphur dioxide alone. Since the normal sulphites and the esters, $C_2H_5 \cdot SO_2 \cdot O \cdot C_2H_5$ and $SO(OC_2H_5)_2$, are both diactinic, it is inferred that sulphurous acid *per se* is non-absorbing both in the ionized and unionized condition.

The diminution in the absorbing power of solutions of sulphur dioxide on dilution is traced to a shift from right to left in the equilibrium represented by the equation, $SO_2 \cdot H_2O \rightleftarrows H_2SO_3$.

Normal sulphites were found to show only end absorption in the extreme ultraviolet and when a solution of a normal sulphite was half-neutralized with sulphuric acid, the resulting acid sulphite at first showed only end absorption and then, after a few days, particularly under the influence of light, the band characteristic of sulphur dioxide was observed to develop. On the other hand, when the acid sulphite was formed by mixing solutions of sulphur dioxide and the normal sulphites, the band manifested itself immediately. A solution of potassium metabisulphite, when freshly prepared, was found to exhibit end absorption only, but on standing an absorption band gradually developed. In like manner, sodium methyl sulphite, which in alcoholic solu-

[1] Schaeffer and Koehler: Z. anorg. Chem., 104, 212 (1918).

tion showed only end absorption, in aqueous solution gradually developed the sulphur dioxide band due to hydrolysis into sodium bisulphite and methyl alcohol. Schaeffer and Koehler summarize their views as to the equilibrium conditions in aqueous solutions of sulphur dioxide by the following equations:—

(1) $SO_2 \rightleftarrows SO_2, H_2O \rightleftarrows (O_2S \cdot OH)H \rightleftarrows (O_2S \cdot OH)^- + H^+$

(2) $(O_2S \cdot OH)^- \rightleftarrows (OS \cdot O \cdot OH)^- \rightleftarrows (OS \cdot O_2)^-H \rightleftarrows (OS \cdot O_2)^= + H^+$

They regard the ion, $HSO_3^-$, as unstable and tending to undergo transformation into $H_2SO_3$ and $SO_3^=$, as represented by the equation,

$$2H\,SO_3^- = SO_3^= + H_2SO_3.$$

The resulting sulphurous acid is then assumed to come into equilibrium with hydrated sulphur dioxide, as indicated by the equation,

$$H_2SO_3 \rightleftarrows SO_2, H_2O.$$

In this manner, the authors account for the gradual development of the absorption band in solutions of sulphurous acid. The view is also expressed that the ion, $SO_3^=$, has a symmetrical structure and that this structure also obtains in the normal sulphites.

The equilibria of solutions of the alkali metal bisulphites was also made the subject of special investigation by Baly and Bailey[1] in connection with a study of the additive compounds formed by sodium and potassium bisulphites with aldehydes. These authors concluded that in aqueous solutions of bisulphites there is present in the equilibrium mixture a small proportion of metabisulphite which absorbs light of wave-length $\lambda = 257\mu\mu$. In the absence of oxygen, the solutions were found to be stable in light, but if oxygen or air is present, photo-oxidation of the $HSO_3$ ion occurs, followed by an ionic rearrangement in which normal sulphate, sulphurous acid and hydrated sulphur dioxide are formed. The solution was then found to show the band at $\lambda = 276\mu\mu$, characteristic of hydrated sulphur dioxide. The absorption bands of sulphurous acid, bisulphite and sulphite molecules were shown to lie in the extreme ultraviolet. It was furthermore pointed out, that the characteristic ultraviolet frequencies of sulphur dioxide, hydrated sulphur dioxide and potassium metabisulphite are integral multiples of the fundamental molecular frequency of sulphur dioxide in the infrared. No evidence was found for the existence of isomerism amongst the sulphite molecules.

While all the foregoing investigators are agreed that solutions of sulphur dioxide show a characteristic absorption band at $\lambda = 276\mu\mu$ and that solutions of bisulphites, on standing in the presence of oxygen, gradually develop a band at $\lambda = 276\mu\mu$, their statements relative to solutions of metabisulphites are conflicting.

Thus, Garrett, referring to the gradual development of a band at $\lambda = 276\mu\mu$ in solutions of bisulphites, states that this might be attributed to the formation of metabisulphite according to the equation,

$$NaHSO_3 + NaHSO_3 = Na_2S_2O_5 + H_2O.$$

If this be correct, then, quoting from Garrett's paper, "freshly dissolved metabisulphite ought to exhibit strong selective absorption from the moment

[1] Baly and Bailey: J. Chem. Soc., **121**, 1813 (1922).

of solution. It was found, however, not to be the case. Both sodium and potassium metabisulphite solutions behaved exactly similarly to the hydrogen sulphite solutions, and, in fact, reached the same constant maxima which those solutions had given." Schaeffer and Koehler, on the other hand, found that freshly prepared solutions of potassium metabisulphite exhibited end absorption only, but that on standing a band gradually developed. Baly and Bailey state, that freshly prepared solutions of potassium metabisulphite exhibit a characteristic absorption band at $\lambda = 257\mu\mu$ and that a similar band was observed in freshly prepared solutions of the alkali metal bisulphites. On exposure to light the band at $\lambda = 257\mu\mu$ disappeared and in its place a new band at $\lambda = 276\mu\mu$ gradually developed with marked increase in the absorptive power of the solution.

Again, it is by no means clear whether the progressive change undergone by solutions of bisulphites on standing is due to the action of light in the presence of oxygen, or to the action of light alone. With a view to clearing up these uncertainties the following investigation was undertaken.

*Preparation of Materials.* In preparing the solutions used in these experiments, due regard was had for the importance of purity of both solutes and solvents in spectrographic work. The sulphur dioxide solutions were prepared with gas obtained by the action of sulphuric acid on chemically pure, crystalline sodium sulphite. The evolved gas was dissolved in distilled water which had just previously been boiled to exclude air and carbon dioxide, precautions being taken to protect the solutions from oxidation after preparation. The solutions of sodium sulphite and bisulphite were prepared in a similar manner from chemically pure salts. Garrett states that he experienced difficulty in obtaining pure samples of sodium and potassium bisulphites and ultimately was forced to prepare the salts by passing sulphur dioxide into dilute solutions of the carbonates. It should be stated that the samples of sodium bisulphite used in this series of experiments were obtained from a well-known chemical manufacturer and upon analysis were found to correspond accurately with the formula of the salt. Considerable difficulty was experienced, however, in obtaining a satisfactory preparation of sodium metabisulphite. After examining several samples of this salt, obtained from different sources, and finding them all more or less impure, the attempt was made to prepare the salt by passing pure, dry sulphur dioxide into a solution of sodium ethylate in absolute ethyl alcohol. While a beautiful crystalline product was obtained, it was found upon analysis to be no purer than the commercial preparations previously examined. Ultimately, an excellent preparation of the potassium salt was obtained from a reliable chemical firm which, upon analysis, was found to conform very closely to the formula, $K_2S_2O_5$.

The concentration of the solutions was determined in each case by means of the familiar iodine-thiosulphate method.

*Apparatus.* The extinction coefficients of the various solutions studied were determined by means of a large size Hilger quartz spectrograph in con-

junction with a Judd Lewis ultraviolet sector-photometer, as described by the author in a previous paper[1].

*Experimental Data.* The experimental results are expressed graphically by means of curves in which logarithms of molecular extinction coefficients are plotted against corresponding wave-lengths expressed in millimicrons, $\mu\mu$. The molecular extinction coefficient is defined by the expression $\frac{\log \frac{I_o}{I}}{ml}$

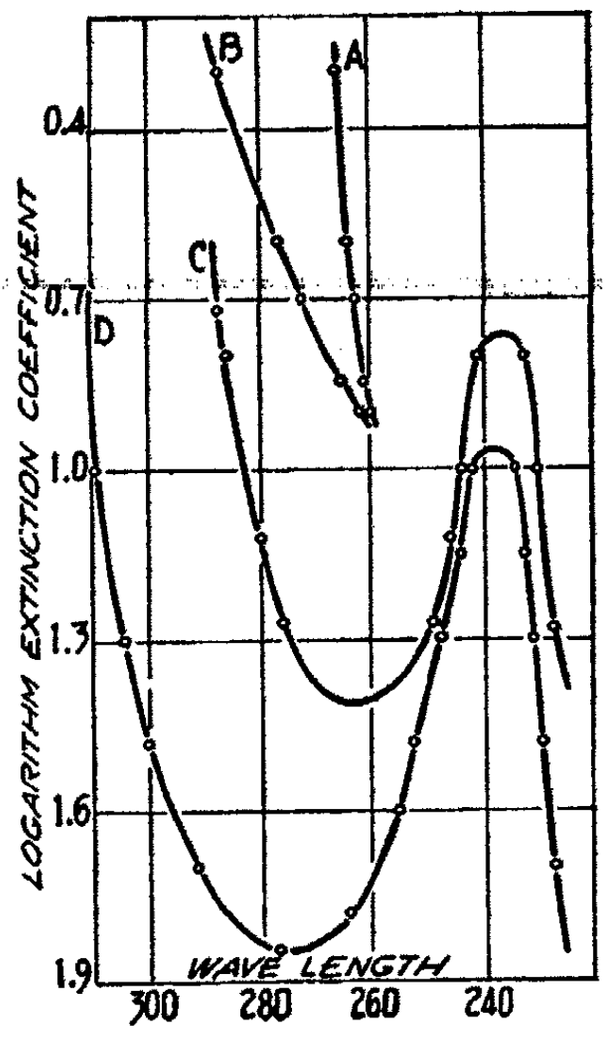



FIG. 1

A 0.05 m Sodium Sulphite
B. 0.05 m Sodium Bisulphite
C 0.02 m Potassium Metabisulphite
D 0.005 m Sulphur Dioxide

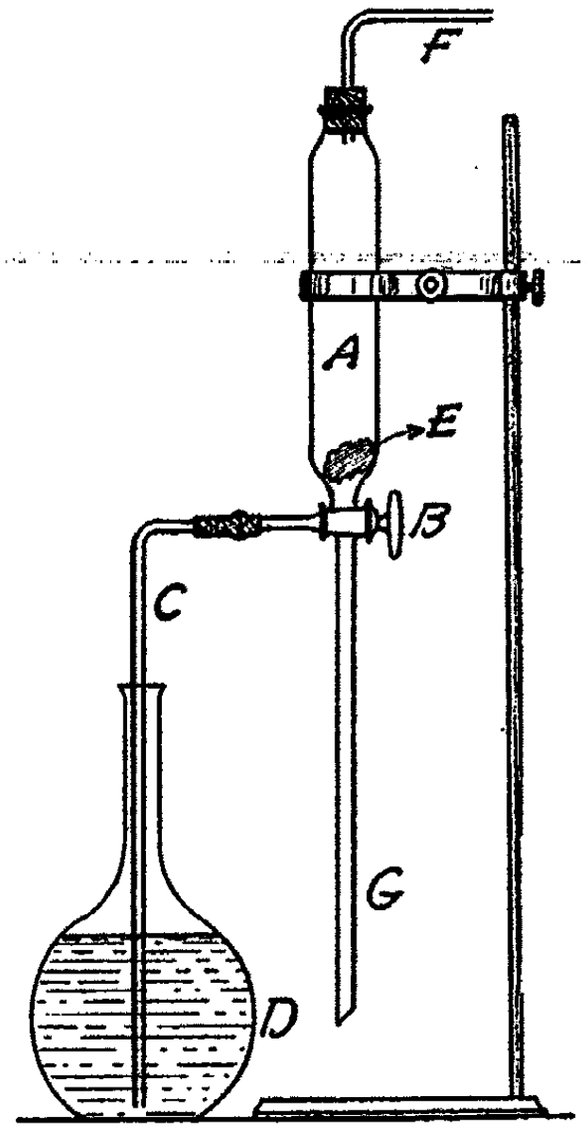



FIG. 2

where $I_o$ and I are the intensities of the incident and transmitted radiation respectively, and where $m$ denotes the concentration of the solution in gram-molecules per liter and $l$ is the length of the column of absorbing medium in cms.

The extinction curve of 0.05 m $Na_2SO_3$ is designated by the letter A in Fig. 1: The position of the absorption band is evidently in the extreme ultraviolet, as was pointed out by Baly and Bailey. Curve B is the extinction curve of freshly prepared 0.05 m $NaHSO_3$ and, as with the normal salt, the absorption band is found to lie in the extreme ultraviolet. The extinction curve of freshly prepared 0.02 m $K_2S_2O_5$ is represented by C. Special pre-

[1] Getman: J. Phys. Chem., 29, 853 (1925).

cautions were taken in the preparation of the latter solution to eliminate both air and carbon dioxide. To this end the apparatus shown in Fig. 2 was employed. A dropping funnel, A, of approximately 70 cc. capacity and fitted with a three-way stopcock, B, was connected through C with a flask, D, containing a large volume of freshly boiled, distilled water. A large clear crystal of potassium metabisulphite, E, was introduced into the funnel, the neck of which was then closed by means of a rubber stopper fitted with a right-angled tube F. The latter was connected with a water pump and B was turned so as to establish communication with the solvent in D. When sufficient water had been aspirated through the funnel to dissolve the surface

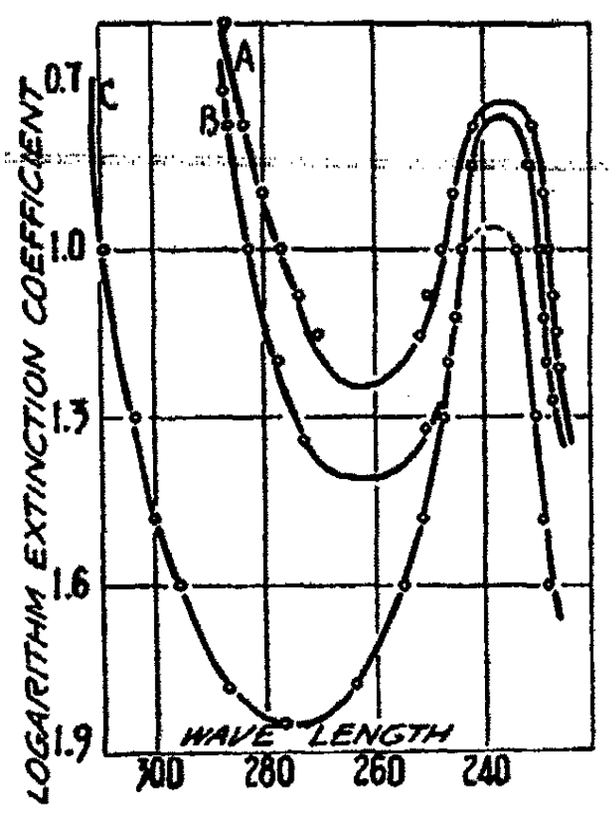



FIG. 3

A 0.025 m Potassium Metabisulphite
B 0.020 m Potassium Metabisulphite
C 0.005 m Sulphur Dioxide

layer of E and to insure the removal of the resulting solution, the stop-cock was closed and the crystal permitted to dissolve. When the bulk of the crystal had diminished to about that required for a solution of suitable concentration for use in the spectrophotometer, the supernatant solution in A was removed by further aspiration and the crystalline residue allowed to dissolve. Connection with the pump was then broken and, after allowing enough of the solution to flow out of the funnel to displace the air in G, the absorption cell was filled and the absorption spectrum immediately photographed. Another portion of the solution was analyzed simultaneously in order to determine its concentration. It will be observed that the solution gives a well-defined absorption band at $\lambda = 263\mu\mu$. The position of the head of this band was checked by repeated experiments. Curve D, Fig. 1, is the extinction curve of freshly prepared 0.005 m $SO_2$. The position of the head of the absorption band at $\lambda = 276\mu\mu$ is in agreement with the results of Baly, Garrett

and others. If due precautions were taken to exclude air and carbon dioxide, the curve for dissolved $SO_2$ could be satisfactorily reproduced. On repeating the experiment with solutions of different concentrations, it was found that Beer's law does not apply to aqueous solutions of sulphur dioxide. This is in agreement with the observations of Garrett.

Further experiments with potassium metabisulphite are summarized in Fig. 3. Curve A represents the results of two series of measurements of the extinction coefficients of 0.025 m $K_2S_2O_5$. Curve B, which is a reproduction

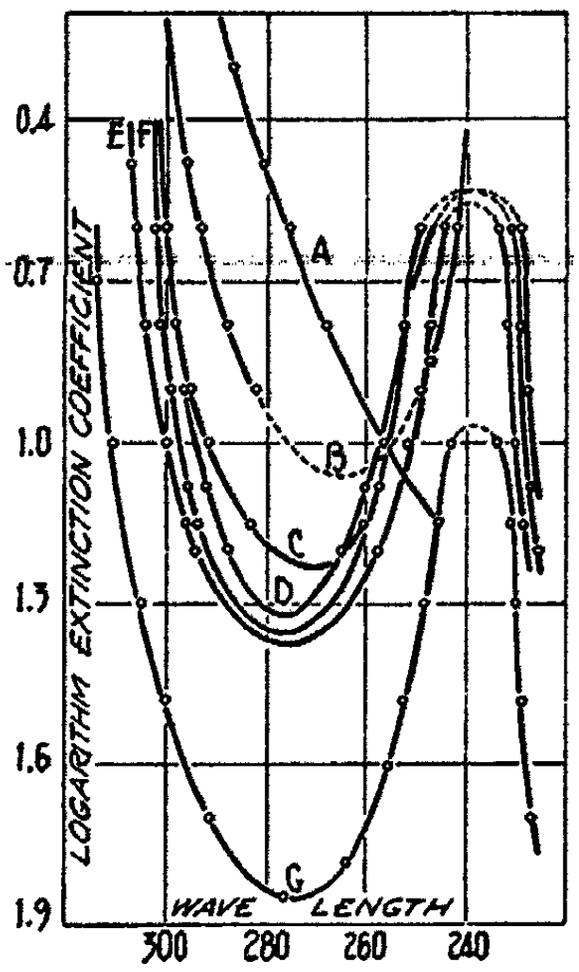



FIG. 4

| | | | |
|---|---|---|---|
| A | 0.05 m | Sodium Bisulphite | (freshly prepared) |
| B | 0.05 m | " " | (after 18 hours) |
| C | 0.025 m | " " | (after 5 days) |
| D | 0.025 m | " " | (after 10 days) |
| E | 0.025 m | " " | (after 20 days) |
| F | 0.025 m | " " | + 0.02 m Sucrose (after 30 days) |
| G | 0.005 m | Sulphur Dioxide | |

of curve C of Fig. 1, serves to illustrate the inapplicability of Beer's law to aqueous solutions of metabisulphites. Although the foregoing experiments confirm the statement of Baly and Bailey, that solutions of metabisulphites give a characteristic absorption band, we have been unable to check their result as to the location of the band. They state that the wave-length corresponding to the head of the band is $\lambda = 257\mu\mu$, whereas we find $\lambda = 263\mu\mu$. Since potassium metabisulphite rapidly decomposes in solution with the formation of sulphur dioxide, it follows that its solutions on standing will develop the band characteristic of dissolved sulphur dioxide at $\lambda = 276\mu\mu$.

The results of the measurements of the extinction coefficients of solutions of sodium bisulphite are brought together in Fig. 4. Curve A was obtained

with freshly prepared 0.05 m $NaHSO_3$. After 18 hours the extinction curve of this same solution was found to have changed to that represented by curve B. As will be seen, the character of the absorption has changed from general or end absorption to selective absorption. In order to follow more closely the progressive change in the composition of solutions of sodium bisulphite with time, a large volume of 0.025 m $NaHSO_3$ was prepared, taking the usual precautions to exclude air and carbon dioxide. With this mother solution, five series of experiments were carried out. In the first series, approximately 100 cc. portions of the mother solution were introduced into flasks of 125 cc. capacity and, after stoppering, the flasks were exposed to light for varying periods of time. In the second series, a number of 50 cc. bottles fitted with ground stoppers were completely filled with the mother solution. After inserting the stoppers, the necks of the bottles were sealed with paraffine and, as in the case of the preceding series, exposed to light for varying periods of time.

The third series resembled the first series in every particular except that to the original solution enough cane sugar was added to make the solution 0.02 molar with respect to that solute.

The fourth series was similar ot the second, except that the composition of solution was 0.025 m $NaHSO_3$ + 0.02 m $C_{12}H_{22}O_{11}$. The last series consisted of partially filled flasks of 0.025 m $NaHSO_3$ which were protected from the action of light. The progressive change in the composition of the solutions was determined both spectroscopically and analytically by examination of the contents of the different flasks and bottles at intervals of from five to ten days. The analytical procedure consisted in titrating the solutions against 10 cc. portions of N/10 iodine to which a few drops of hydrochloric acid had been added to insure complete liberation of combined sulphur dioxide. The results of the analytical examination are given in Table I.

TABLE I

Initial titer, 10 cc. N/10 I = 9.6 cc. $NaHSO_3$

| Interval (Days) | Titer I | II | III | IV | V |
|---|---|---|---|---|---|
| 5 | .... | 9.6 | .... | 9.6 | .... |
| 10 | 12.9 | 9.5 | .... | 9.5 | .... |
| 15 | .... | ... | .... | ... | 9.9 |
| 20 | 27.0 | 9.6 | 24.5 | 9.8 | .... |
| 30 | 62.7 | 9.7 | 31.8 | 9.7 | 10.2 |
| 50 | .... | ... | .... | ... | 10.7 |

As will be seen from columns II and IV of the table, the titer of the solutions from which air had been excluded remains constant, whereas the figures in columns I and III increase, indicating gradual oxidation of the solution. That light plays an important part in the process of oxidation is indicated by the figures of the fifth column. It will be remembered that although this solution was in contact with air it was placed in the dark immediately after preparation. After a period of two months the solution

had not oxidized as much as the same solution had oxidized in ten days under the influence of light. It has been shown by Mathews and Weeks[1] that cane sugar and a number of other organic compounds act as negative catalysts in the oxidation of solutions of sodium sulphite. That a similar action is exerted by cane sugar when dissolved in a solution of sodium bisulphite is revealed by a comparison of the data of I and III columns of the table. Cane sugar was selected from the list of catalysts enumerated by Mathews and Weeks because it was believed that its presence in a solution of sodium bisulphite would produce little or no alteration in the characteristic absorption spectrum of the salt.

The progressive change in the absorption of 0.025 m $NaHSO_3$ is depicted by the curves of Fig. 4. It is apparent that after standing for ten days the head of the absorption band becomes constant at $\lambda = 276\mu\mu$, the wave-length characteristic of dissolved sulphur dioxide. The retarding action of cane sugar on the process of oxidation is clearly shown by the fact that 0.025 m $NaHSO_3$ twenty days after preparation has greater absorbing power than the same solution containing 0.02 gram-molecule of cane sugar thirty days after preparation (curves E and F).

*Discussion of Results.* In reviewing the foregoing experimental data it is apparent that aqueous solutions of sodium bisulphite are stable in light provided oxygen is excluded, but if oxygen or air is present, photo-oxidation ensues and, after five days, the solution shows the characteristic absorption band of dissolved sulphur dioxide at $\lambda = 276\mu\mu$. Since the absorption curve of 0.025 m $NaHSO_3$, five days after preparation, corresponds very closely with that of a mixture of equal volumes of 0.05 m $SO_2$ and 0.05 m $Na_2SO_4$, it may be fairly assumed that the progressive change in the solution under the influence of light consists in the photo-oxidation of the anion of sulphurous acid, $HSO_3^-$. The successive steps in the process may be represented by the equations:—

$$NaHSO_3 \rightleftarrows Na^+ + HSO_3^-, \qquad (1)$$

$$Na^+ + HSO_3^- \xrightarrow[\text{light}]{(O)} Na^+ + HSO_4^-, \qquad (2)$$

$$Na^+ + HSO_4^- \longrightarrow Na^+ + H^+ + SO_4^=, \qquad (3)$$

The resulting ions then react with the ions of (1) in the following manner:—

$$Na^+ + H^+ + SO_4^= + Na^+ + HSO_3^- \longrightarrow 2Na^+ + SO_4^= + H^+ + HSO_3^-, \qquad (4)$$

$$H^+ + HSO_3^- \rightleftarrows H_2SO_3 \rightleftarrows SO_2, H_2O. \qquad (5)$$

Freshly prepared solutions of potassium metabisulphite have been found to give a well-defined absorption band at $\lambda = 263\mu\mu$, provided precautions are taken to exclude air and carbon dioxide. This fact proves that, initially, solutions of metabisulphites and bisulphites are not identical, as has been claimed by several investigators. Solutions of metabisulphites rapidly hydrolyze as indicated by the equilibrium equation,

$$K_2S_2O_5 + H_2O \rightleftarrows 2KHSO_3, \qquad (6)$$

[1] Mathews and Weeks: J. Am. Chem. Soc., 39, 635 (1917).

and the resulting bisulphite then undergoes photo-oxidation, as indicated in the preceding paragraphs.

No indication of the existence of a band at $\lambda = 257\mu\mu$, in freshly prepared solutions of sodium bisulphite, as claimed by Baly and Bailey, was obtained, but the fact that they prepared their solutions of sodium bisulphite by half-neutralization of sulphurous acid with sodium hydroxide, whereas a pure dry salt was used in the present investigation may easily account for this discrepancy. In this connection it may be mentioned that although Garrett took extreme care in the preparation of his solutions he failed to record the existence of any band at $\lambda = 257\mu\mu$ in solutions of the bisulphites. Baly and Bailey estimate that in 0.025 m $NaHSO_3$ there is probably less than three percent metabisulphite, indicating that the equilibrium in reaction (6) lies toward the right side of the equation.

Baly and Bailey apply to the two absorption bands observed by them at $\lambda = 257\mu\mu$ and $\lambda = 276\ \mu\mu$, a relationship previously established by the senior author[1]. By means of a mathematical deduction from the quantum theory, Baly showed that if $\nu_x$ is the wave-number of the characteristic infra-red vibration of a compound, then radiant energy can only be reabsorbed at the wave-numbers $\nu_1$, $\nu_2$, $\nu_3$, etc., where $\nu_1$, $\nu_2$, $\nu_3$, are successive integral multiples of $\nu_x$. In the present example, $SO_2$ is the absorbing molecule and this has been found to exhibit a characteristic absorption band corresponding to each of the three following states:—(a) gaseous $SO_2$, (b) $SO_2.H_2O$, and (c) $K_2SO_3.SO_2$. As Baly and Bailey have shown, the fundamental wave-number of gaseous $SO_2$ is 135.1 and therefore, according to the above generalization, the wave-numbers of the three bands should be integral multiples of this fundamental quantity. The following table is taken from their paper.

TABLE II

| Multiple | $1/\lambda$ | $\lambda$ (calc) | $\lambda$ (obs.) | Origin of band |
|---|---|---|---|---|
| $25 \times 135.1$ | 3377.5 | $296.1\mu\mu$ | $296.1\mu\mu$ | $SO_2$ |
| $27 \times 135.1$ | 3647.7 | 274.1 | 276.0 | $SO_2 \cdot H_2O$ |
| $29 \times 135.1$ | 3917.9 | 255.2 | 257.0 | $K_2SO_3 \cdot SO_2$ |

If the fundamental wave-number of $SO_2$, 135.1, be multiplied by 28 instead of 29, as in the table, the calculated value of the wave-length of potassium metabisulphite becomes $\lambda = 264.3\mu\mu$, which is in quite as good agreement with our observed value, $\lambda = 263.0\mu\mu$, as is Baly and Bailey's calculated with their observed value.

*Summary of Results.* The results of the foregoing investigation may be briefly summarized as follows:—

(1) Aqueous solutions of sulphur dioxide show a characteristic absorption band at $\lambda = 276\mu\mu$. The absorption is attributed to hydrated sulphur dioxide, $SO_2.H_2O$, formed from the anion of sulphurous acid. The extinction curve for sulphur dioxide solutions of the same concentration is easily re-

[1] Baly: Phil. Mag. (6) **27**, 632 (1914); **29**, 223 (1914); **30**, 510 (1915).

producible, provided oxygen and carbon dioxide are excluded. Beer's law does not apply to aqueous solutions of sulphur dioxide nor to any of its derivatives.

(2) Freshly prepared solutions of potassium metabisulphite give a characteristic absorption band at $\lambda = 263\mu\mu$. On standing, this band disappears and in its place the sulphur dioxide band at $\lambda = 276\mu\mu$, gradually develops. The fact that metabisulphite solutions give a well-defined band at $\lambda = 263\mu\mu$, is taken as evidence of the existence of the undecomposed salt in solution.

(3) Solutions of sodium sulphite do not show selective absorption.

(4) Freshly prepared solutions of sodium bisulphite show end absorption only, but on standing in the light, if oxygen is present, photo-oxidation of the ion, $HSO_3^-$, occurs with the simultaneous development of the band at $\lambda = 276\mu\mu$ characteristic of dissolved sulphur dioxide. The magnitude of the absorption coefficient continues to increase for about thirty days when a constant maximum is attained.

(5) The presence of cane sugar in solutions of sodium bisulphite has been shown to retard the process of oxidation.

(6) Light has been found to be an essential factor in the oxidation of bisulphite solutions.

(7) Baly's relationship connecting ultraviolet frequencies with a fundamental frequency in the infra-red has been found to be applicable to the bands at $\lambda = 263\mu\mu$ and $\lambda = 276\mu\mu$, characteristic of $K_2S_2O_5$ and $SO_2.H_2O$ respectively.

*Hillside Laboratory,*
*Stamford, Conn.*

# ORIGIN OF THE FORMATION OF DEPOSITS IN GOUT AND OTHER DISEASES AND THE CAUSE OF SWELLING IN BERIBERI

BY N. R. DHAR

Gout has been defined "as a disorder of metabolism associated with retention of uric acid, and of other purin bodies in the system, characterised clinically by attacks of acute arthritis, the deposition of sodium biurate in and about the joints and by the occurrence of irregular constitutional symptoms"[1]

The veins around the painful joint first appear swollen and shortly the whole joint becomes swollen, tense, shining and of a deep red colour. The subcutaneous tissues are oedematous and pit on pressure.

An attack of acute gout is commonly preceded by some troubles of digestion—acidity, flatulence, loss of appetite, constipation, and scanty, high coloured urine. Before and at the commencement of the attack the output of uric acid is generally low, but rises to normal or above with full establishment of the arthritis. There is a remarkable parallelism in the output of uric and phosphoric acids both during and between the attacks.

It is believed that these joint affections are dependent on the precipitation and deposit of sodium biurate crystals in the cartilages, ligaments, synovial membranes, bursae, and other structures forming part of, or in proximity to, the articulation. In some of the most distressing forms of chronic gout, the joints of the fingers, and less frequently those of the toes, become surrounded by massive deposits of sodium biurate which sometimes ulcerate slowly through the skin. It has been observed that masses as large as horse beans are discharged.

Small deposits of sodium urate are also often observed on the margins of the ears and occasionally on the insides of eyelids, on the arches of the pallets and elsewhere. The most serious manifestations of gout are the cardiovascular and renal changes that are determined by the gout state.

The crystalline urates precipitated in the cartilaginous and fibrous structures of the joints necessarily act as foreign bodies. They excite irritation, clog the lymph channels, exercise pressure on the tissue elements and impede their nutritive operations; hence the inflammation, pain, swelling and subsequent regenerative changes in the joints.

According to newer views gout is regarded as the disturbance of purin metabolism, or a perversion of the general metabolism of the tissues. It is believed then that uric acid plays only a secondary part in the causation of gout and is a mere weapon of the disease. That its excess in the blood is probably due to diminished oxidation in the system; that somewhere in the body a ferment is produced which normally is necessary for the proper oxidation of uric acid, and that owing to some organ or organs failing to produce this ferment, proper oxidation of uric acid does not occur, and it consequently

[1] Osler: "Principles and Practice of Medicine", 417 (1912).

accumulates in the blood. It is certain that an excess of uric acid in the blood cannot alone be regarded as the cause of the deposition of sodium biurate or of uric acid in the tissues, for in leukaemia there is a notable increase of uric acid in the blood, yet it is not usual to find biurate or uric acid deposition in the tissues.

Thus the modern tendency is to believe that ferments play an important part in the formation and destruction of uric acid in the blood. It is suggested that it is formed partly by oxidative processes from the nucleo-proteins, and partly by a synthetic process in the liver.

Gout is due to a disorder of elimination, a defect or feebleness in the function or functions of the elimination of the waste products of nutrition.

The value of alkalies in the treatment of gout has been almost universally accepted. "Alkalies" testifies, Professor Whitla[1] "by forming soluble salts with uric acid, which salts, acting as diuretics, are freely washed out in the urine, cause marked elimination of uric acid, and are the most valuable of the gouty remedies."

I am of the opinion that alkalies also help in the increase of metabolism in the system. We have repeatedly observed in the laboratories that the oxidation of carbohydrates by air at the ordinary temperature in presence of reducing agents like $Fe(OH)_2$, cerous hydroxide etc., is greatly increased by the increase in the concentration of the alkalies. It is now well known that acidity of the system is associated with disturbance of digestion and that acidosis is essentially connected with insufficient metabolism and is mainly responsible for the causation of gout.

From my researches on colloids, I am convinced that sparingly soluble substances like uric acid, calcium phosphate, calcium oxalate etc., remain in the colloidal condition in the system due to the presence of protecting albuminous substances. When these colloidal substances are coagulated and are crystallised in tissues we get diseases like gout, renal colic, oxaluria, lithiasis, phosphaturia, gallstones, etc., which are diseases caused by the deposition of the sparingly soluble substances in various parts of the body.

How this coagulation takes place? The coagulation of peptised substances can take place due to one or more of the following causes:—

1. Increment of electrolytes in the system.
2. Decrease of the peptising influence either by loss or dilution of the protecting agent.
3. Decrease of temperature.
4. Increase of concentration of the substance which is being peptised.
5. Adsorption of the peptised substance by some solid adsorbent.

We have proved definitely that substances like $BaSO_4$, freshly precipitated $Fe(OH)_3$, $PbCrO_4$, etc. can adsorb appreciable quantities of sols of various substances. Hence we are convinced that the bone or the cartilage of the system can surely adsorb the peptised uric acid, calcium oxalate calcium

[1] Whitla: "Dictionary of Treatment", p. 306.

phosphate, etc. existing in the system; consequently the deposition of these substances is certainly very favourable round about the bones, cartilages and in joints. It is a well-established fact that the presence of solids favour the formation of a precipitate from a colloidal matter or from a solution.[1]

I have already emphasised that an attack of gout is commonly preceded by some troubles of digestion—acidity, constipation, scanty and high coloured urine, etc. I believe that when the system is not working in the proper condition and the excretions are not normal, we get an extra amount of water in the system and this water acts as a diluent of the protective agents and hence the amount of uric acid or calcium phosphate or calcium oxalate held in the colloidal condition is decreased due to the decrease in the concentration of the protective agents (albuminous substances) in the system caused by dilution.

I am of the opinion therefore that an important cause in the formation of the deposits of uric acid, calcium phosphate, calcium oxalate, etc. is the presence of an extra amount of water which in normal circumstances should have been eliminated from the system, but when a person is suffering from constipation, scanty urine, etc., the water does not come out of the system in normal quantities, but dilutes the peptising agent (albuminous matter) and hence substances like uric acid, calcium oxalate, calcium phosphate, etc., which normally remain in the peptised condition in the system become coagulated.

We have shown that the amount of silver chromate held in suspension by gelatin decreases with the decrease in the concentration of gelatin; similarly the amount of lead chromate or lead iodide remaining in the colloidal solution increases with the increase in the concentration of agar.[2]

Moreover in the case of gout the acidity which is usually associated with an attack of gout plays a very important part in the separation of uric acid. From the researches of Pauli and Samec we know that the solubility of sparingly soluble substances is increased by the presence of serum albumin and other protective agents, whilst the solubility of readily soluble substances are decreased due to the presence of albuminous substances. Bechhold and Ziegler have shown that the solubility of uric acid is much greater in serum albumin than in water, whilst that of sodium urate is decreased due to the presence of serum albumin. It seems certain that in gouty blood sodium urates should also be present along with uric acid. Now if the blood becomes acid due to insufficient oxidation and causation of acidosis, the sodium urate will be decomposed by the acids (lactic, phosphoric etc.) thus generated and uric acid will be set free, which, being more sparingly soluble than sodium urate is likely to come out as a precipitate due to the presence of the already existing urate ions. Consequently the acidity caused by the lack of proper metabolism helps in the precipitation of uric acid in gout.

---

[1] Compare Dhar and Chatterji: J. Phys. Chem. 28, 41 (1924).

[2] Compare Sen and Dhar: Kolloid-Z. 34, 270 (1924).

It is well known that the swelling of organic substances, like gelatin, albumin, etc., in water is greatly accelerated by the presence of small quantities of free acid or alkali; consequently the acidity produced in the system due to want of proper metabolism helps in the retention of water by the tissues and thus facilitates the dilution of the protecting agent (albuminous matter, etc.) and causes the separation of uric acid. Consequently our theory of the causation of gout, oxaluria, phosphaturia, renal colic, lithiasis etc., where deposits are formed in the system is exactly on the same line as that of Martin H. Fischer for the formation of oedema.

It will be interesting to note that practically the same treatment has been recommended by medical men in gout, oxaluria, renal colic, phosphaturia, lithiasis, gallstones, uninary calculi, oedema, etc., Alkalies like sodium bicarbonate, potassium bicarbonate, etc., have been recommended for the treatment of all these diseases. Alkalies help the oxidation of food stuffs in the body and hence they prevent the formation of acids and check acidosis. Moreover, they neutralise the acids already formed and consequently fight the above diseases. Flushing of the system with large quantities of water has also been recommended; this certainly causes the solution or mechanical carrying away of the precipitates by large volumes of water.

Purgatives have been found to be effective in the treatment of gout and according to our theory they should be effective, because they help the elimination of large quantities of water, purin bodies, etc.

It is well known that gout is prevalent in cold and humid climates; this becomes clear from our point of view because loss of water by perspiration, evaporation, etc., is much less in humid and cold climates than in warm dry climates and hence the retention of water and consequent dilution of the protective agents in the system is facilitated in humid and cold climates. Moreover, decrease of temperature markedly decreases the amount of solids which a certain amount of protective agent can hold in suspension. We have repeatedly observed that the amount of lead iodide or lead chromate which a certain weight of agar can hold in suspension is much greater at higher temperatures than at ordinary temperatures. Hence a lowering of body temperature helps in the formation of a deposit of uric acid, calcium phosphate, calcium oxalate, etc.

We have observed that the addition of alcohol makes a sol say of $Ag_2CrO_4$ peptised by gelatin unstable towards electrolytes. Hence we believe that alcohol would help the coagulation and separation of uric acid crystals in the system and that is why alcohol has been generally recognised as bad for gout.

It will be interesting to discuss in this connection the etiology and causation of beri-beri. It is now well-known that want of vitamin B in food stuffs leads to the causation of beri-beri. I am of the opinion that vitamin B acts as an accelerator or promoter for the oxidation of carbohydrates by air in presence of enzymes. Consequently want of vitamin B would lead to insufficient metabolism and acidosis, and the presence of acids will help in the retention of water in the animal economy. It is well-known that in beri-beri water is retained in various parts of the body and causes swelling. I am

of the opinion, therefore, that the swelling in beri-beri is due to the presence of acids caused by the deficiency in metabolism or carbohydrates of food-stuffs and alkalies ought to be beneficial for patients suffering from beri-beri, and I should request medical men to treat beri-beri with food materials rich in vitamin B together with some alkali to neutralise the acid generated by insufficient metabolism. It is very interesting to note that beri-beri is most common in nations who have to depend mainly on foods rich in carbohydrates. This explanation of the swelling in beri-beri is on the same line as that of Martin Fischer for oedema.

## Summary and Conclusion

1. Gout, oxaluria, renal colic, phosphaturia, gallstones, lithiasis, etc., are mainly due to insufficient metabolism and deficiency of elimination of waste products.

2. An important cause in the formation of the deposits of uric acid, calcium phosphate, calcium oxalate, etc., is the presence of an extra amount of water due to want of proper elimination and this water dilutes the peptising agents and thus leads to the deposition of the above substances.

3. Acids generated in the system due to insufficient oxidation plays an important part in the deposition of uric acid by the decomposition of urates and by helping in the retention of water by the tissues and the albuminous parts of the body and the water thus retained dilutes the peptising agents and causes the precipitation of uric acid, calcium oxalate, etc.,

4. I am of the opinion that uric acid and not urates forms the main deposit in gouts.

5. Beri-beri is most probably due to insufficient metabolism of carbo-hydrates in the system due to the want of vitamin B in food stuffs. The acids generated in the system due to insufficient oxidation helps in the retention of water and causes swelling of different parts of the body.

*Chemical Laboratory,*
*Allahabad University,*
*Allahabad, India,*
*April 29, 1925.*

## NEW BOOKS

**Chemistry in Modern Life.** *By Svante Arrhenius. Translated by C. S. Leonard. 22 × 16 cm; pp. xvi+286. New York: D. Van Nostrand Company, 1925. Price: $3.00.* In the preface the author says: "The bitter experience given us by the World War, and by the after years of exigency, demonstrated with hard-fisted emphasis the necessity for chemical industry. So we see today how the nations are trying to develop this branch of science for the best possible improvement of their situation. The most practical way to repair the heavy losses caused by the war lies in the application of chemistry."

This is a popular book on chemistry and the chapters are entitled: ancient ideas about the constitution of matter; the ground-work of scientific chemistry; fire, oxidation, and reduction; tools and metals; the cultural value of silica; the chemistry of the earth's crust; ores and fossil fuels; the chemistry of water and air; sources of energy, electricity and chemistry the course of a chemical process; dyes, perfumes, and drugs; cellulose and rubber; chemistry and the bread question; housekeeping with the treasures of nature.

"It should be noted that Lavoisier had numerous predecessors who came near to a correct conception about combustion. We have mentioned the genius, Leonardo da Vinci (1452-1519). This man, who accomplished marvellous work in all the arts and sciences of his time, also suggested a theoretical explanation of the problem of combustion. According to Leonardo air was consumed in the process of burning, and animals could not live in an air which, after bodies had been burned therein no longer could support combustion. Thus Leonardo discovered the fact that air consisted of two parts, of which one, now called oxygen, could support combustion and was necessary for the respiration of animals, while the other, now called nitrogen lacked these properties," p. 24.

"A very remarkable statement has been found by Klaproth in a Chinese manuscript of the eighth century. The author, Mao Khoa, reported therein that air was composed of two constituents, yin and yang. Yin could be removed from the air by the use of divers metals, or by sulphur, or carbon;—it must therefore have been oxygen. Yin could also be prepared from a certain mineral, the name of which is given. Klaproth presumes that this word meant saltpeter, but is not sure of this.

"The Byzantines very probably knew of gunpowder in the seventh century, the Chinese surely in the tenth century. Saltpeter is a constituent of this. From China the use of gunpowder passed to Persia and Arabia, where saltpeter was called the Chinese salt, or Chinese snow. The Arabs probably taught the Europeans the art of handling gunpowder," p. 25.

"Flint lends itself to use for tools because of the sharpness of its edges. Flint is an amorphous, which is to say a noncrystalline, substance. Amorphous substances, of which glass is best known, are characterized by a shell-like, or scale-like, mode of fracture, and as a result of this the edges formed by the fracture are very sharp. That is why one can so easily cut oneself on bits of broken glass, while pieces of the coarsely crystalline rocks, such as granite, are not at all dangerous when broken. In primitive times men sometimes used a true glass, volcanic in origin, called obsidian, for making edged-tools, and because of the traditional age of such tools, the Jews, today, use knives of obsidian for religious purposes. Flint also possesses the necessary hardness for use as a tool. It is very widespread, too, in its occurrence in chalk-formations all over the world," p. 60.

"The making of pottery vessels has been of the greatest importance in the development of a sense of beauty in man, for undoubtedly clay objects were an incentive to the use of ornamentation. It was probably noted that the impressions from the fingers that resulted from working the clay were found to remain after firing and to be permanent. Next a pleasure was found in designing an ornament by applying such finger marks in a regular arrangement, see Fig. 15. Later it was preferred to make the marks needed for ornamentation of the clay by the use of pointed objects. A fine example of what could be made even in the stone age by means of this simple technique may be seen in Fig. 16, which is a picture, 1/6 size, of a clay urn found on the island of Moen in Denmark," p. 86.

"There is no question but that the art of fabricating glass arose in Egypt about 5000 years ago. Articles of glass were first brought into Greece by the mercantile and sea-going

peoples such as the Phoenicians, who, like the Assyrians, early learned how to work glass. The Greeks are not known to have practiced the art before the days of our calendar. Thus the Egyptians and the Phoenicians were looked upon at that time as the great masters of glass technique, and Alexandria was world-renowned for the remarkable glass articles sold in its markets.

"In the Roman state glass manufacture was first taken up on a large scale in the days of the Caesars, and the products were marketed even in the far East. In China the art of glass manufacture was first learned about the middle of the fifth century A. D. In spite of the high reputation held by Roman glass it was rather highly colored, having a green or yellow tint, like the simplest kinds of glass of today, and moreover it was full of small blow-holes and nodules. On this account it was generally colored deeply or made opaque by the addition of chemicals and was used mainly for decorative purposes, and for jewelry, such as the cameo, and also for mosaics, etc. Only in very isolated cases was it used for windows; such use may be seen in the excavations at Pompeii. In the first century A. D. glass began to be used to a greater and greater extent for church-windows, but this glass was not clear, and consisted of small colored bits, which transmitted only a mystic half-light. The manufacture of glass next passed over to Constantinople and the Mohammedan Orient. The art returned to Europe during the Middle Ages. Venice became its chief center. When the Renaissance came and progress began again, glass factories, like all else, were influenced by the general desire to find artistic expression and the glass-industry of Venice reached a very high point in the 16th and 17th centuries. From Italy the art spread to France, which country was destined next to take the leading place in this branch of human culture. Even in Germany, and especially in Bohemia at the same period a great glass industry began to develop. In the last half-century Germany has stood at the top in this field. More and more all cultural lands have attained high proficiency in the art," p. 96.

"From lime-glass which is long heated to a high temperature there separates long crystals of pseudo-wollastonite (calcium silicate). As a result the glass acquires a porcelain-like appearance. Such glass is named after Réaumur who first noted the property. Attempts have been made to use this glass as porcelain but it is found to be very brittle so that it has little use. Zinc oxide can be dissolved in glass to such an amount that, on cooling, it crystallizes out in long needles. These can be colored a green or blue color by adding nickel or cobalt, which enter into the zinc silicate crystals. This fact is made use of for the preparation of artistic glazes on porcelain. Aventurine glass is characterized by the presence of small red copper crystals embedded in the glass. It results from the presence in the glass of both copper silicate and ferrous oxide. The latter during a slow cooling of the glass is oxidized at the expense of the copper oxide out of the silicate, so that copper [?] precipitates in crystalline form," p. 105.

Arrhenius seems to be rather impressed by the work of Ross, p. 110. "The chemist, William Ross, at the University of Washington in Seattle, has investigated a process which appears to be most promising. He first tried to get potash from potash felspar by heating the rock with a steam at 500° C. and under the enormous pressure of 1450 atmospheres. This experiment was unsuccessful. Next he heated the felspar with lime in water at 300° under about 90 atmospheres of steam pressure. He then found that a large part of the potash had been displaced by the lime, and had dissolved in the water. When the lime was made double the amount of the felspar, practically all the potash was freed. He now added still more lime so that the mass remaining after leaching out the potash would have about the same composition as the mixture from which Portland cement is made. (Felspar is about 25% low in alumina in comparison with the silica content, but this seems to make little difference in the value of the product). He investigated the potash yield at different temperatures. It was found that at 2000° and 16 atmospheres pressure, 93% of the potash could be separated. At higher temperatures higher yields were possible, but it was convenient and more practical to work at the low temperature of 200°. So it should be comparatively simple to design an economically advantageous process along these lines, first removing the potash, then making cement from the remaining mass."

"Many rocks such as granites are buried under the surface of the earth and cannot therefore have given off their gas-content to the air. The gases are still locked up in the stone. If the stone is crushed and pulverized and the powder heated, the gases pass out. So much gas is occasionally present that the stone explodes when it is struck by a hammer. This is true of the red quartz from Branchville, Conn. Similarly granite from Monson, Mass., is let stand some time after quarrying, and little particles of stone often fly at high velocity from its surface as the gas pressure is relieved. The gas content of the Branchville rock is made up of 98% carbon dioxide, the rest nitrogen with a trace of other gases. Granites and gneiss give off gas amounting to 2.5 to 7 times and even up to 18 times their own volume, measured at 18° C. and atmospheric pressure. These gases are mainly hydrogen and carbon dioxide with a little methane, carbon monoxide, nitrogen, and hydrogen sulphide. Water is not generally present, though at times it may be the chief constituent. Gautier calculated that a cubic centimeter of a granite which he investigated gave off 20 liters of gases when heated to 1000° C., and 80 liters of water measured at 1000° and atmospheric pressure. Very often the vapors from volcanoes attack rock masses lying nearby, setting free carbon dioxide from the limestone, and hydrogen sulphide from sulphur compounds," p. 113.

"The flakes of lime that are precipitated by organisms contain a little magnesium, and on the average this amount is one per cent. Many algae remove even more magnesium carbonate, in some cases up to thirteen per cent (according to Högbom). From such material magnesia-limestones are formed. Högbom has further shown that when such rock is weathered by carbonated water, lime dissolves out faster than does magnesium and so the residue approaches nearer and nearer in composition to dolomite, $MgCa(CO_3)_2$. Also water containing magnesium salts in solution can wash calcium carbonate out of limestones and replace it with magnesium carbonate. Dolomite, and dolomite limestones are widely distributed rock material.

"These rocks often contain iron, partly due to the action of plants, which may cause iron carbonate to be precipitated along with the lime and magnesia. Iron carbonate can replace calcium carbonate just as can the magnesium salt when solutions containing iron come into contact with limestones. In this way large areas of iron-spar or siderite (iron carbonate) are formed. In the presence of water containing oxygen this mineral easily changes to limonite (iron hydrate) and this, by the action of heat and pressure, to hematite, $Fe_2O_3$, or to magnetite, $Fe_3O_4$. The remarkable, huge, iron deposits around Lake Superior are believed to have been formed in this way from original deposits of siderite," p. 122.

"If a radium preparation is preserved in a glass vessel this glass becomes colored a dark violet color. When the glass is heated the color disappears. This coloration results from the action of the radiation from the radium, and it develops more rapidly the more rays the preparation sends out. It has been known for a long time that many minerals such as tourmaline and mica display under the microscope dark spots in their layers, which are called 'pleochroic halos,' (places which under polarized light show various colors). Joly in 1907 discovered that these dark places were due to radiations from little, enclosed kernels of radioactive material, containing uranium. From measurements of the size and the uranium content as well as by intensity of the color of these spots, it was determined that these preparations which came from rock of the Devonian period had an age of about 400 million years," p. 124.

"Concern about our raw materials casts its dark shadow over mankind. Those states which lack throw lustful glances at their neighbors, which happen to have more than they use. Still more tempting is the desire for gain from lands on the other side of the seas, inhabited by uncivilized natives, with interest unawakened to guardianship. Historical research of the future will demonstrate how much desire for raw materials was a cause of the recent great misfortune whose effects mankind, or better, the so-called civilized nations, are still undergoing. It is clear that some day we must come to forbid national egotism, equally with the profit-seeking of industries, from seeking a solution of the problem of the proper use of raw materials. Mankind must finally come to the viewpoint that in every possible way it will spare these raw materials for the future and that it will make use in-

stead of the great power for work poured out by the sun above us in apparently undiminishing amount; or else will use the sun indirectly by employing the energy which is collected together in the form of water-flow, and in the green plants; for these are sources which can renew themselves," p. 143.

"Calcium carbonate precipitates from sea water partly as crystalline limestone, as one can see at the mouth of the Rhone river, or along the Florida coast, but by far the greater part is removed by organisms—corals, mollusks and pteropods. Their limy-shells and skeletons contain crystalline calcium carbonate. It is calculated that yearly 2300 million tons of chemical substances are precipitated in the ocean, of which the largest portion, about 1300 million tons consists of calcium carbonate, while of the remaining 1000 million about one-third is silica, which is removed by organisms, and the rest consists of about 280 million tons of magnesium carbonate, 60 million tons of potash, 75 million tons of iron oxide and various other related oxides, and a residue of sulphate, which for the most part becomes reduced to metallic sulphides. The carbon dioxide content of sea water varies with the depth. At the surface it amounts to about 43 mg. per liter. Below the surface it decreases rapidly so that at 50 meters depth (150 ft.) only 34 mg. are present per liter. At the bottom of the great deeps of the sea it again has increased to nearly 47 mg. per liter. One result of this increase in carbon dioxide concentration with great depth is that the flakes and shells of lime which are continually being produced by the organic life in the upper layers are generally dissolved on sinking into the lower layers of high carbonate concentration. At a depth of over 3000 meters (9000 ft.) no pteropod shells are to be found, while the more strongly built shells of globigerina are still present 5000 meters below the surface. On the ocean bottom less and less lime is to be found the greater the depth. At 900 meters the calcium content of the bottom mud is not less than 86%, at 4000 meters it is only 47%, at 6000 meters it is scarcely one percent, and in yet deeper regions there lies a red mud, colored by iron oxide," p. 145.

"In more recent years an experimental station with five mirrors of giant dimensions (60 by 4 meters) has been worked near Cairo, Egypt, with practical results. The builder was an American engineer named Shuman. The steam-pan was horizontal, as was the mirror axis. It was automatically turned so that the mirrors received the greatest possible radiation at all times of day. This plant was studied in 1913 by an authority, Ackermann. He found that its effectiveness was 60 h. p. per acre of earth-surface, over which the mirrors were mounted. The mirrors, in order not to hide one another in the morning and afternoon, must have space three times greater than their own actual open surface. Ackermann believed that the efficiency of these engines could easily be raised to 50%. In this event, and with the cost of construction and operation counted in, a horse power hour would cost about twenty cents and if the energy was changed to electric power this, in Cairo, should cost about 3.5 cents per kilowatt hour. This is a very moderate price. In Stockholm just before the war the price of lighting current was eight cents and power current four cents," p. 170.

"Great tracts of land in the Mediterranean countries, particularly areas near Avignon in France, which for many years previously had made great profit out of the growing of madder root, were forced by the competition of the synthetic product [alizarine] to give up this crop and had to be converted to the growing of other crops, naturally with great economic loss. However, seen from a more general point of view than that of the Avignon madder growers this must be looked upon as a benefit, for a fruitful district was thus returned to the ranks of bread-producing regions.

"Yet greater economic interests were ruined by the successful artificial production of indigo. This most important of all the dyestuffs has been in use from the grey dawn of antiquity by the Egyptians, the Phoenicians, and the Greeks. Indigo can be prepared from many different plants of which the most important is *Indigofera tinctoria*, a plant which originated in the East Indies but today is spread by cultivation into many parts of the tropics, in Asia, Africa and South America. Another indigo plant, *Isates tinctoria*, the *woad*, is much hardier and is to be found growing in Europe as far north as Sweden. It was formerly, especially around the year 1300, an object of intensive cultivation in France and

Germany, but as indigo began to be imported from the East Indies its European cultivation died out. Probably ancient man in Europe used the woad for a blue dye from very early times. The Pictish people of North Britain, when found by the Romans, were in the habit of painting their bodies for battle with woad. Indigo production in India in the past century was one of the most important sources of revenue of that country (and in consequence, of England). In 1897 the total value of natural indigo production was 20,000,000 dollars, and the amount was 6 million kilos of pure indigo, of which 90% came from British India," p. 219.

"The results [of the experiments on synthetic indigo] were most satisfying to the persevering workers. The importation of indigo into Germany sank from a value of fifty million dollars in 1896 to a value of eighty thousand dollars in 1911, while the export from that country for the same period mounted from thirteen to one hundred million dollars in spite of a drop in price to less than one-fifth. At the same time the value of the export of indigo from British India sank from seventeen to one million dollars. At one time the surface given over to the growing of indigo plant in India was not less than 1,480,000 acres," p. 220.

There are a few slips. Arrhenius still believes in the formation of a definite compound with caustic soda, p. 242, when cotton is mercerized. The translator says, p. 62, that bronze is made by adding a little copper to tin instead of the other way round. The proof reading is not very good and the translator shows a true Gallic freedom as to the spelling of proper names. Also, in English we do not speak of the beautiful blue Donau. The book is a very interesting one and Arrhenius preaches enthusiastically the doctrines of conservation.

*Wilder D. Bancroft*

**Farbkunde.** *By Wilhelm Ostwald. 22 × 15 cm; pp. xvi+313. Leipzig: S. Hirzel, 1923.* The book is divided into two parts: the general theory of color; and applications of the theory of color. In the first part the chapters are entitled: history of the theory of color; light; the process of seeing; the dull colors; the color circles; the symmetrical color triangle; the color fields; the doctrine of the color sector. Under applications we find three subdivisions: measurement of colors, with chapters entitled measurement of the dull colors, measurement of the color tint, measurement of the white and black content of the bright colors, and indirect measurements; physical-chemical relations, with chapters entitled the mixture of colors, physical chemistry of pigments and dyes, and the media for colors; psychophysical relations, with chapters entitled the physiology of the eye, color as a means of representation, and the harmony of colors.

Ostwald recognizes eight main colors: yellow, orange, red, violet, ultramarine blue, ice blue, sea green, and leaf green. He omits the orthodox indigo which only very few people see and splits blue and green into two colors each. Each one of these main colors he divides into three, red into vermilion, carmine, and the purple of the dark red roses; and ultramarine blue into the blues of ammoniacal copper solution, of ultramarine, and of the blue of the sky, p. 91. Starting with 3-5% solutions of quinoline yellow, eosine, rose Bengale, wool blue, and Neptune blue, one can duplicate almost any pure color by dipping pieces of white filter paper either into these solutions or into suitable mixtures of them, p. 76.

Ostwald constructs triangular diagrams with white, black, and any pure color in the three corners, p. 94. He calls attention to the great beauty of the clear colors with a good deal of black in them and claims that the beauty of the old church glass is due either to dust which blackens them or to the presence of magnetite in them to darken them. While this is undoubtedly true to a great extent, strine and irregularities in thickness add also to the beauty of the old glass as was shown conclusively by LaFarge.

Ostwald lays great stress on the theoretical significance of what he calls the "Farbenhalb" or color sector, p. 117. The best yellow is not one which transmits only the spectrum yellow; but one which transmits all the light from red to sea-green so that one gets the synthetic yellow from red and green superposed on the spectrum yellow. In other words the important color sector is the one which includes the colors on either side which make the color under discussion when combined.

The color sectors of the warm colors, leaf-green, yellow, orange (which Ostwald calls Kress) and red contain a good deal of white, which one does not notice as such, while the color sectors of the cool colors, violet to sea-green contain a good deal of black. In fact it is the presence of white in the saturated colors of one class and of black in the saturated colors of the other class which gives rise to the terms warm and cool.

Ostwald points out, p. 126, that when one mixes two complementary colors by means of a rotating disc, the resulting white is spread over twice the surface and is therefore actually gray. If colored lights are mixed, one can get either white or gray, according to the background. On p. 186 Ostwald shows that the colors from orange to blue all move towards the green on dilution while red moves towards the violet. Ostwald believes strongly in five-color printing as against three-color printing, p. 192, if one wishes to reproduce colors satisfactorily.

On p. 202 Ostwald states that white lead is a mixture of lead carbonate and lead hydroxide, and that the two can be distinguished under the microscope. This is of course a mistake. White lead is basic lead carbonate. The commercial pigment may contain an excess of lead carbonate or of lead hydroxide; but that is not what Ostwald said. The reviewer also finds it impossible to accept Ostwald's remarks on luster, p. 36. "Most actual surfaces lie between the two extremes of complete specular reflection and completely matte surfaces. If the specular reflection is recognizable, one calls the surface lustrous, the luster increasing with the amount of specular reflection. Fatty luster, vitreous luster, adamantine luster, and metallic luster are arranged in the order of increasing specular reflection."

Warm glazing colors remain transparent even in thick layers while the black in cold glazing colors makes them look black in thick layers, p. 207. Ostwald proposes to take as the standard of reduction with white the amount of zinc oxide which must be added to one gram of a pigment to give an optical white content of fifty percent. This will be 0-30 with the mineral pigments and may run over 1000 with the dyes, p. 212.

When a pigment is ground, there is a grain size for which the color is most intense, because too much white is reflected when the pigment surface is increased too much. It follows from this that the pigments which can stand the most reduction with white can stand the finest grinding. For cobalt glass the most effective grain size is 0.5-1.0 mm.

Ostwald is an authority on the theory of colors; but he slips up when he talks about dyeing, p. 247. Basic and acid dyes are not colloidal and they don't dye cotton direct. Substantive dyes do dye cotton direct and are in colloidal solution. No one would guess from what Ostwald says that sodium sulphate acts in three ways with the three classes of dyes: basic, acid, and substantive. There is another unfortunate statement on p. xvi. "The blue color of the sky is due to physical and not to special chemical causes. All earthly objects on the other hand show chemical colors." Ostwald has forgotten or never known about the blue feathers of birds, the moonstones, the iridescent feathers, the temper colors on steel, etc.

Ostwald lays down the general rule, p. 271, that in all fields of art law is harmony. "In a book entitled "The Harmony of Forms," which appeared in 1922, I tried out the experiment thoroughly. The classification was found to cover all the previous laws of ornamentation and of beautiful forms as they have been worked out by artists during thousands of years and it also enabled the prediction of an infinite number of beautiful forms which the creative phantasy of all the people in all times had not originated, and there was not a single ugly one among them," p. 273.

It is often said by dressmakers and decorators that white and black harm no colors. Otswald takes issue with this, p. 282. He claims that white goes well only with the bright clear colors. One can combine white with pink or sky blue, with vermilion or ultramarine blue; but one cannot combine white with bottle green, a blackish blue, or a yellow containing black. One corollary is perhaps subject to the decrees of fashion. "Another case is that children and very young girls can wear white while it is not suitable as the chief color for older women. The reason for this is that from about twenty-five years on the skin becomes darker due to increase of coloring matter in the surface cells, and this increasing amount

of black makes the complexion appear muddy when contrasted with white, whereas colors containing more black make the skin appear clearer."

Conversely, black goes well only with colors which are poor in white. Since red is the one of the bright colors which can most easily be obtained in a deep shade with a low white content this accounts for the fondness people have for combining black and red.

*Wilder D. Bancroft*

**A System of Physical Chemistry.** *Vol. II. Thermodynamics. Fourth edition. By W. C. McC. Lewis. 22 × 15 cm; pp. viii+489. New York and London: Longmans, Green and Co., 1925. Price: $4.75; 15 shillings.* Whilst all chemists who are not faddists agree that a knowledge of Thermodynamics is useful and even necessary in a proper understanding of the modern science, they will also admit that perhaps no other branch of the subject offers such difficulties to the average student. It may not be impossible that these difficulties are introduced by a particular treatment of the subject. By avoiding terse and clear-cut statements, adopting a discursive style, interpolating explanatory paragraphs to break up an argument, and returning to a subject again and again after having given the impression that it has been brought to a conclusion, modern thermodynamics might conceivably be robbed of its main terror, that of being a science capable of leading, by strictly logical development from two general laws of experience to a great number of special results without the aid of loose analogical or ingenious but shaky hypotheses. There is little doubt that a logical way of treating the subject is distasteful to the average student of chemistry and the author of a successful textbook will, in the interests of popularity, be careful to avoid it.

Professor Lewis's book is too well known to need description. In its fourth edition he has made certain slight alterations and has added new sections which much enhance its value. A readable account of recent American work is given, but European contributions are not altogether neglected. In some cases the treatment has been made rather stricter, notably in the direction of the equation of maximum work. Whilst this is perhaps desirable on scientific grounds it will reduce to some extent the popularity of the book, since the new treatment is rather more difficult to follow than the old, although more accurate. No attempt is made to preserve a consistent set of symbols throughout, but although this might puzzle a mathematical student it will perhaps enhance the clearness of the work to a student of chemistry. This result is also inevitable if the author's practice of quoting original papers almost *verbatim* is followed. The symbols are always clearly defined.

Sections which may be especially commended are those on electromotive force, on activities (in which the recent memoir of A. A. Noyes on the Debye-Hückel theory is reproduced *verbatim*), theory of membrane equilibria, and chemical affinity. A special feature is the inclusion of modern work, and numerical results are freely quoted. This makes the book very useful for reference purposes. Whilst it has not the wealth of numerical data of Lewis and Randall, nor the strict but arid mathematical elegance of Gibbs, it succeeds in giving the impression, by a skilful interweaving of theory with the results of experiment, that thermodynamics is a living science of great value to chemists. This is a really praiseworthy achievement, for which the author deserves, and will receive, the congratulations of his fellow-chemists.

*J. R. Partington*

# THE CHEMICAL ACTION OF $\alpha$ PARTICLES ON ACETYLENE

BY W. MUND AND W. KOCH

Having found in previous work[1] that acetylene gas when mixed with radon is slowly converted into a pale yellow powder, we investigated further[2] by a simple method the rate of such polymerization. The quantitative results were worked out:

1. Knowing the number of $\alpha$ particles emitted by a given quantity of radon with equilibrium amounts of RaA and RaC (1 curie gives $3 \times 1.772 \times 10^{10} (1 - e^{-\lambda t})$ particles.

2. Taking into account the partial absorption of the $\alpha$ particles by the walls, RaA and RaC being wholly deposited.

The formula we used[3] rested upon the validity of Geiger's ionization law. We calculated thus that, at 0°C and at a pressure of about 70 cm. of mercury, every $\alpha$ particle emitted by radon (range 3.94 cms.) brings about the condensation of $4.38 \times 10^6$ gaseous molecules. The total ionization along the path of an $\alpha$ particle in acetylene being $2.13 \times 10^5$, it follows that for each ion, 20.5 molecules fall out.

As S. C. Lind[4] first suggested, the ratio M/N is often near unity, M being the number of reacting molecules and N the number of ions produced. This led M. Bodenstein[5] to correlate the radiochemical reactions which follow the rule with his primary photochemical reactions. In the case of acetylene, however, the M/N ratio is much larger than in most other primary reactions, though much smaller, indeed, than in the HCl synthesis, which Bodenstein compares with a photochemical secondary reaction. Thus arose the question to which class the acetylene polymerization would belong from other points of view, namely, as regards the influence of oxygen, pressure and temperature.

## I. The Influence of Oxygen

A system of two identical bulbs, $B_1$ and $B_2$, surrounded by melting ice was connected by a U shaped tube, which acted as a differential manometer, Fig. 1. Acetylene was admitted, its pressure being at first equal on both sides. While mercury in connection with $B_1$ was kept at constant height, its level slowly rose in the other branch of the manometer as soon as a known quantity of radon had been introduced into $B_2$ (by a device not shown on Fig. 1). The difference of height being h and the difference of volume $V - V'$, the pressure in $B_2$ reduced to constant volume is expressed by

$$P' = (P - h)\, V'/V$$

[1] Mund and Koch: Bull. Soc. chim. Belg. 34, 119 (1925).
[2] Bull. Soc. chim. Belg. 34, 241 (1925).
[3] Mund: Ann. Soc. scient. Bruxelles, 64, 336 (1925).
[4] Lind: J. Phys. Chem. 16, 564 (1912).
[5] Bodenstein: Z. physik. Chem. 85, 390 (1913).

The experiment was started without any oxygen in $B_2$. At time $t_1$ and $t_2$, the pressures $P'_1$ and $P'_2$ were noted showing (c.f.i.) that $4.07 \times 10^6$ molecules condensed per $\alpha$- particle (of range 3.94 cm). The agreement with former experiments is close enough to exclude accidental disturbance.

The same experimental contrivance (not shown in Fig. 1) that had provided for the introduction of radon, was now used to bring into $B_2$ about 8 cm³ of air (i.e., 2 cm³ of $O_2$). As will be seen from the table below, the decrease of pressure is at first slightly accelerated. After a few hours, however, it proceeds at its primitive rate. Counting time from the introduction of the air, we found between $t_1 = 8h.10'$ and $t_2 = 21h.30'$, a rate of condensation of $4.22 \times 10^6$. Between $t_1 = 10h.40'$ and $t_2 = 31h.15'$ after a second introduction of air we found $4.17 \times 10^6$.

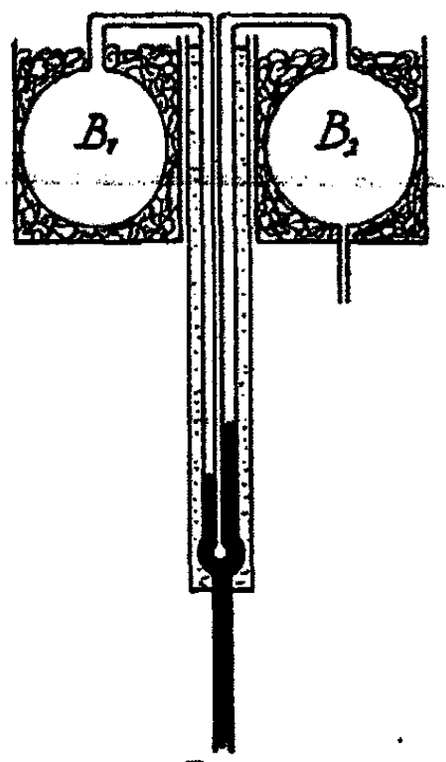


FIG. 1

The small increase of reaction velocity just after the addition of air might easily be explained. The air entering $B_2$ at a temperature of about 20°C, cools down and contracts. Further on, part or totality of its oxygen will perhaps be adsorbed as one knows that cuprene does retain large amounts of it.

Let M be the number of $C_2H_2$ molecules condensing and L the number of $\alpha$-particles which—running undisturbed through the whole range (of 3.94 cm. in air)—would supply such ionization or chemical effect as really happened in $B_2$. The number M of molecules brought into reaction by each of these $\alpha$-particles will be

$$m = M/L$$

M is a product of three factors: (1) the proportional decrease of pressure; (2) the number of gram-molecules in $B_2$; (3) the Avogadro number (as given by R. Millikan). Thus:

$$M = \frac{P'_1 - P'_2}{P'_1} \times \frac{V P'_1 273}{22412(273+t)76} \times 6.06 \times 10^{23}$$

Putting $V = 550$ cm³ and $t = 0$

$$M = (P'_1 - P'_2) \times 1.957 \times 10^{20}$$

L is given by

$$L = N_0 (1 - e^{-\lambda t})F$$

$N_0$ is the number of radon atoms present at the outset ($t - 0$) and is equal to $1.772 \times 10^{16}$ times the initial number of curies. F is calculated from the following formula which takes account of the $\alpha$-particles from RaA and RaC as well as of the absorption undergone by $\alpha$-particles hitting the wall. Let r, r', r'' be the ranges of $\alpha$-particles from radon, RaA, RaC, respectively. As long as the diameter 2 R of the bulb $B_2$ exceeds r'', we have:

$$F = \left\{ 1 + \tfrac{1}{2}\left(\frac{r'}{r}\right)^{2/3} + \tfrac{1}{2}\left(\frac{r''}{r}\right)^{2/3} - \frac{9r + 3\left(\frac{r'}{r}\right)^{2/3} r' + 3\left(\frac{r''}{r}\right)^{2/3} r''}{20\,R} + \frac{81}{3520}\left(\frac{r}{R}\right)^{3} \right\}$$

In air at 0°C and normal pressure $r = 3.94$; $r' = 4.50$; $r'' = 6.57$.
The stopping power of acetylene amounts to 112/100.

$$F = 2.249 - 0.989\, r/R + 0.023\, (r/R)^3.$$

The range r should be calculated from the mean pressure
$P_m = 0.5\,(P'_1 + P'_2)$ by the relation

$$r = \frac{3.94}{1.12} \times \frac{76}{P_m} \times \frac{273}{273 + t} \quad (t = 0)$$

This involves no other assumption than inverse ratio between the range and the number of molecules encountered per cm by the *a*-particle.
$N_0 = 1.0146 \times 10^{15}$ (0.05726 curie); $P = 67.65$.

| Time: t | Corrected pressure: P′ | m |
|---|---|---|
| $t_1 = 47.50$ hours | 64.23 cm. | $4.07 \times 10^6$ |
| $t_2 = 43.75$ | 63.86 | |
| (first introduction of air) | | |
| $t_3 = 44.00$ hours | 65.06 cm. | |
| $t_4 = 44.42$ hours | 64.98 cm. | |
| $t_5 = 44.75$ " | 64.90 " | |
| $t_6 = 45.33$ " | 64.77 " | |
| $t_7 = 46.08$ " | 64.64 " | |
| $t_8 = 46.90$ " | 64.55 " | |
| $t_9 = 47.75$ " | 64.42 " | |
| $t_{10} = 49.25$ " | 64.17 " | |
| $t_{11} = 51.92$ " | 63.74 " | $4.22 \times 10^6$ |
| $t_{12} = 65.25$ " | 61.74 " | |
| (second introduction of air) | | |
| $t_{13} = 65.70$ hours | 62.86 cm. | |
| $t_{14} = 66.17$ " | 62.75 " | |
| $t_{15} = 66.90$ " | 62.66 " | |
| $t_{16} = 67.80$ " | 62.55 " | |
| $t_{17} = 70.25$ " | 62.24 " | |
| $t_{18} = 73.47$ " | 61.77 " | |
| $t_{19} = 75.93$ " | 61.46 " | $4.17 \times 10^6$ |
| $t_{20} = 96.50$ " | 59.03 " | |

## II. Influence of Pressure

As the decrease of pressure owing to the progress of the reaction amounts easily to 40% (with the size of bulb $B_2$ and the radon at our disposal), it will suffice to run the experiment a fairly long time (without adding air) in order to ascertain the effect of changing pressure. The following data refer to an experiment which lasted 17 days. Though fluctuating, the values of m do

not vary in a systematic manner. It may thus be said that the rate of reaction is not appreciably affected by change of pressure. (At very low pressures recoil atoms would of course play their rôle.)

$N_0 = 1.022 \times 10^{15}$ (0.0661 curies); P = 67.75 cm.

| Time t | | Corrected Pressure P′ | | m |
|---|---|---|---|---|
| $t = 0$ | hours | 67.75 cm. | ..... | $4.24 \times 10^6$ |
| $t_1 = 24.66$ | " | 62.33 | ..... | $4.17 \times 10^6$ |
| $t_2 = 48.16$ | " | 58.27 | ..... | $4.33 \times 10^6$ |
| $t_3 = 72.00$ | " | 54.83 | ..... | $4.30 \times 10^6$ |
| $t_4 = 121.16$ | " | 49.73 | ..... | $4.27 \times 10^6$ |
| $t_5 = 167.66$ | " | 46.62 | ..... | $4.45 \times 10^6$ |
| $t_6 = 239.50$ | " | 43.52 | ..... | $4.23 \times 10^6$ |
| $t_7 = 312.00$ | " | 41.88 | ..... | $4.67 \times 10^6$ |
| $t_8 = 409.08$ | " | 40.63 | ..... | |

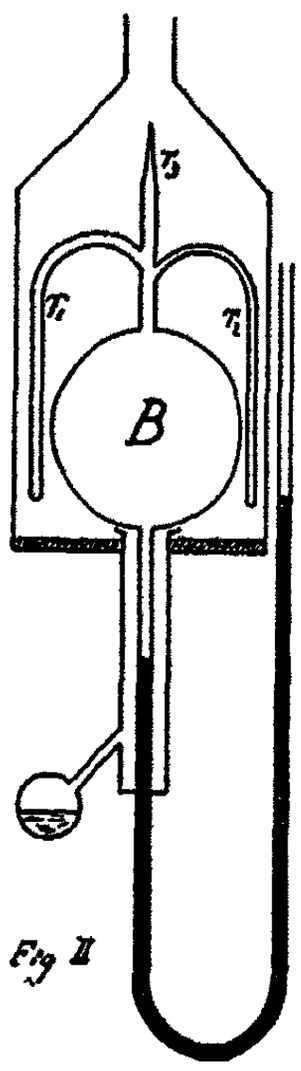



FIG. 2

### III. Influence of Temperature

Our apparatus[1] (Fig. 2) was an open air manometer connected with a glass sphere B (R = 3.40 cm.) In the upper part of this sphere ended:

1. Two small pieces of glass tubing, bent downwards, and closed at the other end; one of them, $T_1$, immersed in liquid air, held an adequate quantity of $C_2H_2$ in the condensed state. The other, $T_2$, contained a known amount of well-purified radon enclosed under a capillary column of mercury.

2. A drawn-out tube, $T_3$, connecting B with a Langmuir vacuum pump.

The bulb, B, having been evacuated, the tube $T_3$ was sealed off, and the tube $T_2$ was heated till all the mercury boiled over to B causing the radon to diffuse. Then the liquid air was withdrawn allowing the acetylene in $T_1$ to evaporate and to fill B at nearly atmospheric pressure.

The bulb B, along with the tubes, $T_1$, $T_2$ and $T_3$ and the copper part of the manometer tube, was then kept at 100°C by means of a steam bath securing a very good constancy of temperature. Pressure measurements at 100°C having been completed, the steam was removed and another set of readings was taken at 20°C and at 0°C.

The volume of the sphere B was only 164 cm³, but taking into account the capacity of $T_1$, $T_2$, $T_3$ and of part of the manometer stem, the total volume V of the gaseous mixture amounted nearly to 190 cm³. The initial and final pressure, $P_1$ and $P_2$, of every measurement were given by the manometer, the

[1] For full details see Mund and Bogaert: Bull. Soc. chim. Belg. **39**, June (1925).

atmospheric pressure being read at the same time on a good mercury barometer.

The number m was calculated as before by the relation $m = M : N_o(1 - e^{-\lambda t}) F$.

In the experiment at 100°, the factor F could be calculated by the formula applying when $2R > r''$, but at 20°C and at 0°C the pressure was so far reduced as to require another formula fitting the conditions $r'' > 2R > r'$, namely:

$$F = 1 + \tfrac{1}{2}\left(\frac{r'}{r}\right)^{2/3} + 1/2\left(\frac{r''}{r}\right)^{2/3} - \frac{9r + 3\left(\frac{r'}{r}\right)^{2/3} r' + 3\left(\frac{r''}{r}\right)^{2/3} r'' - 3\left(\frac{r''-2R}{r}\right)^{2/3}(r'' - 2R)}{20\,R} + 81/3520\ (r/R)^3$$

In every case, however, the factor F had to be corrected owing to the fact that 26 cm³ (i.e., 13.6% of the total volume of 190 cm³) did not belong to the sphere B but were contained in narrow shaped glass tubes. This resulted in a loss of ionization which could be estimated and for which allowance was made by reducing the factor F to 9/10 of its value. It will be gathered from the results that change of temperature as well as of pressure has but little, if any, influence on the reaction velocity.

$N_o = 8.1725 \times 10^{14}$ (0.04612 curie)

| Time | Pressure | Temperature | m |
|---|---|---|---|
| $t_1 = 12.16$ hr. | 87.18 cm. | 100°C | $4.17 \times 10^6$ |
| $t_2 = 20.16$ " | 73.68 | " | " |
| $t_3 = 20.75$ " | 65.63 | 20°C | $4.28 \times 10^6$ |
| $t_4 = 44.33$ " | 59.08 | " | " |
| $t_5 = 60.75$ " | 49.94 | 0°C | $4.41 \times 10^6$ |
| $t_6 = 67.92$ " | 48.86 | " | " |

## Conclusions

I. No variation exceeding experimental error could be detected in number of molecules of acetylene polymerized per pair of ions produced in the system (1) at different pressures; (2) at different temperatures; 0°C, 20°C, and 100°C; and (3) in the presence of small quantities of air.

II. Taking the general mean value of eleven measurements (without oxygen) obtained in this study and two concordant measurements previously reported, the ratio of the number of molecules of acetylene polymerized per pair of ions produced ($-MC_2H_2/N$ total) is 20.2.

*Louvain*
*Laboratory of Physical Chemistry*
*of the University,*
*September, 1925.*

# THE INFLUENCE OF IONS CARRYING THE SAME CHARGE AS THE DISPERSED PARTICLES IN THE INVERSION OF EMULSIONS

BY S. GHOSH AND N. R. DHAR

In previous papers[1] we have emphasised that the stability of a sol depends a great deal on the adsorption of ions carrying the same charge as the sol. We have also suggested that ions carrying the same charge as an emulsion influence the stability of the emulsion markedly. In this paper we shall show that ions carrying the same charge as the emulsoid particles have a considerable influence on the inversion of the type of an emulsion.

The investigations of Lewis,[2] Ellis,[3] Powis[4] and others show that the emulsoid particles are charged and that their stability depends upon the electric potential at the surface of the globules, just as colloids remain suspended due to their electric charge.

Powis studied the effect of KCl, $K_4$ Fe(CN)6, $BaCl_2$ $AlCl_3$ and $ThCl_4$ on the velocity of oil particles dispersed in water under an electric field. For the pure emulsion, the velocity, of the particles first increased when KCl or $K_4Fe(CN)_6$ was gradually added and with greater amounts of these electrolytes it fell. A similar maximum was observed by Ellis in the presence of 0.001N NaOH. On the other hand, the velocity of the oil globules gradually fell when $BaCl_2$, $AlCl_3$, or $ThCl_4$ were added and finally they moved in the opposite direction showing a reversal in charge. Similar results were obtained by Powis using $As_2S_3$ sol and KCl, Kruyt[5] with $As_2S_3$ sol and KCl, and Freundlich and Zeh[6] with $As_2S_3$ sol and $K_4$ Fe(CN)$_3$, and with Fe(OH)$_3$ sol and $\left[\left(NH_3\right)_4 Co\left\langle \begin{matrix} NH_2 \\ OH \end{matrix} \right\rangle Co\left(NH_3\right)_4\right]Cl_4$ where first an increase in velocity was observed on the addition of the electrolytes.

We have already indicated that this increase in velocity is a direct consequence of the adsorption of an ion carrying the same charge as the suspended particles on the addition of these electrolytes, in spite of the fact that there exists an electric repulsion due to the sameness of the electric charge. Let us consider the fate of an electrolyte say KCl, when added to a negatively charged colloid. Now, if the tendency for adsorption of similarly charged Cl′ ions is greater than the force of repulsion due to the sameness of electric charge, the charge on the colloid particles will increase as chloride ions are adsorbed, when small quantities of KCl are added. This increase in velocity, however, reaches a limit when the adsorption of chloride ions is maximum and

[1] Ghosh and Dhar: J. Phys. Chem., 29, 435 (1925); Ghosh, Bhattacharya and Dhar; Kolloid-Z. (1925).

[2] Phil. Mag. (6) 15, 509 (1908).

[3] Trans. Faraday Soc. 2, 14 (1913).

[4] Z. physik. Chem. 89, 91 (1914).

[5] Kolloid-Z. 22, 81 (1918).

[6] Z. physik Chem. 114, 65 (1924).

the adsorption of the oppositely charged K ion increases. If, however, the adsorption of chloride ions cannot counter-balance the repulsive effect due to the sameness in electric charge we may not get any marked increase in the velocity of the colloid particles in an electric field, but the fall in the velocity of the colloid particles when KCl is added to the sol will not be rapid. On the other hand, if the adsorption of similarly charged chloride ions is comparatively small or nil, the fall in the velocity of the colloid particles will be rapid on the continued addition of small quantities of KCl.

Consequently, from the results of Powis we can infer that oil particles in water are negatively charged and appreciably adsorb ions carrying the negative charge from such electrolytes as KCl, $K_4Fe(CN)_6$, etc.

It has already been indicated that emulsions closely resemble colloidal suspensions. From the existing literature we find that emulsions behave abnormally towards electrolytes on dilution that is become more stable towards electrolytes on dilution. This behavior is certainly due to the adsorption of ions carrying the same charge as the oil globules. It is expected therefore that such emulsions would also show (i) abnormality towards a mixture of electrolytes i.e. show an antagonistic effect when coagulated by a mixture of electrolytes of varying valency, and (ii) the phenomenon of acclimatization.

Bhatnagar's[1] results on the coagulation of aniline emulsion show that it becomes stable on dilution towards electrolytes such as KCl, $BaCl_2$ and $Al_2(SO_4)_3$. His results are given in Table I.

TABLE I

| Electrolyte added | | Time of Perceptible Change in Emulsion | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Grms equivs. per litre | | Emulsion | | Twice diluted | | Three times diluted | | Four times diluted | |
| | | Mins: | Secs. | Mins. | Secs. | Mins. | Secs. | Mins. | Secs. |
| KCl | (a) 0.1 | 41 | 0 | 56 | 1 | 115 | 5 | 133 | 10 |
| | (b) 0.139 | 12 | 8 | 20 | 5 | 41 | 0 | 63 | 9 |
| $BaCl_2$ | (a) 0.029 | 10 | 0 | 18 | 7 | 27 | 5 | 40 | 0 |
| | (b) 0.040 | 2 | 0 | 4 | 6 | 7 | 0 | 13 | 2 |
| $Al_2(SO_4)_4$ | (a) 0.002 | 10 | 0 | 11 | 1 | 13 | 5 | 15 | 9 |
| | (b) 0.005 | 2 | 0 | 2 | 53 | 3 | 58 | 7 | 2 |

We have shown that with all the suspensoids so far studied in this laboratory the tervalent $Al'''$ ion always behaves normally towards dilution. Thi- behavior of $Al'''$ ion with aniline emulsion will be discussed later on.

In the following pages more evidence will be advanced in favour of the view that an emulsion can adsorb an ion or a micelle carrying the same charge as the emulsiod particles and it will be shown that our generalisation already referred to is more or less followed by emulsions.

Very little systematic work has been done on the coagulation of emulsions by electrolytes. Hence it is difficult to draw very definite conclusions regarding the effect of anions on the precipitation of an emulsion.

[1] J. Phys. Chem. 25, 735 (1921).

It is obvious that when an emulsion is formed of two immiscible liquids say water and oil, it is possible to get two kinds of emulsion viz, (i) oil dispersed in water and (ii) water dispersed in oil. The existence of such two types of emulsions has been recognised by Ostwald,[1] Robertson[2] and other. Bancroft[3] has shown that sodium oleate emulsifies oil in water and calcium oleate emulsifies water in oil. The systematic work of Newman,[4] Briggs and Schmidt,[5] Clowes[6] and others on the inversion of oil-in-water emulsion to water-in-oil type has thrown considerable light on this question.

Clowes has shown that an oil-in-water emulsion produced in the presence of sodium soap can be inverted into water-in-oil emulsion by the addition of a calcium salt. The transformation of an oil-in-water emulsion to a water-in-oil emulsion by means of a calcium salt has been followed microscopically. It is noted that the oil globules in water are first distorted, then elongated and as the critical point for inversion of phases approaches the Brownian movement is very marked, and finally on complete conversion of the system into an emulsion of water in oil, the Brownian movement of these oil particles dispersed in water entirely ceases. From these observtions it can be concluded that at the critical point of the inversion of the type the coagulation of oil-in-water emulsion has set in and that the emulsion is extremely unstable.

It seems that up till now very little attention has been paid to the question of charge on emulsoid particles. Several workers have shown, however, that the usual charge on the suspended oil particles is negative. We are of the opinion that when the electrolytes like KCl, NaCl, etc., are added to such an emulsion, at first preferential adsorption of the negative ions takes place and consequently the negative charge on the oil globules increases. If the concentration of such electrolytes is increased the influence of the oppositely charged ion becomes more prominent and the charge on the oil globules is neutralised and is followed by the coalesence of the oil globules to form bigger drops and separation into two layers. This phenomenon is the same as the coagulation of a sol by the addition of an electrolyte.

It is interesting to note that reversion of emulsion oil-in-water to water-in-oil hardly takes place with KCl, NaCl, etc., but phase-reversal of oil emulsions takes place readily with bivalent and trivalent cations and H ions. Consequently, we are of the opinion that in water-in-oil emulsion the dispersed water particles are positively charged. This is further supported by the observation of Bancroft that in the presence of sodium or potassium oleate oil-in-water emulsion is obtained, whilst in the presence of calcium or magnesium oleate water-in-oil emulsion is formed. Moreover Bhatnagar[7] has obtained phase-reversal of water-in-oil by KOH, $K_3PO_4$, etc.

---

[1] Kolloid-Z. 6, 103 (1910); 7, 64 (1910).
[2] Kolloid-Z. 7, 7 (1910).
[3] "Applied Celloid Chemistry," 267 (1921).
[4] Phys. Chem. 18, 34 (1914).
[5] J. Phys. Chem. 19, 478 (1915).
[6] Proc. Soc. Exp. Biol. Med. 11, 1 (1913); J. Phys. Chem. 20, 407 (1916).
[7] J. Chem. Soc. 129, 1760 (1921).

This is due to the fact that the oil particles have a tendency to adsorb oleate ions and pass into negatively charged oil-in-water emulsion, whilst water particles have a tendency to adsorb $Mg^{\cdot\cdot}$ or $Ca^{\cdot\cdot}$ ions and pass into positively charged water-in-oil emulsion. There are certain points of resemblance between the phase-reversion of emulsion and charge-reversal of colloids. It is well known that the charge reversal of a sol usually takes place by a bivalent or a polyvalent ion or $H^{\cdot}$ or $OH'$ ions; similarly, reversion in phase of emulsion also occurs with bivalent and polybalent ion or $H^{\cdot}$ and $OH'$ ions. Let us see what happens when $CaCl_2$ is added to an emulsion of oil-in-water. The $Ca^{\cdot\cdot}$ ion will be adsorbed by the particles of the oil on charge-neutralisation and coalesence of the oil globules will take place. Just before the separation of the substances in two layers, the water particles, which have a greater affinity for $Ca^{\cdot\cdot}$ ions than that of oil particles for the same ion, will take up $Ca^{\cdot\cdot}$ ion and pass into positively charged water particles forming a water-in-oil emulsion, provded the system is shaken well. This is possibly the mechanism of phase-reversal of an emulsion by a polyvalent ion. It is evident that in the case of charge reversal of a sol only the charge on the suspended particles is changed, whilst in the case of phase reversal the dispersed phase is different in the two conditions.

Clowes showed that in the case of emulsions of olive oil in water stabilised by NaOH, the addition of $CaCl_2$ leads to the inversion of the type. Table II gives the results obtained by Clowes with olive oil emulsion containing free oleic acid.

TABLE II

| Vol. of M/10 NaOH added. c.c. | Vol. of M/10 $CaCl^2$ employed. c.c. | | | |
|---|---|---|---|---|
| | 0.25 | 0.5 | 0.75 | 1.0 |
| 1 | R | W-O | W-O | W-O |
| 2 | O-W | R | W-O | W-O |
| 3 | O-W | O-W | R | W-O |
| 4 | O-W | O-W | O-W | R |

O-W = Oil-in-water emulsion.
W-O = Water-in-oil emulsion.
R = Critical (inversion) point.

These results show that the greater the concentration of the added NaOH the, greater is the amount of $CaCl_2$ required to bring about the inversion of the emulsion. On plotting the logarithims of NaOH added as abscissae and the logarithims of the corresponding amounts of $CaCl_2$ to bring about the inversion of the emulsion as ordinates, we find that the graph is a straight line, showing that the adsorption formula of Freundlich,[1] $x/m = KC^n$, where $x$ = the amount adsorbed by $m$ grams of the adsorbent, $C$ = concentration of the solution and $k$ and $n$ are constants, is strictly followed. This therefore, simply proves that the stabilisation of the oil-in-water emulsion is due to the adsorption of $OH'$ ions from NaOH or oleate ions from sodium oleate formed by the action of NaOH and free oleic acid.

[1] Kolloid-Z. 3, 212 (1908).

Clowes has also shown that the adsorption of ions is the underlying factor in emulsion equilibrium. Besides $CaCl_2$ Clowes has observed that bivalent salts of Mg,$^{\cdot\cdot}$ Sr$^{\cdot\cdot}$ and Ba$^{\cdot\cdot}$ and trivalent salts of Al$^{\cdot\cdot\cdot}$ and Fe$^{\cdot\cdot\cdot}$ exert an effect similar to that of Ca$^{\cdot\cdot}$, whilst KOH, LiOH, etc., may be substituted for NaOH.

The effect exerted on emulsions by KCl, NaCl, sodium citrate, etc., is very interesting. It has been observed by Clowes that NaCl in small quantities promotes the formation of emulsions of oil-in-water and improves the dispersion of the oil, so that more $CaCl_2$ is necessary to bring about the inversion of the emulsion in the presence of small amounts of NaCl. Apparently this has to be ascribed to the preferential adsorption of negatively charged Cl$'$ ions from NaCl by the negatively charged emulsoid particles or by the soap film adhering to the oil particles. He has also shown that when NaCl is added to an emulsion up to a concentration of 0.1M preferential adsorption of chloride ions takes place and thus facilitates the formation of oil emulsion and dispersion of oil globules. At higher concentrations of NaCl the adsorption of negative ions in excess to that of positive ions does not occur to the same extent, and at 0.35 M to 0.40 M NaCl the emulsion separates in two layers; that is, coagulation sets in.

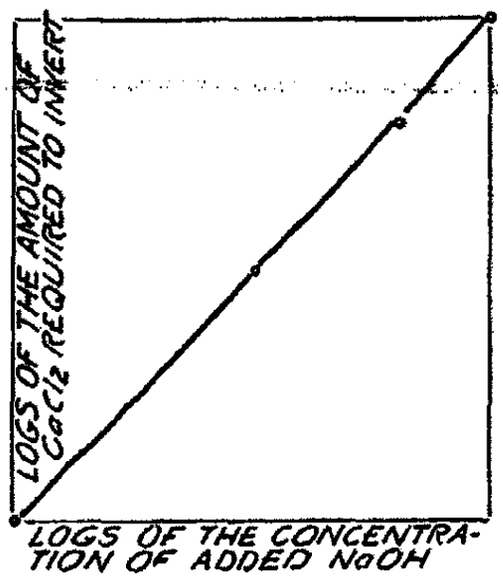



FIG. 1

These observations of Clowes are in support of our postulation that (i) stability of the sols and emulsions towards dilution when coagulated by certain electrolytes (ii) antagonistic effect observed on coagulation towards a mixture of electrolytes and (iii) the phenomenon of acclimatization are all due to the adsorption of an ion carrying the same charge as the suspended particles and are essentially connected and go hand in hand. It is well known that when $As_2S_3$ sol[1] is coagulated by a mixture of KCl and $BaCl_2$, LiCl, and $BaCl_2$, etc., the previous addition of KCl or LiCl makes the sol stable, and more of $BaCl_2$ is necessary to bring about coagulation than when $BaCl_2$ coagulates the sol alone. In a previous paper we have observed that this is due to the adsorption of chloride ions by $As_2S_3$ sol from KCl, when added in small quantities, in spite of the fact that there exists an electric repulsion due to the sameness in the electric charge. As the amount of KCl added is gradually increased the adsorption of chloride ions reaches a maximum. On the further addition of KCl, the adsorption of K ions greatly exceeds that of the chloride ions and the sol is finally coagulated by KCl. It is, therefore, obvious that a point of maximum stability exists as KCl is gradually added to the sol. From the experiments of Linder and Picton, Weiser and others, it will be seen that the amount of $BaCl_2$ or $SrCl_2$ necessary for the

[1] Linder and Picton: J. Chem. Soc. **67**, 67 (1895); Weiser: J. Phys. Chem. **25**, 665 (1921); Ghosh, Bhattacharya and Dhar: loc. cit.

complete coagulation goes on increasing with the increase in the concentration of KCl up to a limiting value. After this limiting value is attained if the concentration of KCl is further increased the amount of $BaCl_2$ or $SrCl_2$ necessary for complete coagulation gradually diminishes.

From these results a very interesting point has been drawn out in a previous paper.[1] It is well known that keeping the amount of the adsorbent constant, the greater the concentration of the electrolyte which will be adsorbed the greater is the amount of adsorption. Now, as the concentration of the electrolytes KCl, LiCl, etc. is increased the adsorption of Cl ions goes on increasing and thus the sol becomes more and more stable. We expected that up to this maximum stability the Freundlich exponential formula for adsorption should be followed, where the concentration of KCl added may be roughly taken as the final concentration of the electrolyte and the excess of $SrCl_2$ necessary for coagulation in the presence of KCl as the amount proportional to the adsorption of chloride ions. Beyond this maximum stability the adsorption of K ions becomes more prominent and, therefore, the adsorption formula need not be followed. We have shown that on plotting a graph with Linder and Picton's result by taking the logarithims of the excess of $SrCl_2$ necessary for complete coagulation as ordinates and the logarithims of the amount of KCl added as abscissae a straight line is obtained. This proves conclusively that chloride ions are preferentially adsorbed by $As_2S_3$ sol. The similar graph obtained for the inversion of oil-in-water emulsion by $CaCl_2$ in the presence of NaOH shows that this stabilisation of the emulsion in presence of NaOH is not materially different from that of $As_2S_3$ sol in the presence of KCl, though more markedly.

Clowes has classified electrolytes into two main groups (1) promoting dispersion of oil-in-water salts of monovalent cations Li, Na, K, etc., alkalies, salts of divalent and trivalent anions, (2) promoting dispersion of water-in-oil—salts divalent and trivalent cations Ca, Ba, Sr, Fe, Al, etc. It has been already indicated that the system water-in-oil may be looked upon as coagulated oil-in-water emulsion, and therefore can be compared to a jelly, where water is dispersed in the continuous solid phase.

Hardy[2] believed that the concentrated gelatine jellies consisted of drops of water suspended in a gelatine-rich phase. Many workers are, however, of the opinion from the ultramicroscopic observations that jellies have a sponge structure and not a honeycomb structure peculiar to emulsion jellies, where water is the dispersed phase; but it is now believed that we cannot distinguish between the two cases by means of the ultramicroscope.[3]

If we regard a water-in-oil emulsion as coagulated oil-in-water emulsion, salts like NaCl, KCl, $K_4Fe(CN)_6$ etc., promote the formation of the emulsion oil-in-water due to the adsorption of similarly charged ions like $Cl,'$ $Fe(CN)_6'''$ etc., whilst the salts of bivalent and trivalent cations can easily coagulate

[1] Ghosh and Dhar: J. Phys. Chem. 29, 435 (1925).
[2] Z. physik. Chem. 33, 326 (1900).
[3] Compare Bachmann: Kolloid-Z: 23, 89 (1918).

the oil particles and help the dispersion of water particles as a positively charged water-in-oil emulsion.

Clayton[1] has also observed that monovalent salts like KCl, NaCl, etc., help the emulsification of oil in water. He has observed that 1% NaCl greatly facilitates the formation of margarine emulsion in water. This is ascribed by Clayton to the adsorption of chloride ions from NaCl and subsequent liberation of NaOH, which forms soap with the free oleic acid already present. Similar effects of monovalent cations have been observed by Ayres[2] and Herschel[3] on the formation of oil-in-water emulsion. We are of the opinion that in all these cases the charge on the oil particles and the degree of dispersions are increased due to the adsorption of small quantities of Cl′ ions. Briggs[4] on the other hand has observed that NaCl possesses no emulsion-producing property with benzene.

Recently Rosner and Narrat[5] have shown that a 25 cc mixture of rape oil and mineral oil forms a stable emulsion with 25 cc of sea water, where water forms the continuous phase. The emulsion is fairly stable showing that the emulsification is greatly helped by the NaCl of sea-water. Increase in the amount of sea water is unfavourable towards emulsification. Harkins and Keith[6] have also shown that the addition of potassium iodide or sodium chloride decreases the size of the dispersed oil particles; and this shows that an oil emulsion is stabilised by the addition of monovalent electrolytes due to the adsorption of the similarly charged anions.

The experiments of Parson and Wilson[7] are also of much interest from this point of view. Using emulsions of pure mineral oil 'Nujol' in the presence of a dilute sodium oleate solution, they found that 0.22 M NaCl and 0.24 M $Na_2SO_4$ are necessary to precipitate an oil emulsion and separate it into two layers. It will be seen that if the concentration of these electrolytes are expressed in equivalents far greater quantities of $Na_2SO_4$ are required to precipitate the emulsion than NaCl, which points to the fact that anions have a marked effect on the precipitation of the negatively charged emulsions. They have also studied the inversion of oil-in-water emulsion to water-in-oil emulsion by various electrolytes. Aqueous solutions of $MgSO_4$, $MgCl_2$, $FeSO_4$, $Al_2(SO_4)_3$ and $FeCl_3$ were used. With magnesium salts no absolutely sharp inversion point was found, but, rather, a time-period of instability during which inversion took place. Complete inversion took place with trivalent electrolytes. This shows that the trivalent cations are more effective precipitants and invertors of type than Mg; consequently, more magnesium salts are necessary to bring about the inversion in the type of the emulsion.

The first effect observed on adding a magnesium salt was to lower the viscosity of the oil-in-water emulsion. This was followed by an increase in

[1] "Margarine," 72 (1920).
[2] Chem. Met. Eng. 22, 1061 (1920).
[3] U. S. Bur. Standards, Tech. Papers No. 86, 17 (1917).
[4] J. Ind. Eng. Chem. 13, 1009 (1921).
[5] "Petroleum," 19, 611 (1923).
[6] Science, 59, 463 (1924).
[7] J. Ind. Eng. Chem. 13, 1119 (1921).

viscosity, with oil appearing as the external phase. The initial drop in the viscosity of the oil emulsion can be attributed to the adsorption of ions carrying the same charge as the emulsion and consequent increase in the degree of dispersion. In a recent paper Dhar has emphasised that, keeping other variables constant, the increase in charge on suspended particles in water results in the partial dehydration so that there is a fall in viscosity which is intimately connected with the amount of bound and free water. Such initial drop in the viscosity on the addition of small quantities of electrolytes like NaOH, KCl and NaCl to sodium palmitate solution has been observed by Farrow.[1] On the addition of more electrolyte the viscosity increases very rapidly. More or less similar results have been obtained by Woudstra[2] with $Fe(OH)_3$ sol, though less markedly. It has been observed by Clowes that chloride ions are appreciably adsorbed by soap films from NaCl solution and McBain and Salmon[3] have also observed that both Cl′ and OH′ ions are adsorbed by soap. The increase in viscosity is certainly due to the coagulation of the sol with the increasing concentration of the electrolyte and the subsequent abstraction of the free water by the coagulam. It is therefore, clear that an increase in viscosity on the addition of magnesium salts to 'Nujol' emulsion is due to the dispersion of water-in-oil medium and this can be compared with a jelly of the so called 'hydrophile colloids' in which water is dispersed in the solid medium.

Bhatnagar[4] has made several experiments on the inversion of the two types of emulsion by electrolytes. It has been observed by him that the greater the concentration of KOH the greater is the amount of $Ba(NO_3)_2$ required to complete the inversion. On plotting a graph with his results, it is found that the Freundlich exponential adsorption formula is strictly followed as has been already shown with the results obtained by Clowes. Bhatnagar has got the following order Al > Cr > Ni > Pb > Ba > Sr, Ca, Mg beginning with the cation possessing the greatest influence on the inversion of phase. The coagulating power of these cations with $As_2S_3$ sol as obtained by Linder and Picton[5] is in the order Al > Pb > Ba > Sr > Ca, Mg > Ni beginning with the cations possessing the highest coagulating power.

It will be interesting here to consider some results of Bhatnagar[6] on the effect of dilution towards the inversion of the type of emulsion by different electrolytes with a paraffin-in-water emulsion.

Amount of sodium oleate in each sample = 0.101 millimole

| 20 cc emulsion | $BaCl_2$ in millimole at the inversion point | $Al_2(SO_4)_3$ in millimole at the inversion point |
|---|---|---|
| Standard emulsion. | 0.050 | 0.015 |
| " (twice diluted) | 0.0798 | 0.025 |
| " (thrice diluted) | 0.112 | 0.040 |
| " (four times diluted) | 0.156 | 0.057 |

[1] J. Chem. Soc. **101**, 347 (1912).
[2] Kolloid-Z. **8**, 73 (1911).
[3] J. Chem. Soc. **119**, 1369, 1374, 1669 (1921).
[4] J. Chem. Soc. **119**, 61, 1760 (1921).
[5] Burton: "Physical Properties of Colloid Solutions," 158-160 (1920).
[6] J. Chem. Soc. **119**, 61, 1760 (1921).

The results in the above table indicate that greater the dilution of the emulsion the greater is the concentration of the electrolytes necessary to bring about an inversion in phase. The most striking point observed in these results is that more abnormality is observed with $Al^{...}$ ion than with $Ba^{..}$ ion. The concentration of $BaCl_2$ required to invert the phase of four times diluted emulsion is about three times the concentration of $BaCl_2$ required to invert the strongest emulsion, whilst the concentration of $Al_2(SO_4)_3$ required to invert the phase of the diluted emulsion is about four times the concentration of $Al_2(SO_4)_3$ required to invert the strongest emulsion. This peculiar behaviour of $Al^{...}$ ion cannot be easily explained from the point of view that the stability of a sol entirely depends upon the increase in distance between the particles on dilution. This view advanced by Kruyt and Spek,[1] Mukherji and coworkers[2] and others indicates that the effect will be more marked with $K^{.}$ ion, less with $Ba^{..}$ ion, and still less with trivalent $Al^{...}$ ion. Kruyt and Spek, Burton and Bishop[3] and others have observed that on diluting a collodial solution more of uni-valent salts like KCl, NaCl, etc., are necessary to coagulate a dilute sol than a concentrated one and the amount of tervalent ions from salts like $AlCl_3$, $CrCl_3$, required to coagulate a sol decreases with the decreasing concentration of these electrolytes, whilst practically constant amounts of such salts as $BaCl_2$, $SrCl_2$, etc., are necessary to coagulate a strong or a dilute sol.

We are of the opinion that the results of Bhatnagar do not support the view that the stability of an emulsion is due to an increase in the distance between the dispersed particles. The following explanation, which is based on the assumption that the abnormal dilution effect, i.e. more of an electrolyte is necessary to coagulate a dilute sol or emulsion than a concentrated one is a direct consequence of the adsorption of an ion carrying the same charge as the sol or emulsion, can satisfactorily explain the behaviour of $Ba^{..}$ and $Al^{...}$ ion. When an electrolyte say AB is added to a sol or an emulsion carrying a negative charge, it is well known that if it can adsorb the anion B′ carrying the same charge as the sol or emulsion appreciably, it will tend to increase the stability of the sol or emulsion and the process will follow the ordinary adsorption law. Now, if the sol is diluted twice, it is well known that the amount of adsorption of the anion B′ is always greater than half the amount of adsorption by the concentrated sol or emulsion, consequently the amount of adsorption of anion B′ adsorbed by an unit mass of the suspended matter is greater for the dilute sol or emulsion than the concentrated one. The dilute sol or emulsion is, therefore, stabilised to a greater extent than the concentrated one due to the greater adsorption of anion B′. Hence, more of an electrolyte is necessary to coagulate a dilute sol than a concentrated one in the presence of AB if the anion B′ is appreciably adsorbed and stabilises the sol.

The following experiments with silver sol prepared by Kohlschütter's method will show that more abnormality is observed in the presence of an

[1] Kolloid-Z. 25, 3 (1919).
[2] J. Chem. Soc. 115, 461 (1919).
[3] J. Phys. Chem. 24, 701 (1920).

alkali. It is well known that AgOH is not completely decomposed by hydrogen and free OH ion is always present, which peptises the sol.

Concentration of the sol = 0.08 grm of Ag per litre Sol A = 4 cc made up to 8 cc; volume = 8 cc.

Immediate change in colour is observed.

| Concentration of the sol. | $KNO_3$ N/8 c.c. | $KNO_3$ N/8 in presence of 0.1 c.c. NaOH N/5. |
|---|---|---|
| A | 0.8 | 1.2 |
| 3A/4 | 0.9 | 1.4 |
| A/2 | 1.0 | 2.10 |

From this table it will be seen that the amount of $KNO_3$ required to coagulate the sol increases with the decreasing concentration of the sol, but the phenomenon is more marked in the presence of NaOH which is known to stabilise the sol in small quantities.

It has already been observed that in the presence of KCl, $KNO_3$, etc., more $BaCl_2$ or $AlCl_3$ is necessary to coagulate the sol of $As_2S_3$. This antagonistic effect of KCl towards $BaCl_2$ has been ascribed by us to the adsorption of chloride ions carrying the same charge as the sol from KCl. It has been already shown that more of chloride ions are adsorbed by a dilute sol than a concentrated one; consequently, the antagonistic effect of KCl towards $BaCl_2$ or $AlCl_3$ will be more marked with a diluted sol of $As_2S_3$ than a concentrated one. This has been already shown by Sen[1] that the antagonistic effect of NaCl towards $CaCl_2$ is more marked for the dilute sol than the concentrated one.

We have already cited in this paper that NaOH or soap exert an antagonistic effect on the inversion of an oil emulsion by $Ba(NO_3)_2$. Briggs[2] has shown that soaps are markedly adsorbed by benzene-water interface and it is clear that this adsorption will be more marked when the emulsion is diluted; consequently, more marked antagonism will be observed with a diluted emulsion than a concentrated one, so that more of an electrolyte is necessary to invert a dilute emulsion than a concentrated one.

The abnormal behaviour of $Al'''$ ion towards the coagulation of aniline emulsion is more due to the peptising effect of $OH'$ ion obtained from the dissolved aniline than due to the adsorption of the ion carrying the same charge as the emulsion from $Al_2(SO_4)_3$ because the concentration of $SO''_4$ ion is very small. Now, when an aniline emulsion is diluted the amount of $OH'$ ions in a given volume of the emulsion increases because more of aniline dissolves due to an increase in the amount of water phase. It is well known that $OH'$ ions stabilise a negatively charged emulsion and the phenomenon is more marked with a diluted sol than the concentrated one. This is the probable explanation of the abnormal behaviour of $Al'''$ towards dilution of aniline emulsion as observed by Bhatnagar.

[1] Private communication.

[2] J. Phys. Chem. 19, 210 (1915).

Bhatnagar has studied the effect of various soap solutions on the stability of paraffin oil emulsions and his results indicates that soaps can be arranged in order of their protective effect. It is found from his results that the stability of the emulsion increases with the increase in the concentration of the added soap and that on allowing for experimental errors straight lines are obtained when the logarithims of the concentrations of the soap solution are plotted as ordinates and the logarithims of the corresponding of amounts of the electrolytes required to bring about the inversion as obscissae.

This shows that here we are dealing with the pure adsorption phenomenon and subsequent stabilisation due to the adsorption of the highly colloidal soap micelles. It will be interesting at this stage to describe the experimental results of Briggs on the adsorption of soap in the interface between benzene and water. Briggs has shown that the amount of soap adsorbed agrees fairly well with Freundlich's adsorption formula. It is, therefore, certain that the formation of an oil-in-water emulsion depends upon the adsorption of the highly charged soap micelles, just as $Fe(OH)_3$ is peptised to a celloidal solution by an acid due to the preferential adsorption of hydrogen ions. The greater peptising effect of a soap solution than that of an alkali is due to the colloidal nature of soap. It has been shown by us[1] that an adsorbent like $BaSO_4$ can adsorb colloids in greater quantities than molecules or ions from molecular solutions.

In a recent paper Seifriz[2] has studied the reversibility of hydrocarbon oil emulsions prepared from hydrocarbons of varying densities. It has been shown that heavier petroleum oils form water-in-oil emulsion in the presence of casein. The author has observed that the relative potency of ions in their ability to reverse the stable water in oil type to oil in water type is in the order $Na(OH) > Ba(OH)_2 > Th(NO_3)_4 > Al_2(SO_4)_3$, whilst NaCl and $BaCl_2$ cannot reverse the type at all. Seifriz concludes from these results that there is nothing to suggest the effect of valency of electrolytes on emulsions. On careful consideration we find that the above order of the electrolytes is quite reasonable as will be evident from the following point of view:

It is well known that the stability of a suspensoid or an emulsion is chiefly due to the electric charge on the suspended particles. It is, evident that the greater inverting influence of either NaOH or $Th(NO_3)_4$ is certainly due to the marked adsorption of $OH'$ or of polyvalent $Th''''$ ions by the particles of oil. The experiments of Powis in which he has shown that $Th''''$ ions can reverse the charge of oil globules has been already cited. NaCl and $BaCl_2$ on the other hand possess no marked inverting effect because chloride ions are not so markedly adsorbed as $OH'$ ions and the other cations are also not as effective as $Th''''$ ion. It is quite probable that the oil-in-water emulsion obtained with an hydroxide is negatively charged and that obtained with $Th(NO_3)_4$ or $Al_2(SO_4)_3$ is a positively charged emulsion.

---

[1] Compare Ghosh and Dhar: Kolloid-Z. 35, 144 (1924).

[2] J. Phys. Chem. 39, 587 (1925).

## Summary

1. It is shown that an oil emulsion closely resembles a colloidal suspension and the generalisations advanced for a sol is followed by an emulsion.

2. The separation of oil-in-water emulsion into two layers can be regarded as the coagulation of the dispersed oil globules. The reversal of phase of oil-in-water is probably the dispersion of water particles carrying a positive charge in the oil.

3. From the experimental results of various workers it is concluded that salts like NaCl, KCl, Na citrate, NaOH, etc., favour the formation of an emulsion of the type oil-in-water. This shows that anions viz, Cl′, Cit‴, OH′, etc., are appreciably adsorbed by the oil globules.

4. It has been deduced that the adsorption of the anions is mainly responsible for the antagonism observed between the electrolytes of monovalent cations like NaCl, KCl, NaOH, etc., towards salts of bivalent and trivalent cations like $Ba(NO_3)_2$ $AlCl_3$, $Al_2(SO_4)_3$, etc., on the inversion of an oil emulsion.

5. It is shown that the (a) abnormal dilution effect i.e. more of an electrolyte is necessary to coagulate a dilute emulsion than a concentrated one and (b) the antagonistic effects observed between salts of monovalent cations and bivalent cations on the inversion of the types of the emulsion are essentially connected and go hand in hand. This generalisation has already been advanced by us in a series of papers for ordinary sols.

6. It has been emphasised that the stability of an oil emulsion in the presence of soaps mainly depends on the electric charge of highly adsorbed soap micelles.


*Chemical Laboratory,*
*University of Allahabad,*
*Allahabad, India.*
*June 24, 1925.*

# GEL STRUCTURE*

BY WILLIAM C. ARSEM

## Introduction

Gels are of very common occurrence and of great importance biologically and technically. Practically all the tissues of living matter have gel structure, and the study of the behavior and properties of typical animal and plant gel-forming substances is assuming ever increasing importance.

Gel phenomena occur in the great industries of soap, leather, rubber, celluloid, paint, varnish, textiles, bread, glass, lubricants, photography and many others. Important problems of these industries are related to the swelling and shrinkage of gels, and their reversible or irreversible transformations into other states of aggregation.

## Historical

There still exists considerable disagreement as to the number and relationship of the phases in a gel. Many writers appear still to hold the view that a gel is a homogeneous system. The evidence for this view is discussed by Katz.[1] Other investigators consider a gel to be a heterogeneous system composed of two mingled phases, either liquid-liquid or solid-liquid. Wo. Ostwald held that a gel was made up of two liquid phases, but this view now seems untenable. No two-phase emulsion is known which has the properties of a gel. Hatschek[2] has shown mathematically that the elastic properties of gels are not easily accounted for by this type of structure. The two-phase solid-liquid theory is very old, and many variants of it have been advanced. Thus various writers have pictured the solid phase as having a honeycomb, network, sponge or fibrillar structure.

Bütschli (1902) tried to render gel structure visible by the microscope, and described a foam-like appearance which is presumed by others to have been simply an optical effect. Ultramicroscopic study beginning with the work of Zsigmondy (1912) has shown that many gels are apparently without structure, but that in some cases where structure is seen, the solid phase is not a honeycomb, but a mass of straight fibrils intersecting and joined at their points of intersection. This structure has been observed in gels of soap, barium malonate and fibrin.

J. O. W. Barratt[3] has shown that fibrils in a solution of fibrinogen can be made to increase by growth at the expense of the liquid until a diameter of 1 $\mu$ has been reached. On the other hand all gels which show a structure under the ultramicroscope are not fibrillar. Gelatine and cellulose appear to consist of minute portions joined in a somewhat irregular manner according

---

*Read at Milwaukee meeting of American Chemical Society Sept. 1923.

[1] Kolloidchem. Beihefte, 9, 1-182, (1917).

[2] Trans. Faraday Soc. 12, 17 (1917).

[3] Trans. Faraday Soc. 16 appendix, p. 49, (1920-1921).

to Harrison[1] who photographed them with a Zeiss cardioid condenser using direct sunlight. The fibrils in soap gels are probably crystalline. Gelatinous crystals can also be observed in the gels obtained from concentrated solutions of benzopurpurine and chrysophenine. (Harrison[1]).

Evidences of slow crystallization in gelatin gels and silica gels have been observed by S. C. Bradford[2]. Zsigmondy[3] believed that silica gel had an extremely fine porous structure with amicroscopic pores. The adsorption and drying isotherms of silica gel in presence of water, alcohol and benzene were studied by J. S. Anderson[4] who considered that his results might seem to indicate the existence of pores with a diameter of 2.62 to 5.55 $\mu\mu$.

## The Nature of Gels

The view which I wish to present is as follows:

A normal gel consists of two phases which may be distinguished and designated as

a. The associated phase
b. The free phase

The associated phase is a single large molecule having the same shape and volume as the entire mass of the gel. It is made up of molecular units held in combination by the same kind of forces as those which function in the formation of a crystal lattice. (The term "molecular unit" is used for the grouping of atoms corresponding to the empirical formula. For example, NaCl is the molecular unit from which the large molecule or crystal $(NaCl)_n$ is built up, and $SiO_2$ is the molecular unit of the associated phase of silica gel.) These forces are, in fact, the residual valences of the molecular units. The associated phase differs from a normal crystal lattice in that the molecular units are irregularly oriented, only a fraction of the residual valences are employed in holding the structure together, and the lattice is, in consequence, much expanded and contains an extremely large number of voids of approximately molecular unit dimensions. The associated phase is thus conceived as an attenuated or expanded solid.

The free phase permeates the associated phase and fills the voids in it. In special cases, molecules of the free phase substance may take part in forming the lattice structure of the associated phase just as water does in hydrous crystals.

A normal gel may also be regarded as a uniformly porous, imperfect crystal filled with a fluid; or as an intimate mixture of two continuous phases, one solid, the other fluid, the solid phase being continuous in the special sense indicated.

## Types of Gel

We may distinguish two types of gel, the special characteristics of which will be made clear in the discussion which follows.

---

[1] Trans. Faraday Soc. 16 appendix, p. 37, (1920-1921).
[2] Trans. Faraday Soc. 16 appendix, p. 56, (1920-1921).
[3] Z. anorg. Chem. 71, 356 (1911).
[4] Z. physik. Chem. 88, 191 (1914).

1. Normal gels, which have a uniform space distribution of the molecular units of the associated phase, with voids of approximately molecular dimensions.

2. Segregated gels, which have a non-uniform distribution of the units of the associated phase, which consequently has a relatively coarse structural framework in which the voids are much larger than molecular dimensions.

## Effect of Progressive Association on a Dissolved or Dispersed Substance

*The formation of crystals.*

In a solution, the dissolved substance is completely dispersed in single molecular units or small aggregates having an association factor not far from unity. If the solution is saturated, and a change of condition is made which tends to cause separation of the solute, then progressive association of molecular units occurs through the union of residual valences. If conditions favor crystallization, normal crystal lattices are built up, and solid crystals result. This is especially true when concentration of the solution proceeds slowly, and its viscosity is low. Thus, R. W. Moore[1] was able to produce large perfect crystals of Rochelle salt by regulated cooling of a saturated solution. Such conditions favor the building of a perfect lattice, and large crystals tend to form.

If these conditions are departed from, there is a tendency toward irregular arrangement of the units in the building up of the lattice, the crystals are irregular, twinned, hopper-shaped, etc., and mother liquor is included. The inclusion of water in a crystal is some evidence of departure from the regular close-packed arrangement of atoms which is characteristic of a normal lattice, with the consequent formation of voids filled with liquid. A crystal containing included liquid may contain a certain proportion of gel structure.

*The formation of gels.*

In many cases when a substance separates from solution, conditions do not favor the building of a normal and regular crystalline lattice structure. This is especially true when the substance has a high molecular weight or great complexity, or when the solution from which it separates is greatly supersaturated. Many proteins, proteoses and carbohydrates form gels readily because their large and unsymmetrical molecular units do not orient themselves regularly upon separation from solution, so that an expanded lattice is built up with its units irregularly arranged and not closely packed.

When a normally insoluble substance like $SiO_2$, $Fe_2O_3$, $Al(OH)_3$, etc. is produced by a chemical reaction the velocity of separation from the supersaturated solution may prevent regular orientation and cause gel formation.

## Irreversible Changes in the Solid Phase

*Syneresis.*

The structural arrangement of units in a gel is inherently unstable. A further condensation of the associated phase is possible through the re-orienta-

[1] J. Am. Chem. Soc. 41, 1060 (1919).

tion of units, the release of loosely combined molecules of the liquid phase, and the union of previously non-functioning residual valences. If complete re-orientation of all units is possible, the associated phase eventually becomes crystalline and the gel reverts to a mixture of crystals and free liquid. Syneresis may be defined as shrinkage of the solid phase caused by progressive association and re-orientation of molecular units.

*Segregation.*

The associated phase of a normal gel may undergo segregation instead of shrinkage. When this occurs, the molecular units may gather into groups, the configuration of which will depend on the structure of the units. Such substances as soaps with long chainlike molecules might be expected to segregate into threadlike groups and thus produce the fibrillar framework which has been observed. The elements of this framework, the fibrils themselves, may still have normal gel structure, which must necessarily be richer in associated phase than the original gel. If segregation continues, the framework may shrink still more and fracture at numerous places to make possible the formation of such aggregates as curds, clots and precipitates which are more concentrated than the original gel.

## Reversible Changes in the Solid Phase

*Stiffening and softening.*

These changes in rigidity of the solid phase are due to changes in the proportion of free residual valences. They are essentially dissociation phenomena. A gel with a given concentration of associated phase may exist in a whole range of modifications characterized externally by different degrees of rigidity. This is because the proportion of residual valences of the solid phase substance which function as lattice-forming bonds may vary in accordance with the thermal history of the sample, and with the presence or absence in the free phase of substances capable of fixing these bonds, and thus preventing lattice formation. Such changes in rigidity may be brought about by temperature changes, H or OH ions, certain salts, dehydrating agents, and by mechanical means.

## Reversible Changes involving both Phases

*Swelling and shrinkage.*

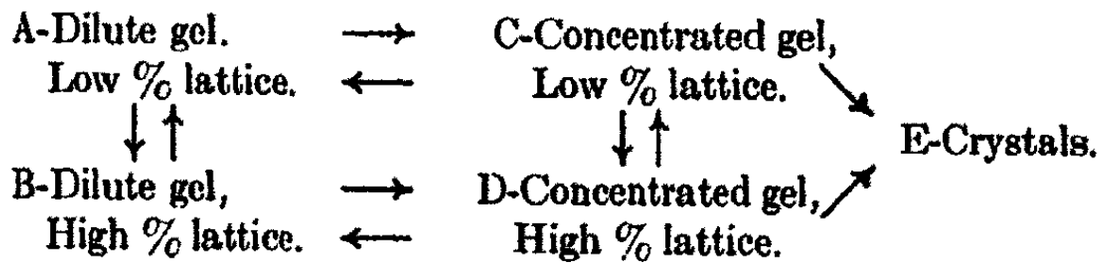
In order to explain the swelling process it is necessary to have some theory of the process of solution. When a crystalline substance goes into a true solution, it seems permissible to suppose that the lattice-forming residual valence bonds are separated and appropriated by the superior combining power of the solvent molecules, so that the crystal structure is entirely broken down and the molecules individually dispersed. In a gel, however, some of the residual valences function permanently as lattice bonds while others remain free and can hold or release molecules of free phase in accordance with surrounding conditions. Swelling, then, is the result of the combination of the molecules of a fluid with the free valences of a gel lattice.

The effect of hydrogen ion concentration on the degree of swelling of amphoteric gels like gelatin may be explained thus. On the acid side of the isoelectric point the amphoteric union of $NH_2$ and COOH is broken when the basic group is fixed by the anion of the added acid, leaving the equivalent amount of COOH free to take up water molecules, and vice-versa.

## Relations and Transformations of Gel States

The associated phase may have all possible degrees of rigidity, and the gel may contain varying percentages of the free phase. In consequence, gels may exist with all degrees of rigidity from relative fluidity as in a cellulose nitrate solution, to high rigidity as in a glass, asphalt, or resin. Often a gel may be modified so as to have any desired rigidity by altering the proportions of the phases or by changing the temperature. Silica gel[1] exists in dilute forms which will flow, and in concentrated forms which are brittle and can be powdered. In cellulose nitrate "solutions" the fluidity decreases rapidly with increase of concentration and there is a definite yield value. The transition from viscous to plastic flow occurs at concentrations less than 1% according to work of W. L. Hyden quoted by Bingham.[2] On warming a solution of cellulose nitrate in acetone, the friction in terms of shearing force becomes zero at 43°C, so that above this temperature such solutions are true fluids, while below it they are soft solids.[3] Certain other gels probably have erroneously been considered to be sols because of their mobility. Such mobile gels still act like solids in many respects. For example, a hot 10% solution of gelatine can not be mixed with a hot 2% solution of agar.[4]

To make clear the relations of gel states as indicated by the lattice theory, we may consider the diagram:




Examples of these types are:

A. Warm dilute gelatin "solution". Most of lattice-forming bonds free, and gelatin in sol or solution state chiefly.

B. Cold dilute gelatin gel, completely set.

C. Warm concentrated gelatin "solution."

D. Cold concentrated gelatin gel, completely set.

The changes A $\rightleftarrows$ C and B $\rightleftarrows$ D are usually reversible, and involve both phases. They can be carried out by drying or swelling processes, and are accompanied by characteristic changes in rigidity. There is probably no

[1] Van Bemmelen: "Die Absorption", 196, 214, 232 (1910).
[2] "Fluidity and Plasticity", 291 (1922).
[3] Bingham: "Fluidity and Plasticity", 243 (1922).
[4] Beijerinck: Kolloid-Z. 7, 16 (1910).

change in the number of lattice-forming bonds. A familiar example is the drying or swelling of pieces of gelatin jelly by evaporation or absorption of water.

The changes A $\rightleftarrows$ B and C $\rightleftarrows$ D are changes in the associated phase involving the number of lattice-forming bonds. They are reversible in some cases and not in others. As examples of reversible changes may be cited the effect of temperature changes on gelatin jellies, cellulose nitrate "solutions", asphalts, pitches, gums and resins.

The effects of temperature changes on gels bears an interesting relation to their effects on crystalline bodies. When a pure simple substance crystallizes by freezing, there is no gel structure in the liquid phase, and a sharp separation of solid from liquid occurs. When a melted gel is cooled, however, lattice structure begins to form throughout the mass long before the material as a whole becomes solid. This accounts for the indistinct melting point of a gel-forming substance.

Probable examples of irreversible changes A $\longrightarrow$ B and C $\longrightarrow$ D are: the coagulation of albumen by heat, the thickening of drying oils by heat, and the hardening of synthetic resins of the Bakelite type.

There are many examples of irreversible gel formation in which an additional reagent is involved, among which may be mentioned the vulcanization of rubber in which sulphur assists the formation of a gel lattice by linking the molecular units together; also the setting and drying of oils in paints and varnishes, in which oxygen plays a similar role.

By mechanical working, rubber can be depolymerized. In this way many of the residual valence unions of the lattice are broken by stresses which exceed the elastic limit, and thus the pseudo-solid associated phase of the gel is broken into smaller aggregates in the same way that an ordinary solid is pulverized by grinding.

An example of the change D $\longrightarrow$ E is the devitrification of a glass. Another possible example is the crystallization of a metal or alloy under repeated stresses.

*Schenectady, N. Y.*

# THE APPARENT VISCOSITY OF SOLUTIONS OF NITRO COTTON IN VARIOUS SOLVENTS

BY J. W. McBAIN, C. E. HARVEY, AND L. E. SMITH

The object of the present investigation, which has extended over the past six years, was to study all the factors which affect the viscosity of nitro cotton in various solvents with a view to testing the suggestion of H. Schwarz[1] that comparative fluidity is a criterion of solvent power—a suggestion which accords with the results of later workers and ourselves. The course of the investigation has increasingly emphasized the favorable effect upon solvent power of suitable admixtures so that frequently an ordinary specimen of solvent may owe a large part of its solvent power to impurity. The work has resulted in a definite theoretical conception of the processes operative in the formation of solutions and jellies of such substances as nitro cellulose.

The most important previous investigation was that of F. C. Baker[2]. Whereas Baker, probably relying upon the earlier work of C. Piest[3] had assumed that the viscosity of a solution of nitro cellulose in various solvents exhibited a definite value, A. M. Bakr and C. S. Salmon and R. D. Reid, in this laboratory in 1919, found that all the factors enumerated below affect viscosity. Thus, the viscosities previously recorded refer only to particular solutions of a given unspecified history, and change in conditions may alter their magnitude several fold.

We must emphasize at the outset that, if the technique of measurement is sufficiently standardized and the various factors suitably controlled, the apparent viscosity of a solution of nitro cotton is definite and the results are reproducible by different experimenters within a few per cent. The apparent viscosity is not a true viscosity because it is not independent of the rate of shear; nevertheless the value of the results is only slightly impaired by the fact that they are not universal constants but subject to correction when the conditions are widely varied. Such results will be shown to be both useful and significant.

## Table of Contents

I. General experimental information on method, units and materials.
II. Factors which influence apparent viscosity of a sol of nitro cotton.
  1. Concentration.
  2. Temperature of measurement.
  3. Method, period and temperature of preliminary drying of nitro cotton.
  4. Previous mechanical treatment.

[1] Kolloid-Z., 12, 32-41 (1913); J. Soc. Chem. Ind., 32, 191 (1913).
[2] J. Chem. Soc., 103, 1653-1675 (1913).
[3] Z. angew. Chem., 24, 968-972 (1910).

5. Temperature of preparation of the solution.
6. Exposure to light.
7. Actual specimen of nitro cotton (nearly all the experiments here recorded refer to one specimen).
8. Purity of solvent; impurities and admixtures with other solvents and non-solvents.
9. Nature of solvent.
10. Degradation of nitro cotton.
11. Age of the solution.
12. Temperature of storage of solution.

III. Effect of preliminary treatment with acetone or aqueous acetone.
IV. Alcohol as a solvent.
V. Properties more or less parallel with solvent power.
VI. General Summary.
VII. General Conclusions.

## I. General Experimental Information on Method, Units and Materials

*a. Materials.*

For most of the chemicals used we are indebted to Messrs. Nobel's Explosives Co., Ltd. In a number of cases, successive samples were supplied and more stringent precautions were taken in purifying them, so that in most cases our latest measurements refer to the purest obtainable materials. Increasing purity definitely impaired the solvent power of most of these solvents and greatly increased the viscosity of nitro cotton therein. Furthermore, it was found that, in keeping specimens of solvents for a few years, in most cases, the viscosity of solutions made from them became less, evidently through slight decomposition. A few of the solvents were procured from British Houses and a few from Kahlbaum, and one sample of diethyl phthalate from Eastman Kodak Co.

Table I gives a list of the solvents used and indicates the constants of the purest samples received from each source.

*b. Preparation and storage of solutions.*

There is no apparent limit to the concentrations of these solutions which can be made up, but above 10% they are quite solid.

The method of preparation of a solution greatly affects its whole subsequent history. For instance, even the order of mixing has its effect. When nitro cotton is placed in an empty tube and solvent added the nitro cotton (where wetted) almost instantaneously turns to a hard lump of jelly which frequently sticks obstinately to the glass, requiring long continued violent shaking to dislodge and dissolve it. For the same reason a narrow neck or corners must be avoided in the tube used for the preparation as they provide

TABLE I

Densities and viscosities of pure solvents used. (Temp. 55°C)

| Chemical | Firm | Date supplied | Date measured | Density $D^{55°}_{4°}$ | Viscosity (poises) |
|---|---|---|---|---|---|
| Acetone | Purified | 1924 | 1924 | 0.7865 | 0.003039 (25°) |
| Acetophenone | Nobels | 6/11/22 | 1924 | 1.000 | 0.0103 |
| Benzophenone | Nobels | 2/4/25 | 1925 | 1.081 | 0.04647 |
| Benzophenone | Kahlbaum | 1925 | 1925 | 1.081 | 0.04688 |
| Benzyl formanilide | Nobels | 16/2/25 | 1925 | 1.100 | 0.1163 |
| Benzyl phenyl urethane | Nobels | 12/3/24 | 1925 | 1.076 | 0.1096 |
| Diethyl phthalate | Nobels | 1923 | 1924 | 1.087 | 0.04184 |
| Diethyl phthalate | Kodak | 1925 | 1925 | 1.087 | 0.04180 |
| Ethyl formanilide | Nobels | 1924 | 1925 | 1.024 | 0.02418 |
| Ethyl phenyl urethane | Nobels | 1923 | 1924 | 1.013 | 0.02760 |
| Formanilide | Nobels | 1/5/24 | 1925 | 1.114 | 0.08794 |
| Formanilide | B. D. H. | 1924 | 1924 | 1.114 | 0.08624 |
| Form-o-toluidide | Nobels | 2/2/22 | 1924 | 1.086 | 0.1291 |
| Methyl phenyl urethane | Nobels | 8/8/23 | 1924 | 1.012 | 0.0255 |
| Methyl cyanilide | Nobels | 6/11/22 | 1924 | 1.040 | 0.02037 |
| Methyl ethyl ketone | Purified | 1924 | 1924 | 0.8013 | 0.004976 (25°) |
| Nitrobody | Nobels | 1922 | 1922 | 1.392 | 0.0787 |
| Ortho-tolyl urethane | Nobels | 1924 | 1925 | 1.061 | 0.07425 |
| Ortho-tolyl oxamic ester | Nobels | 1922 | 1922 | 1.126 | 0.1566 |
| Phenyl urethane | Nobels | 1923 | 1925 | 1.085 | 0.8535 |
| Phenoxyacetic ester | Nobels | 1922 | 1924 | 1.071 | 0.0262 |
| Triacetin | Nobels | 1922 | 1925 | 1.119 | 0.04790 |
| Triphenyl phosphate | Nobels | 22/2/22 | 1922 | 1.202 | 0.0950 |

One sample of nitro cotton was used throughout. It was prepared by Messrs. Nobel's Explosive Co., Ltd. by the displacement process and supplied on March 27, 1919 and kept cold and wet in a dark stove. It had been freed from calcium carbonate, with acetic acid; nitrogen content 12.10% solubility in ether-alcohol 99.45%, ash 0.27%. Where not expressly stated it was dried for three hours at 60° though dried samples were often kept before use in a tightly stoppered bottle in a desiccator over phosphorus pentoxide at room temperature before use.

a lodgement for the half-dissolved gel. A great difference is noted in the behavior of good and poor solvents in the time taken for the viscid gel to disperse throughout the solution. An excellent solvent may do this in a few minutes, where, under the same conditions, a poor solvent may require a week or more.

Throughout the present work, tubes of practically the same diameter, 2 cms., were used, but the method of mixing the nitro cotton and the solvent was as follows:—

About 3 ccs of the solvent were first added to wet the lower half of the tube, and the nitro cotton weighed in by difference from a glass bulb of approximately 10 cc. capacity, fitted with a delivery tube about 6 cms. in length, so that no nitro cotton touched the inside of the tube which had not been wetted by the solvent. More solvent was then added to make up to the required strength, the tube sealed, and placed in the shaker at 55°C in the dark. In this way, the lump of gel formed is easily detached or comes away from the sides of the tube, and floats about in the solvent from the commencement of the shaking. One hour after ageing has commenced, the shaking is started and continued for 22 hours, when the tube is removed, opened and the sol filtered through a special sieve made from very fine gauze of pure silver, folded into four layers to eliminate any nitro-cotton impurities and fibres. The tube containing the filtered sol was covered with tin foil to prevent access of light, and after allowing it 15 minutes to acquire the temperature of the 60° electric oven, 5 ccs. each for the viscosity measurement and the preparation of the diluted solutions for the concentration curve at 24 hours age were extracted, and the tube, carefully sealed with a cork, was suspended in the 55° thermostat.

Since the time required for the production of homogeneous sols is greatly influenced by mechanical shaking, it is necessary that the "shaker" dimensions be known in order that the results may be reproduced at will. The essential dimensions for the shaker used as determined by Bennett are given in Table II.

TABLE II

The dimensions of the shaker

| | |
|---|---|
| Length of shaker arm | 41 cms. |
| Length of stroke (distance centre of tube moves) | 6.8 cms. |
| Number of strokes per minute with one tube fixed | 610-620 (single) 305-310 (double) |

Two methods were used for diluting the solutions. In one case a small bottle was weighed empty, then a quantity of solution was added and again weighed, to this was added the requisite amount of solvent to make up to either 0.1% or 0.2% approximately. In the other case the storage tube itself was used instead of the bottle, thus doing away with the necessity of transference of the solution from the bottle to the tube. Latterly the second

method was used almost entirely. In each case the dilution was carried out as quickly as possible, the solutions being well shaken and put in the thermostat without delay.

Sufficient original solution was made up, and sufficient diluted to last for several (at least five) viscosity determinations. It was thought to be an advantage to have solutions of exactly the same concentrations for successive ageings. All solutions were preserved in sealed tubes similar to those used in the preparation of the sols. After each determination of viscosity the solution was poured carefully from the viscometer into the ageing tube.

*c. Design of viscometers.*

The special designs of the accurate viscometers used for this work were based upon a study of the work of F. Baker[1], Grüneisen[2], Appleby[3], Washburn and Williams[4], and Bingham[5]; and were such that they obeyed Poiseuillle's law to within 0.1% accuracy when the time of flow was slightly greater than 200 seconds. Bungenberg de Jong[6] has also published a useful summary and discussion of this subject. The most convenient reference is British Eng. Standards Association, No. 188 (1923) "Determination of Viscosity in Absolute Units." The kinetic energy correction, which Bingham regards as highly important for absolute values, was made practically negligible by suitable design.

*d. Standardization of viscometer tubes.*

All viscometers were thoroughly cleaned with acetone before use, since this is the best solvent for the nitro cotton sols, and were then carefully dried with dust-free air and allowed to stand for 15 minutes in the 60° electric oven together with the calibrated pipette (made to deliver 5 ccs. at 55° to within 0.01 ccs). Two rubber tubes about 25 cm long were then attached to the two openings of the viscometer to prevent access of condensed vapor, the viscometer suspended in the 55° thermostat and securely held in a clamp so that the capillary limb appeared vertical when viewed from two directions at right angles. The viscometer was allowed 15 minutes to acquire the temperature of the thermostat before the time of flow of the liquid was measured. The temperature of the thermostat could be kept constant at 55° within 0.02°C. The correct value for the time of flow at 55.00° was obtained by interpolationg the times of flow and the various temperatures recorded.

Table III gives the values obtained for the viscometer constants by H. B. Bennett, P. R. Edwards and L. E. Smith together with the dimensions required for any kinetic energy correction. The repeated standardization was

[1] J. Chem. Soc., 103, 1653 (1913).
[2] Wiss. Abh. phys. techn. Reichsanstalt, 4, 151 (1904).
[3] J. Chem. Soc., 97, 2000 (1910); 103, 2167 (1913).
[4] J. Am. Chem. Soc., 35, 738 (1913).
[5] "Fluidity and Plasticity," (1922).
[6] Rec. Trav. chim. 42, 1-24 (1923).

TABLE III

Dimensions and constants of viscometer tubes at 55°C

| Viscometer | Length of capillary (cm) | Volume of bulb (cc) | Tube constant Bennett K | Bennett log K | Edwards K | Edwards log K | Smith K | Smith log K |
|---|---|---|---|---|---|---|---|---|
| 1AG | 13.0 | 3.24 | 24.05 | $\bar{4}.3811$ | 24.00 | $\bar{4}.3802$ | 24.00 | $\bar{4}.3802$ |
| 2BG | 13.0 | 3.24 | 24.80 | $\bar{4}.3945$ | 25.23 | $\bar{4}.4019$ | 25.23 | $\bar{4}.4019$ |
| 3AG | 13.0 | 3.24 | 48.16 | $\bar{4}.6826$ | — | — | — | — |
| I (rep) | 6.3 | 1.5 | 57.18 | $\bar{4}.752$ | — | — | — | — |
| I | 6.3 | 2.7 | (51.89) | $\bar{4}.7151$ | — | — | — | — |
| 4AG | 13.0 | 3.24 | 75.86 | $\bar{4}.8800$ | — | — | — | — |
| P | 13.0 | 3.24 | 92.55 | $\bar{4}.9663$ | 91.96 | $\bar{4}.9636$ | 91.96 | $\bar{4}.9636$ |
| N | 6.0 | 2.5 | 96.27 | $\bar{4}.9835$ | — | — | — | — |
| O | 6.3 | 2.0 | 111.7 | $\bar{3}.0480$ | 111.7 | $\bar{3}.0480$ | 111.7 | $\bar{4}.0480$ |
| T | 5.6 | 1.1 | 510.9 | $\bar{3}.7084$ | — | — | — | — |
| R | 6.6 | 1.56 | — | — | 18.29 | $\bar{4}.2622$ | 18.29 | $\bar{4}.2622$ |
| $V_2$ | 7.0 | 3.5 | — | — | 61.25 | $\bar{4}.7872$ | — | — |

based upon 60% sucrose supplied by Bureau of Standards, Washington, using Bingham and Jackman's value[1] at 55.0°. The concentration of all sucrose solutions was checked by a determination of their density.

## II. Factors which influence Viscosity of a Sol of Nitro Cotton

1. *No accepted formula represents the dependence of viscosity upon concentration.*

As a first approximation, the logarithm of the viscosity of solutions of nitro cotton at 55° follows the Arrhenius rule in being proportional to the concentration. Our more careful work has been carried out with solutions seldom exceeding 1% and generally 0.5% and when the logarithm of the relative viscosity is plotted against the number of grams of nitro cotton per 100 grams solvent there is a distinct deviation from the straight line in that the more concentrated solutions are less than proportionately viscous. Since the solutions are so dilute this discrepancy cannot be obviated by plotting concentrations in true per cent nor can it be ascribed to errors of calibration, etc., since it invariably appears when one actual solution is repeatedly diluted and passed through the same viscometer tube.

The deviation is in the opposite direction from that observed in solutions of proteins which Arrhenius was able to explain away by ascribing it to hydration. Hatschek[2] has pointed out that F. Baker's curves[3] deviate from the straight-line Arrhenius formula, the deviation being in the same direction and of the same magnitude as in our work. Hatschek points out that graphs of viscosity slope for solutions of rubber may diverge from a straight line to an

[1] Bureau of Standards Bull. **14**, 83 (Table XV).
[2] Biochem. J., **10**, 325 (1916).
[3] J. Chem. Soc., **108**, 1653 (1913).

equal extent in either this or the opposite direction. The Arrhenius formula is therefore invalid and it is a merely empirical approximate rule. Bingham's suggested rule that the fluidity should be linearly proportional to the concentration is far more widely at variance with the facts as Bingham himself has shown. Mardles[1] likewise found no simple relation between either viscosity or fluidity and concentration.

This real discrepancy introduces an unavoidable difficulty in comparing the slopes for different solvents or for different conditions. We have therefore arbitrarily taken the mean value of the slope for solutions up to 0.5%. It is

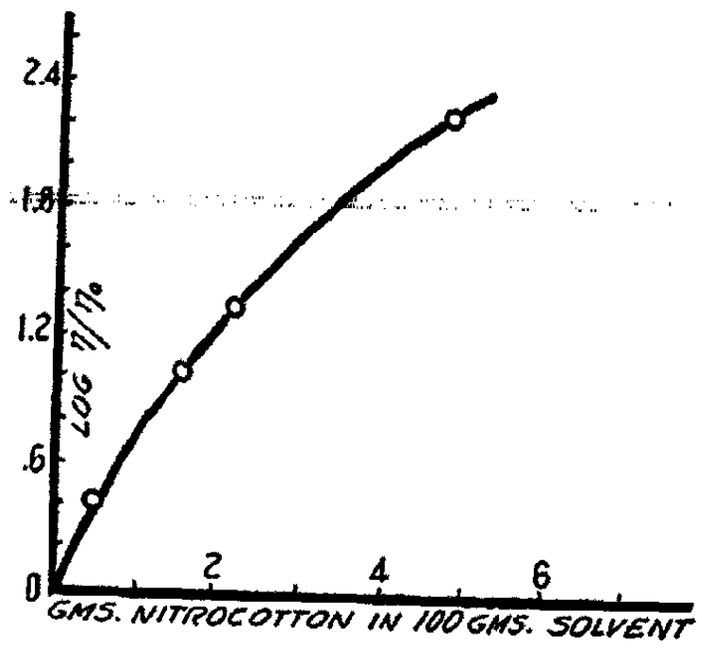



FIG. 1

Change with concentration of relative apparent viscosity of nitro cotton in ethyl formanilide at 55°.

this slope; that is, logarithm of the viscosity of the solution divided by that of the solvent, calculated per gram of nitro cotton in 100 grams solvent that is recorded as the representative value in each case.

It is difficult to dissolve large amounts of nitro cotton in the purer solvents now in use but Fig. 1 shows the results obtained by L. E. Smith using the latest technique for solutions up to 5% in one of the best available solvents, ethyl formanilide. This graph confirms all of the data obtained during the last few years with fresh solutions in that the curvature is undeniable. Solutions which have been allowed to age for long periods show viscosity much more nearly proportional to the concentration.

2. *The high temperature coefficient of viscosity.*

The viscosity of solutions of nitro cotton shows an extremely great temperature coefficient such as is found in the case of other gelatinising colloids, for example soap solutions. It is difficult to adduce a temperature coefficient which is not arbitrary owing to the interplay of the other factors under discussion but the magnitude of the effect may be illustrated by quoting W. A.

[1] J. Chem. Soc., **123**, 1951 (1923).

Squance's data for 0.4% solution of nitro cotton in ethyl phenyl urethane which at 30° is 0.368 and at 55° is 0.065; that is, a change of six-fold when the temperature is lowered only 25°.

3. *Method and period and temperature of preliminary drying of nitro cotton.*

In a paper entitled "Researches on Cellulose and its Ethers" II. 'The Stability and Viscosity of Nitrocelluloses' I, J. Duclaux[1] describes a series of experiments with 47 different varieties of nitrocellulose. The effect of heating the samples for various periods from 0-23 hours at temperatures of 100° to 110°C was measured by the loss in weight of the sample, and the resulting effect on the viscosity of the nitro cellulose solutions. Duclaux summarised his conclusions as follows:—

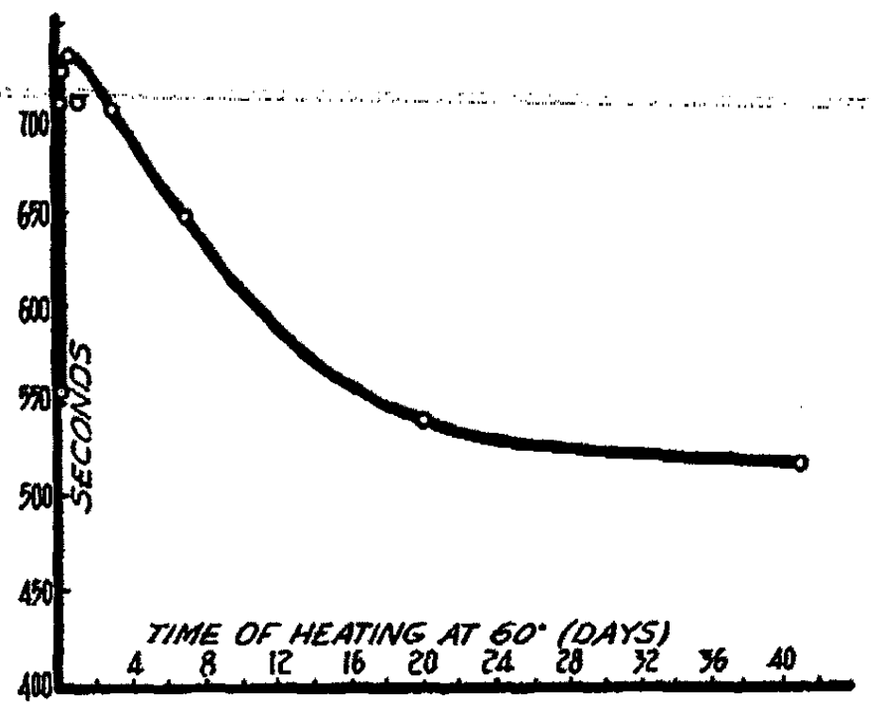



FIG. 2

Viscosity of solutions of 1 gram nitro cotton in 100 cc ethyl formanilide at age 24 hours at 55°; made from nitro cotton heated to 60° for various periods (the pure solvent about 100 seconds).

1. When nitrocellulose is heated, the viscosity of its solutions diminishes. This fall in viscosity is an absolutely general fact.

2. There is a direct relation between the fall in viscosity and the loss of weight of the nitrocellulose. In practice, the knowledge of one of these two quantities is sufficient to determine the other.

3. The study of the variations in the viscosity of a nitrocellulose during a prolonged heat treatment gives a very good method of following the degradation of that nitrocellulose and consequently of determining its stability.

4. This method of determining the stability, depending on viscosity measurements, offers important advantages over the current methods and does not appear to be inferior to them from the standpoint of sensitiveness.

Duclaux's treatment was however very drastic and nitro cotton can be maintained at 60° for long periods without appreciable loss of weight.

[1] Bull., 29, 374 (1921).

L. E. Smith has recently carried out a series of measurements using ethyl formanilide as solvent. The nitro cotton was heated in an electric oven at 60° for 41 days and from time to time specimens were removed and made up by weighing one gram of the nitro cotton into 100 cc of ethyl formanilide the solutions being prepared and measured in the usual way at 55° at age 24 hours. The results are given in Table IV and Fig. 2 and show a maximum viscosity when the nitro cotton has been heated about 12 hours falling off at about 70% of the maximum value in 41 days.

TABLE IV

Relation between viscosity of solutions of nitro cotton and the time of previous drying at 60°

| Amt. of heating at 60°C (hours) | Age of solution (hours) | Time of flow (seconds) |
|---|---|---|
| 1 | 24.1 | 556.6 |
| 3 | 24.1 | 707.9 |
| 7 | 24.0 | 724.6 |
| 12 | 24.0 | 734.0 |
| 24 | 24.0 | (709.0) |
| 3 days | 24.1 | 704.6 |
| 7 | 24.0 | 647.8 |
| 20 | 23.9 | 539.8 |
| 41 | 24.1 | 517.4 |

A result obtained by P. R. Edwards for a sample of nitro cotton dried in a vacuum of 10 mm. mercury over phosphorus pentoxide for ten days at room temperature shows that nitro cotton can be dried effectually without heating.

4. *Violent shaking during solution greatly diminishes the viscosity.*

The dependence of viscosity on previous mechancial treatment is a commonplace in colloid chemistry particularly in the two cases of gelatinising sols and of sols which have been prepared by the swelling of colloidal material. It is the second case with which we are dealing here and it would be readily intelligible if the degree to which the structure of the fibres of nitro cotton is broken down were to depend on the intensity of the mechanical disintegrating forces applied. It would appear quite possible for nitro cotton to swell to an almost indefinite size in a suitable solvent without being disintegrated; that is, whilst still retaining certain bonds of union throughout, just as a starch granule may swell in the water to an enormous bulk and still retain some trace of its original structure.

Bakr, Salmon and Reid carried out experiments in this connection, using ethyl phenyl urethane and methyl phenyl urethane which showed that if nitro cotton were dissolved with very gentle stirring such as mere tilting of the solution from end to end of the tube, that its viscosity was twice as great as if placed for 2 hours in a shaking machine with moderate shaking even though the comparison was carried out a week afterwards.

Most of our experiments involve violent shaking until the solution is homogeneous and thereafter a comparison is made between solutions which are subjected to a continuation of the same shaking and those which are merely allowed to rest. The results in Table V show quite clearly that the prolongation of this thorough shaking produces no further effect.

TABLE V

Effect of continuation of standard shaking beyond the time of complete solution at 55°

| Time shaken | Time of standing | Age measured | Concn. % | Viscosity slope |
|---|---|---|---|---|
| | | *Benzophenone. (Edwards)* | | |
| 24 hours | 0 hours | 24 hours | 0.3445 | 1.636 |
| $5\frac{3}{4}$ | $8\frac{1}{2}$ | 24 | 0.4308 | 1.590 |
| | | *Methyl phenyl urethane (Smith)* | | |
| 4 | 20 | 24 | 0.4119 | 1.766 |
| 20 | 32 | 23.2 | 0.3761 | 1.861 |
| 23 | 1 | 24 | various | 1.879 |
| 20 | 27.6 | 47.6 | 0.3761 | (1.775) |
| 40 | 8.6 | 48.6 | 0.3761 | (1.781) |
| | | *Phenyl urethane (Smith)* | | |
| 24 | 23 | 47 | 0.3811 | (1.655) |
| 46.5 | 2.3 | 48.8 | 0.3811 | (1.659) |

Smith has recently carried out experiments which test directly the observations of Bakr, Salmon and Reid. Two kinds of shaking were compared; namely, standard shaking and mere tilting of the tubes back and forth once a second at right angles to their axes, Table VI.

TABLE VI

Effect on viscosity at 55° of slow tilting followed by rapid shaking

| Time of tilting | Time of shaking | Time of flow |
|---|---|---|
| | *Ethyl phenyl urethane* | |
| 3 days | None | 542.4 seconds. |
| " | ½ hour | 390.4 |
| 3 days | none | 152.2 |
| " | ½ hour | 132.4 |
| 7 days | none | 843.2 |
| " | 1 hour | 837.0 |
| | *Ethyl phthalate* | |
| 3 days | none | 118.0 |
| " | ½ hour | 116.8 |

The time taken to prepare a homogeneous sol for a good gelatinizer and mild shaking is about $1\frac{1}{2}$ days at 90° and 4 or 5 days at 55°; or, with violent agitation, $1\frac{1}{2}$ hours at 90°, and 4 hours at 55°.

It is quite clear that vigorous mechanical treatment diminishes the viscosity of solutions of nitro cotton at 55° presumably by breaking down residual structure derived from the original fibres. However, if any definite treatment has been applied until it was certain that solution was complete, a further continuation of treatment not more violent has but a negligible effect. Again, violent treatment has its greatest effect at the beginning when the grossest aggregates are being broken up; if applied at a much later period it has comparatively little effect.

5. *The higher the temperature of preparation the lower the viscosity.*

The difference between solutions prepared at say 55° and 90° persists indefinitely showing no signs of disappearing even after a lapse of months. Owing to the fact that the best solvents dissolve nitro cotton so much more quickly than the worst ones it is sometimes possible to prepare solutions in good solvents with a slightly higher viscosity than bad solvents which have taken longer to prepare.

6. *Exposure to light distinctly diminishes the viscosity.*

It was shown in a previous report that light has the effect of slightly decreasing the viscosity of a solution of nitro cotton, the effect depending on the solvent and possibly the concentration of the nitro cotton. The effect is only a few per cent in diffused daylight. Throughout the present work solutions were prepared and kept in the dark. G. W. MacDonald[1] found that 2½% solution of nitro cotton in acetone fell off in viscosity to about half value on exposing the solution for seven days to the diffused light of the laboratory; whereas there was only a slight decrease on keeping the solution in the dark for seven weeks (at room temperature).

Exposure to ultraviolet light is said to increase solvent power of liquids. L. E. Smith found that a suspension of nitro cotton in alcohol is yellowed and decomposed with the result of partial solution. It seems probable that nitration of the solvent combined with denitration of the nitro cotton produces the enhanced solubility.

7. *Unrelated specimens of nitro cotton of similar chemical composition give solutions of very different viscosity.*

It is hardly necessary to quote experimental data in support of the foregoing statement but its significance lies in the clear indication given of the primary importance of physical state, structure and degree of subdivision, not only in the dry state but in the solutions themselves.

8. *Purity of solvent; impurities and admixtures with other solvents.*
(*a*) *Introduction.*

F. Sproxton[2] in summarising work on cellulose esters pointed out that up to 1920 no published investigation was available to show for any binary mix-

[1] J. Soc. Chem. Ind., 30, 785 (1911).

[2] "Third Colloid Report", 84 (1920); Trans. Faraday Soc., 16, Colloid Discussion 72-75 (1921).

ture what the optimum proportions are for maximum solvent power and minimum viscosity. He mentions well known qualitative instances of mixtures which are superior in solvent power to either constituent; such as ether-alcohol, and methyl alcohol containing traces of acetone. Piest in 1910 noted that addition of acetic acid to acetone or to ether-alcohol solution of nitro cotton diminishes their viscosity. By estimating the amount of low nitrogen nitro cotton dissolved by mixtures of alcohol with toluene Sproxton concluded that the optimum mixture in this case has the empirical composition $C_7H_8 . {}_3C_2H_5OH$. The position of this optimum remains unaltered if petroleum spirit is added but the solvent power is steadily decreased. Unlike alcohol, the solvent power of acetone is not enhanced even initially but only diminished by addition of toluene. Using cellulose acetate, mixtures of (non-solvent) alcohol with (non-solvent) n-tetrachlorethane containing 20-60% of alcohol are good solvents. Other similar instances of non-solvents of cellulose acetate which on mixing produce a solvent are cited (possibly from the work of Mardles, Moses and Willstrop) in an article in Chem. Trade Journ. 1923, 10th August, 155-157; thus chloroform and alcohol, ethyl acetate and benzyl alcohol above 40%; similarly "binary mixtures of esters and alcohols including water." Chandelon[1] observed that moist nitro cotton dissolves more readily than dry nitro cotton in ether-alcohol.

The first systematic study was published by Gibson and McCall[2] using ether-alcohol (92% alcohol, 8% water) with different varieties of nitro cotton. They found an optimum proportion of ether and alcohol at which the viscosity was a minimum. This optimum was independent of the concentration of nitro cotton but it does depend to some extent upon the nitrogen content of the nitro cotton. As in our work, definite reproducible values for viscosity were obtained with a given sample of nitro cotton; but these were greatly dependent upon the origin and treatment of the nitro cotton. The optimum concentration of ether-alcohol solvent was not affected by addition of amyl acetate but the latter acts as a diluent or non-solvent and increases the viscosity. Masson and McCall[3] found an optimum solvent for nitro cotton when water is added to acetone, although if more than 12% of water was present the nitro cotton no longer dissolved.

Anna von Fischer[4] (working with Schwartz) used 39 cellulose acetates of 7 different types. The chief experiments were with alcohol-acetone as solvent. The optimum solvent for all good industrial cellulose acetates was 80% acetone-20% alcohol by volume, and the actual value of the minimum was very like for all cases. One however showed minimum viscosity in 70% acetone and one was insoluble in pure acetone. Almost all the technically useless cellulose acetates showed a very high viscosity in 70% acetone and exhibited a minimum in 90% acetone, but in general the minimum was much higher than that for good acetates.

[1] Bull. Soc. chim. Belg., 26, 495-506 (1912).
[2] J. Soc. Chem. Ind., 39, 172-176T (1920).
[3] J. Chem. Soc., 117, 819-23 (1920).
[4] Kolloid-Z., 29, 260-5 (1921).

Addition of 20% and 40% of camphor to pure acetone as solvent always increased the viscosity of the acetate solution and lessened its solubility. Cellulose acetate dissolves very much more readily in acetone to which 10% of triacetin has been added although the absolute viscosity is raised; no data are given for the solvents to enable any conclusion to be drawn as to whether the *relative* viscosity referred to the viscosity of the solvent is raised or lowered. Addition of dichlorhydrin to acetone causes the viscosity of solutions of cellulose acetate to pass through a minimum in some cases. p-Toluene sulphamide in some instances raised, in others lowered, the viscosity. The behavior is so closely linked up with that discussed in the preceding part of the paper that it might possibly be utilized as a factory test of the suitability of various cellulose acetates for the manufacture of celluloid. Turning to nitro cotton (10.4 to 10.6% $N_2$) it was found that nitro cotton suitable for celluloid manufacture showed in alcoholic solution containing two or more grams of nitro cotton a diminished viscosity upon addition of camphor; whereas bad nitro cotton gave solutions whose viscosity was progressively increased by addition of camphor.

Barr and Bircumshaw[1] studied the viscosity of cellulose acetate in 5% solution in pure acetone and in acetone to which water, benzene or alcohol was added in various proportions up to the amount that caused precipitation. Benzene causes a progressive increase in the viscosity whereas addition of water or alcohol gives an initial rapid fall in viscosity, which in the case of water reaches a minimum and then rises fairly rapidly, but with alcohol remains fairly constant at the low value.

Mardles, Moses and Willstrop[2] note that water up to 6% increases the solvent power of acetone for cellulose acetate. Minima in the viscosity of solutions of cellulose acetate in binary mixtures of alcohol with a second solvent were observed with tetrachlorethane, butyl formate, methyl benzoate, nitro xylol, etc., but the optimum mixture varied in composition for different varieties of acetate. No minima were produced by the addition of the pronounced non- solvent hexane to other solvents; whereas the mild non-solvent benzene and alcohol gave minima with benzyl alcohol. The higher the substance in any homologous series the less was the tendency to produce optimum mixtures.

In 27 mixtures of solvents for which curves are drawn in a later paper by Mardles[3] all but three show optima. However, a remarkably different behavior is said to be shown by mixtures of acetone and aniline, which separately are each solvents for cellulose acetate, whereas the mixture in the proportion of 1 mol aniline to 2 mols acetic acid does not dissolve cellulose acetate. For the present purpose we may quote only the results for nitro cotton where optima were obtained with alcohol-benzyl ethyl ether, and with alcohol-aceto-phenone, and with alcohol-acetone (and even with acetone to which was

[1] Trans. Faraday Soc., 16, Colloid Discussion, 72-75 (1916).
[2] Advisory Committee for Aeronautics; Reports and Memoranda, No. 568.
[3] J. Soc. Chem. Ind., 42, 129T (1923).

added a mixture of equal parts of alcohol and benzene). Several instances are given where a mixture of three non-solvents is required to dissolve cellulose acetate.

A further paper by Mardles[1] includes data for nitro cotton with acetone-water, and acetone-alcohol. A table of all binary mixtures hitherto studied with nitro cotton is given in the discussion below.

To sum up, in the great majority of cases, small additions of a second substance enhance the solvent power of a solvent for cellulose esters, as is shown by lowered relative viscosity or increased power of withstanding the precipitating effect of an extreme non-solvent such as petroleum spirit.

(*b*) *Viscosity data in binary mixtures of solvents.*

(1) Acetone-water at 25°C (Edwards)

Methyl ethyl ketone-water at 25°C (Edwards)

The above solvents were used in making solutions of nitro cotton under standard conditions at 55°C though the viscosity was measured at 25.00° (corrected). The results are recorded in Tables VII and VIII. In each case there is an optimum mixture at which not only the absolute viscosity of the solutions of nitro cotton but also the slope of the log viscosity is a minimum. 20% aqueous acetone did not dissolve nitro cotton at 55°C.

TABLE VII

Viscosity of nitro cotton sols in dry acetone and in acetone-water mixtures

(Sols shaken for 22 hours at 55.0°C measured at 25.00° in the dark)

| Concn. water % | Concn. N.C. % | $d_4^{55°}$ of sol gms./cc. | Age hours | $\eta$ poises | log $\eta$ | slope $\frac{\log \eta/\eta_o}{\text{concn.}}$ |
|---|---|---|---|---|---|---|
| 0.00 | 0.000 | 0.7865 | — | 0.003039 | $\bar{3}.4827$ | — |
| | 1.798 | 0.8045 | 26.3 | 0.03502 | $\bar{2}.5444$ | 5.589 |
| 5.734 | 0.000 | 0.8042 | — | 0.00375 | $\bar{3}.5740$ | — |
| | 1.061 | 0.8150 | 24.3 | 0.01061 | $\bar{2}.0257$ | 0.428 |
| 9.649 | 0.000 | 0.8200 | — | 0.004200 | $\bar{3}.6514$ | — |
| | 0.9131 | 0.8290 | 24.0 | 0.01552 | $\bar{2}.1942$ | 0.594 |

TABLE VIII

Viscosity of nitro cotton sols in dry methyl ethyl ketone and in methyl ethyl ketone-water mixtures

(Sols shaken for 22 hours at 55.0° in dark, measured at 25.00°C)

| Concn. water % | Concn. N.C. % | $d_4^{55°}$ of sol gms./cc. | Age hours | $\eta$ poises | log $\eta$ | slope $\frac{\log \eta/\eta_o}{\text{concn.}}$ |
|---|---|---|---|---|---|---|
| 0.00 | 0.000 | 0.8013 | — | 0.004976 | $\bar{3}.6969$ | — |
| | 0.8303 | 0.8096 | 25.3 | 0.01368 | $\bar{2}.1361$ | 0.529 |
| 6.904 | 0.000 | 0.8168 | — | 0.00558 | $\bar{3}.7466$ | — |
| | 0.8555 | 0.8254 | 25.1 | 0.01073 | $\bar{2}.0306$ | 0.332 |
| 28.36 | 0.000 | 0.8660 | — | 0.006332 | $\bar{2}.8015$ | — |
| | 0.9802 | 0.8758 | 27.5 | 0.03866 | $\bar{2}.5872$ | 0.802 |

[1] J. Soc. Chem. Ind., 42, 207-211T (1923).

Harvey and Squance found for slopes in formanilide 1.08, in form-ortho-toluidide 0.1-0.2 and in a 50% mixture of the two 0.78. Hence, the absolute viscosity of the mixture (0.614) is distinctly less than the mean for the two solvents (1.086 and 0.4 or 0.5, mean 0.75 or 0.8).

The addition of six parts of the non-solvent benzene, to one of acetone greatly raises the viscosity slope though it is still equal to that of ethyl phenyl urethane or methyl phenyl urethane.

Smith investigated four mixtures of non-volatile solvents in equal parts by weight at 55° under standard conditions. The results are given in Table IX.

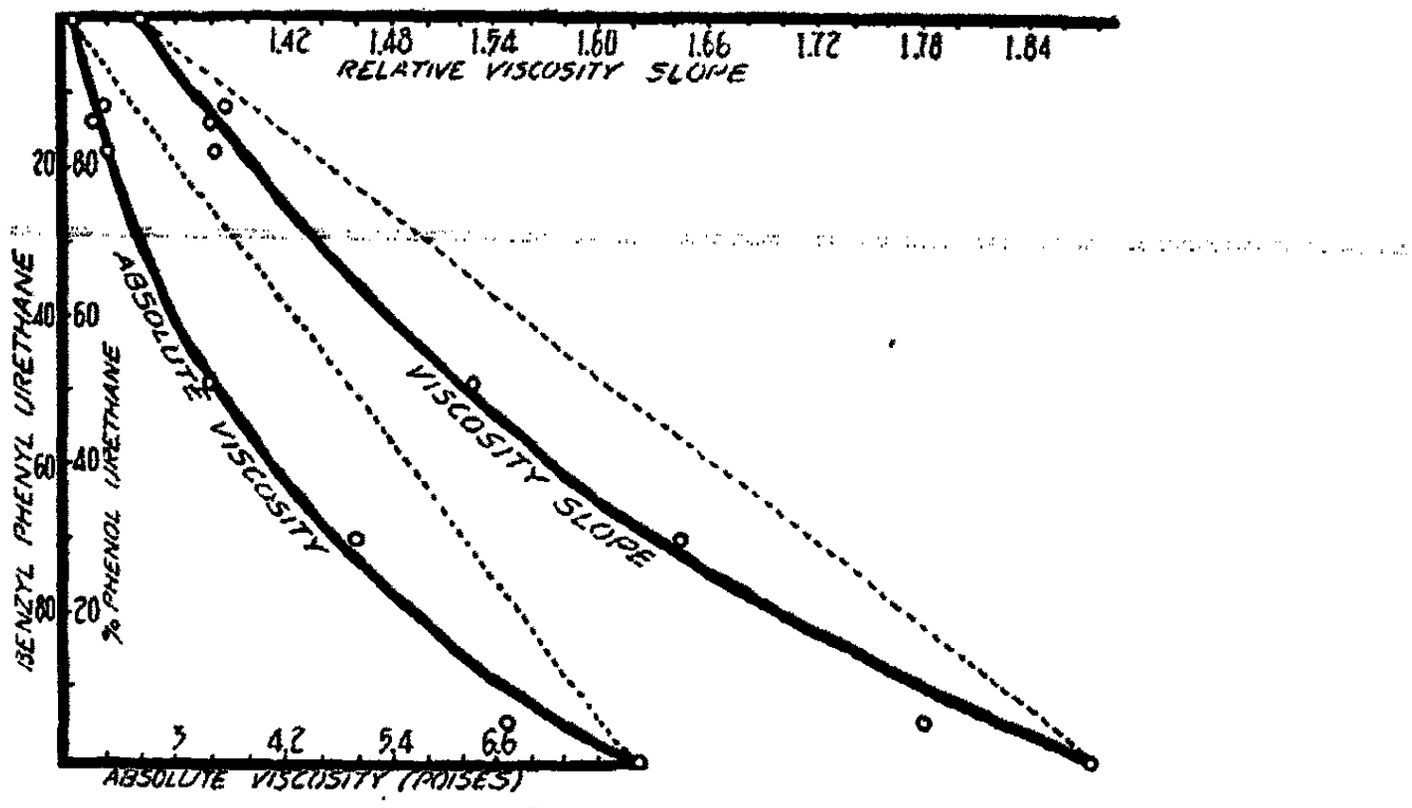



FIG. 3

*Viscosities and slopes of relative viscosities of solutions of nitro cotton in phenyl methane and ortho tolyl methane and their mixtures.*

## TABLE IX

Absolute viscosities and viscosity slopes $\frac{(\log \eta/\eta_0)}{\text{concn.}}$ of solutions in mixed solvents compared with the values in the pure solvents separately

| | Viscosity slope | | | | Absolute viscosity, $\eta$ (poises) | | | |
|---|---|---|---|---|---|---|---|---|
| 1st pure solvent | BPU* | B formanil. | EtPhth. | PU | BPU | B formanil. | EtPhth. | PU |
| | 2.108 | 1.174 | 2.118 | 1.673 | 14.10 | 1.720 | 5.606 | 4.05 |
| 2nd pure solvent | EtPhth. | MeCyanil | Benz. | oTU | Etphth. | MeCyanil. | Benz. | oTU |
| | 2.118 | 1.189 | 1.882 | 2.116 | 5.606 | 0.3148 | 3.534 | 9.616 |
| Mean | 2.113 | 1.186 | 2.00 | 1.895 | 9.853 | 1.0174 | 4.570 | 6.835 |
| Mixture | 2.12 | 1.10 | 1.72 | 1.38 | 8.349 | 0.4987 | 2.258 | 1.963 |
| % decrease | 0% | 7% | 14% | 27% | 15% | 51% | 51% | 71% |

(* Phenyl urethane = PU; ortho-tolyl urethane = oTU; ethyl phthalate = EtPhth.; benzyl phenyl urethane = BPU; benzyl formanilide = B formanil.; methyl cyanilide = MeCyanil.; Benzophenone = Benz.)

Miss M. E. Grant has carried out a series of determinations with mixtures of phenyl urethane and benzyl phenyl urethane in all proportions at 55° under standard conditions. The results are shown graphically in Fig. 3. Both viscosity slope and absolute viscosity of the solutions are plotted (continuous curves) and each is compared with the values found by linear interpolation of the values found for nitro cotton in the two solvents separately. In the case of the viscosity slope this may or may not be legitimate because the observed slopes are necessarily referred to the observed viscosity of the mixed solvents themselves which passes through a maximum value, whereas no such maximum can be taken in predicting the mixed slopes. However, it is seen that the observed slopes are smaller than the slopes expected from the behavior of solutions in the separate solvents.

It will be seen that the absolute viscosities like the slope do not pass through a minimum value, because the viscosities in the separate solvents lie too far apart. However, the observed values for the actual viscosities are unmistakably lower than those obtained by linear interpolation from solutions in the separate solvents. In other words, although there is no optimum solvent the behavior of the mixture is better than would be expected from the behavior of the separate components. Thus, the poorer solvent is less detrimental to solvent power than expected and the better solvent is more beneficial than expected.

Apart from the mixtures which definitely give an optimum solvent, forming solutions of nitro cotton whose viscosity no matter how calculated or compared is less than that of corresponding substances or solutions in either single constituent, it is probable that in all cases the absolute viscosity of the solution in the mixture is definitely lower than that predicted from solutions in the two pure solvents. Absence of a minimum is in some cases due to the fact that the viscosities of the solutions in the separate solvents lie too far apart.

The evidence is overwhelming that in almost all cases a mixture of solvents in suitable proportions has greater solvent power than that of the mean of the two solvents. Our suggested explanation lies in the direction of assuming that certain molecular grouping in each substance have a specific power of combining with definite groupings in the nitro cellulose complex differing from substance to substance. Table X summarises all known cases, including those we have ourselves investigated, where the solvent power for nitro cotton of a mixture surpasses that of any single constituent of the mixture.

TABLE X

The behavior of all known mixtures of solvents for nitro cotton

1. *Optimum solvent from 2 non-solvents.*

Ether-alcohol.
Camphor-alcohol.

(Table X continued on page 328)

2. *Optimum mixtures from 2 solvents.*

Methyl alcohol-acetone.
Acetic acid-acetone.
Acetic acid-ether: alcohol.
Ethyl phthalate-benzophenone.
Phenyl urethane-o-tolyl urethane.
Benzyl formanilide-methyl cyanilide.

3. *Improved solvent by adding a non-solvent to solvent.*

Toluene-alcohol (for a low nitrogen nitro cotton--Sproxton)
Benzene-alcohol (aq.)
Water-acetone.
Water-methyl ethyl ketone.
Water-alcohol at low temperatures (I. Masson)
Water-ether: alcohol.
Amyl acetate-ether: alcohol.
Alcohol-camphor.
Alcohol-acetophenone.
Alcohol-benzyl ethyl ether.
Alcohol-benzyl phenyl urethane.
Alcohol-acetone.
Alcohol-diethyl carbonate.
Butyl alcohol-butyl acetate.

4. *The only mixtures which are not known to give an optimum solvent.*

Benzene-acetone.
Toluene-acetone.
(Formanilide-form-o-toluidide)
(Benzyl phenyl urethane-ethyl phthalate)
Benzyl phenyl urethane-phenyl urethane.

It is interesting to quote from the summary of Mardles' paper[1] on "Solvent Power of Mixtures for Cellulose Acetate and Nitrate":—

"The close correlation of the solvent power of a liquid or mixture of liquids for a cellulose ester, and the viscosity of the solution is, apart from the theoretical interest, of considerable industrial importance. It involves the economy of costly solvents and time in preparation of the cellulose ester varnishes. The optimum solvent mixture dissolves the cellulose ester most rapidly; because the least viscous solutions are formed and the particles diffuse most rapidly away from the dissolving material. The solutions so prepared are also the clearest, the degree of dispersion being usually highest. They are generally the most stable since the tendency to set to a jelly is at a minimum[2]

"That the optimum solvent mixture should possess the maximum fluidity, follows from the fact that with the highest degree of dispersion, there is the

[1] J. Soc. Chem. Ind., 42, 211T (1923).
[2] Cf. E. Mardles: Trans. Faraday Soc., 18, Part 3 (1923).

nearest approach to a true (molecularly dispersed) solution with its characteristically low viscosity."

9. *The viscosity of the solutions of one definite sample of nitro cotton in various solvents under definite conditions at 55° is inversely proportional to their solvent power.*

(*a*) *The data*

Considerations of space forbid publication of our long series of measurements on many hundred independent solutions many of which were kept for long periods and repeatedly studied. Each recorded result was the mean of three determinations and solutions were almost always made up in duplicate so that final values were usually the mean of six determinations. To illustrate the results Table XI is here taken from L. E. Smith's Series II.

The results are all finally expressed in the form of mean slope; that is, the log of the ratio of the viscosity of the solution to the viscosity of the solvent divided by the concentration, it being assumed (merely as a basis for numerical comparison) that this slope has a constant value for solutions up to 0.5% of nitro cotton. Where a series of dilutions were made the slope is usually the mean of three dilutions of two independent duplicate solutions but in Smith's later work it was considered sufficient if good agreement were obtained with two independent duplicate solutions. The age of the solution was taken from the first mixing of nitro cotton and solvent and the duration of the initial standard shaking was 22 hours. Our standard procedure was developed by C. E. Harvey, the final details being fixed by H. B. Bennett and L. E. Smith.

TABLE XI

Smith Series II. Solutions prepared and measured at 55° in the dark. Standard shaking

| N.C. % | $D_4^{55°}$ | Age | Tube | Viscosity (poises) | log $\eta$ | slope $\frac{(\log \eta/\eta_0)}{\text{concn.}}$ |
|---|---|---|---|---|---|---|
| | | *Benzyl phenyl urethane.* | | | | |
| 0.395 | 1.080 | 24.0 hrs. | N | 0.6679 | $\bar{1}$.8247 | 1.98 |
| 0.3374 | 1.0793 | 24.0 | N | 0.5248 | $\bar{1}$.7200 | 2.01 |
| Pure | 1.076 | | 2AG | 0.1098 | $\bar{1}$.0407 | *Mean = 1.995* |
| 0.395 | 1.080 | 14 days | N | 0.3685 | $\bar{1}$.6664 | 1.33 |
| 0.3374 | 1.0793 | 14 | N | 0.3020 | $\bar{1}$.4800 | 1.30 |
| | | | | | | *Mean = 1.315* |
| 0.395 | | 84 | P | 0.1932 | $\bar{1}$.2860 | 0.620 |
| 0.3374 | | 84 | P | 0.1718 | $\bar{1}$.2848 | 0.577 |
| | | | | | | *Mean = 0.599* |
| 0.395 | | 175 | P | 0.1602 | $\bar{1}$.2047 | 0.405 |
| 0.3374 | | 174 | P | 0.1433 | $\bar{1}$.1562 | 0.343 |
| | | | | | | *Mean = 0.375* |

(Table XI continued on page 330)

TABLE XI (continued)

| N.C. % | $D_4^{55°}$ | Age | Tube | Viscosity (poises) | Log $\eta$ | Slope $\frac{(\log \eta/\eta_0}{\text{concn.}}$ |
|---|---|---|---|---|---|---|
| | | | *Ethyl phthalate (Nobel's Dec. 1923)* | | | |
| 0.3522 | 1.0905 | 24.3 hrs. | N | 0.2202 | $\bar{1}.3428$ | 2.04 |
| 0.355 | 1.0905 | 24.0 | P | 0.2266 | $\bar{1}.3353$ | 2.05 |
| Pure | 1.087 | | 1AG | 0.4215 | $\bar{2}.6248$ | *Mean = 2.045* |
| 0.3522 | 1.0905 | 14 days | N | 0.2076 | $\bar{1}.3173$ | 1.97 |
| 0.355 | 1.0905 | 14 | P | 0.215 | $\bar{1}.3325$ | 1.99 |
| | | | | | | *Mean = 1.98* |
| 0.3522 | | 84 | P | 0.1526 | $\bar{1}.1835$ | 1.58 |
| 0.355 | | 84 | P | 0.1485 | $\bar{1}.1718$ | 1.54 |
| | | | | | | *Mean = 1.56* |
| 0.3522 | | 174 | P | 0.1177 | $\bar{1}.0708$ | 1.27 |
| 0.355 | | 170 | P | 0.1173 | $\bar{1}.0693$ | 1.25 |
| | | | | | | *Mean = 1.26* |
| | | | *Ethyl phthalate (Kodak)* | | | |
| 0.4049 | 1.091 | 24.0 hrs. | P | 0.266 | $\bar{1}.4248$ | 1.98 |
| 0.420 | 1.091 | 23.9 | P | 0.2807 | $\bar{1}.4483$ | 1.96 |
| Pure | 1.087 | | 1AG | 0.041 | $\bar{2}.6243$ | *Mean = 1.97* |
| 0.4049 | 1.091 | 14 days | P | 0.2214 | $\bar{1}.3453$ | 1.78 |
| 0.420 | 1.091 | 14 | | | | |
| 0.4049 | | 84 | 1AG | 0.06763 | $\bar{2}.8301$ | 0.534 = *0.534* |
| 0.4049 | | 168 | 1AG | 0.05894 | $\bar{2}.7704$ | 0.362 = *0.362* |
| | | | *Ethyl formanilide (May 1924)* | | | |
| 0.4076 | 1.028 | 24.0 hrs. | 1AG | 0.05495 | $\bar{2}.7400$ | 0.875 |
| 0.4729 | 1.0287 | 24.0 | 1AG | 0.06204 | $\bar{2}.7937$ | 0.87 |
| Pure | 1.024 | | 1AG | 0.02418 | $\bar{2}.3834$ | *Mean = 0.872* |
| 0.4076 | 1.028 | 14 days | 1AG | 0.03673 | $\bar{2}.5651$ | 0.446 |
| 0.4729 | 1.0287 | 14 | 1AG | 0.04118 | $\bar{2}.6146$ | 0.489 |
| | | | | | | *Mean = 0.467* |
| 0.4076 | | 84 | 1AG | 0.02896 | $\bar{2}.4618$ | 0.193 |
| 0.4729 | | 84 | 1AG | 0.03045 | $\bar{2}.4836$ | 0.214 |
| | | | | | | *Mean = 0.203* |
| 0.4076 | | 170 | 1AG | 0.02743 | $\bar{2}.4383$ | 0.111 |
| 0.4729 | | 169 | 1AG | 0.02828 | $\bar{2}.4514$ | 0.144 |
| | | | | | | *Mean = 0.127* |
| | | | *Ethyl phenyl urethane (March 1923)* | | | |
| 0.3743 | 1.017 | 24.0 hrs. | P | 0.1327 | $\bar{1}.1230$ | 1.82 |
| 0.4026 | 1.017 | 23.8 | 1AG | 0.1446 | $\bar{1}.1603$ | 1.78 |
| Pure | 1.013 | | 1AG | 0.02760 | $\bar{2}.4409$ | *Mean = 1.80* |
| 0.3743 | 1.017 | 15 days | 1AG | 0.08408 | $\bar{2}.9247$ | 1.29 |
| 0.4026 | 1.017 | 14 | 1AG | 0.0936 | $\bar{2}.9713$ | 1.32 |
| | | | | | | *Mean = 1.31* |

TABLE XI (continued)

| N.C. % | $D_4^{55°}$ | Age | Tube | Viscosity (poises) | log $\eta$ | Slope $\frac{(\log \eta/\eta_0}{\text{concn.}}$ |
|---|---|---|---|---|---|---|
| | | | *Ethyl phenyl urethane (March 1923) (cont'd.)* | | | |
| 0.4076 | | 84 days | 1AG | 0.04246 | $\bar{2}$.6280 | 0.50 |
| 0.4026 | | 84 | 1AG | 0.05802 | $\bar{2}$.7636 | 0.803 |
| | | | | | | *Mean = 0.651* |
| 0.3743 | | 168 | 1AG | 0.03795 | $\bar{2}$.5791 | 0.369 |
| 0.4026 | | 169 | 1AG | 0.04288 | $\bar{2}$.6322 | 0.476 |
| | | | | | | *Mean = 0.422* |
| | | | *Methyl phenyl urethane (8/8/23)* | | | |
| 0.403 | 1.045 | 24.0 hrs. | N | 0.1131 | $\bar{1}$.0535 | 1.6 |
| 0.3539 | 1.0455 | 24.1 | 1AG | 0.09562 | $\bar{2}$.9806 | 1.61 |
| Pure | 1.042 | | 1AG | 0.02569 | $\bar{2}$.4079 | *Mean = 1.605* |
| 0.403 | 1.046 | 14 days | 1AG | 0.07252 | $\bar{2}$.8605 | 1.12 |
| 0.3539 | 1.0455 | 14 | 1AG | 0.0675 | $\bar{2}$.8293 | 1.18 |
| | | | | | | *Mean = 1.15* |
| 0.403 | | 84 | 1AG | 0.4702 | $\bar{2}$.6723 | 0.652 |
| 0.3539 | | 84 | 1AG | 0.4158 | $\bar{2}$.6188 | 0.591 |
| | | | | | | *Mean = 0.621* |
| 0.403 | | 168 | 1AG | 0.03702 | $\bar{2}$.2984 | 0.395 |
| 90.353 | | 168 | 1AG | 0.03413 | $\bar{2}$.5332 | 0.349 |
| | | | | | | *Mean = 0.372* |
| | | | *Formanilide (Nobel's)* | | | |
| 0.3498 | 1.1175 | 24.9 hrs. | P | 0.1987 | $\bar{1}$.2984 | 1.01 |
| 0.3341 | 1.117 | 24.2 | P | 0.1944 | $\bar{1}$.2888 | 1.03 |
| Pure | 1.114 | | 1AG | 0.08794 | $\bar{2}$.9442 | *Mean = 1.02* |
| 0.3498 | 1.1175 | 14 days | 1AG | 0.1302 | $\bar{1}$.1145 | 0.487 |
| 0.3341 | 1.117 | 14 | 1AG | 0.1260 | $\bar{1}$.1003 | 0.468 |
| | | | | | | *Mean = 0.477* |
| 0.3498 | | 84 | 1AG | 0.1013 | $\bar{1}$.0058 | 0.175 |
| 0.3341 | | 84 | 1AG | 0.09886 | $\bar{2}$.9981 | 0.152 |
| | | | | | | *Mean = 0.163* |
| 0.3498 | | 169 | 1AG | 0.09324 | $\bar{2}$.9696 | 0.073 |
| 0.3341 | | 168 | 1AG | 0.09269 | $\bar{2}$.9670 | 0.068 |
| | | | | | | *Mean = 0.070* |

TABLE XI (continued)

| N.C. % | $D_{4°}^{55°}$ | Age | Tube | Viscosity (poises) | log $\eta$ | Slope $\frac{(\log \eta/\eta_0}{\text{concn.}}$ |
|---|---|---|---|---|---|---|
| | | | *o-Tolyl urethane (15/4/24)* | | | |
| 0.371 | 1.089 | 24.1 hrs. | P | 0.3175 | $\bar{1}$.5018 | 1.7 |
| 0.3963 | 1.065 | 24.1 | P | 0.3583 | $\bar{1}$.5542 | 1.73 |
| Pure | 1.061 | | 1AG | 0.07425 | $\bar{1}$.8707 | *Mean = 1.715* |
| 0.371 | 1.0647 | 14 days | P | 0.2328 | $\bar{1}$.3670 | 1.34 |
| 0.3963 | 1.065 | 14 | P | 0.2617 | $\bar{1}$.478 | 1.38 |
| | | | | | | *Mean = 1.36* |
| 0.371 | | 84 | P | 0.1319 | $\bar{1}$.1202 | 0.672 |
| 0.3963 | | 84 | P | 0.1351 | $\bar{1}$.1306 | 0.665 |
| | | | | | | *Mean = 0.669* |
| 0.371 | | 168 | 1AG | 0.1033 | $\bar{1}$.0010 | 0.352 |
| 0.3963 | | 168 | 1AG | 0.1049 | $\bar{1}$.0208 | 0.379 |
| | | | | | | *Mean = 0.365* |
| | | | *Phenyl urethane (Aug. 1923)* | | | |
| 0.405 | 1.088 | 23.9 hrs. | P | 0.3223 | $\bar{1}$.5083 | 1.42 |
| 0.4093 | 1.089 | 24.2 | P | 0.3337 | $\bar{1}$.5233 | 1.45 |
| Pure | 1.085 | | 1AG | 0.08535 | $\bar{2}$.9313 | *Mean = 1.435* |
| 0.405 | 1.089 | 14 days | P | 0.1745 | $\bar{1}$.2417 | 0.765 |
| 0.4093 | 1.089 | 14 | P | 0.1799 | $\bar{1}$.2551 | 0.792 |
| | | | | | | *Mean = 0.778* |
| 0.405 | | 84 | 1AG | 0.111 | $\bar{1}$.0457 | 0.283 |
| 0.4093 | | 84 | 1AG | 0.1102 | $\bar{1}$.0422 | 0.272 |
| | | | | | | *Mean = 0.277* |
| 0.405 | | 168 | 1AG | 0.09927 | $\bar{2}$.9968 | 0.163 |
| 0.4093 | | 168 | 1AG | 0.09865 | $\bar{2}$.9941 | 0.153 |
| | | | | | | *Mean = 0.158* |
| | | | *Benzophenone (Nov. 1923)* | | | |
| 0.3506 | 1.0845 | 24.2 hrs. | P | 0.166 | $\bar{1}$.2200 | 1.59 |
| 0.351 | 1.0845 | 24.0 | P | 0.165 | $\bar{1}$.2173 | 1.57 |
| Pure | 1.081 | | 1AG | 0.04601 | $\bar{2}$.6629 | *Mean = 1.58* |
| 0.3508 | 1.0845 | 14 days | 1AG | 0.111 | $\bar{1}$.0451 | 1.09 |
| 0.307 | 1.0845 | 14 | 1AG | 0.1132 | $\bar{1}$.0542 | 1.11 |
| | | | | | | *Mean = 1.10* |
| 0.3508 | | 84 | 1AG | 0.06336 | $\bar{2}$.8018 | 0.396 |
| 0.351 | | 84 | 1AG | 0.06503 | $\bar{2}$.8131 | 0.428 |
| | | | | | | *Mean = 0.412* |
| 0.3508 | | 168 | 1AG | 0.05697 | $\bar{2}$.7556 | 0.264 |
| 0.351 | | 168 | 1AG | 0.05902 | $\bar{2}$.7711 | 0.309 |
| | | | | | | *Mean = 0.286* |

TABLE XI (continued)

| N.C. % | $D_{4°}^{55°}$ | Age | Tube | Viscosity (poises) | log $\eta$ | Slope $\frac{\log \eta/\eta_0}{\text{concn.}}$ |
|---|---|---|---|---|---|---|
| | | | *Benzyl formanilide (1/10/20)* | | | |
| 0.4032 | 1.104 | 24.2 hrs. | P | 0.3773 | $\bar{1}.5767$ | 1.29 |
| 0.3512 | 1.1035 | 24.0 | P | 0.3323 | $\bar{1}.5215$ | 1.30 |
| Pure | 1.100 | | 1AG | 0.1160 | $\bar{1}.0647$ | *Mean = 1.295* |
| 0.4032 | 1.104 | 14 days | P | 0.2169 | $\bar{1}.3363$ | 0.67 |
| 0.3512 | 1.1035 | 14 | P | 0.2065 | $\bar{1}.3150$ | 0.71 |
| | | | | | | *Mean = 0.69* |
| 0.4032 | | 84 | P | 0.1760 | $\bar{1}.2455$ | 0.488 |
| 0.3512 | | 84 | P | 0.1784 | $\bar{1}.2263$ | 0.460 |
| | | | | | | *Mean = 0.454* |
| 0.4032 | | 168 | P | 0.1699 | $\bar{1}.2302$ | 0.410 |
| 0.3512 | | 168 | P | 0.1675 | $\bar{1}.2241$ | 0.460 |
| | | | | | | *Mean = 0.432* |
| | | | *Benzyl formanilide (16/2/25)* | | | |
| 0.3632 | 1.1036 | 24.0 | P | 0.3426 | $\bar{1}.5347$ | 1.29 |
| 0.4723 | 1.1047 | 24.2 | P | 0.4171 | $\bar{1}.6202$ | 1.17 |
| Pure | 1.100 | | 1AG | 0.1163 | $\bar{1}.656$ | *Mean = 1.23* |
| 0.3643 | 1.100 | 14 days | | 0.2065 | $\bar{1}.3150$ | 0.687 |
| 0.4723 | | 14 | P | 0.2616 | $\bar{1}.4175$ | 0.744 |
| | | | | | | *Mean = 0.73* |
| | | | *Benzophenone (Kahlbaum)* | | | |
| 0.3554 | 1.0845 | 24.2 hrs. | 1AG | 0.2493 | $\bar{1}.3967$ | 2.04 |
| Pure | 1.081 | | 1AG | 0.03688 | $\bar{2}.6709$ | *Mean = 2.04* |
| | | | *Benzophenone (Nobel's 2/4/25)* | | | |
| 0.3952 | 1.085 | 24.2 hrs. | P | 0.2305 | $\bar{1}.3636$ | 1.76 |
| Pure | 1.081 | | 1AG | 0.04647 | $\bar{2}.6672$ | *Mean = 1.76* |

(*b*) *Discussion of results.*

In the previous section attention was drawn to the fact that the final viscosity of the solutions and hence the viscosity slope was greatly influenced by the purity of the solvent. In general the solvents used latterly have been purer than those used formerly.[1] It has been pointed out that within certain limits the less impure the solvent the lower the slope. The slopes have been systematically raised during later work owing to the increased purity of the solvents.

[1] All were obviously much purer than ordinary commercial solvents.

Considering the solvents as a whole, the slopes vary from about 0.5 to about 2.2, the slopes in the poorest solvents being over four times as great as those in the best solvents. The slopes of the substituted urethanes are of the same order of magnitude, also those of formanilide and the substituted formanilides are of the same order. The similarity of the slopes of similar substances will be further brought out when considering the ageing of these solutions. The substances which do not belong to any definite group are scattered between the extremes of the good and bad "gelatinizers."

It has been assumed that the best time for comparing the viscosities of the nitro cotton solutions is at 24 hours after the mixing of the nitro cotton and solvent. Under the fixed conditions of shaking that are in use, the time taken for the complete solution of the gel in the solvent varies considerably. The time for solution may be taken as being roughly proportional to the slope for the particular solvent (for a given concentration) and not, as might be expected, to the absolute viscosity, 24 hours is a convenient time to take the initial measurement of the viscosity, because all solutions are complete within that time. Formanilide, which is a fairly viscous liquid dissolved 0.5% of nitro cotton in about 2 hours, whereas ethyl phthalate and others which are less viscous require several hours more shaking. If it be considered that 24 hours is not the best time for making the comparison, then this can be done at a greater age; this will be dealt with under the ageing of nitro cotton in a later section (II).

The justification for comparing the viscosity effects for the various solvents through the medium of viscosity slope is given in the following theoretical paper. The whole of the existing data for slopes at 55° at age 24 hours is compiled in Fig. 4. In this graph the various solvents are put in parallel columns in a somewhat arbitrary order but keeping the urethanes and the anilides together. An ordinates the viscosity slopes are employed and the viscosity slope found by each worker is indicated at the appropriate height by a short horizontal line. Furthermore, the results are weighted by the use of lines of various thicknesses and forms to distinguish the most accurate work done under standard conditions. Finally, just above each line is given the letter referring to the specimen of solvent actually used, the specimens having been arranged in chronological order; the earliest, generally the least pure, being given the letter A, Kahlbaum's chemicals being marked K.

Inspection of the graph brings out very clearly the relations between the solvents in spite of all subordinate influences such as degree of possible impurity. First and most important is that the different solvents definitely give different viscosity slopes with the same specimen of nitro cotton. This disproves J. Duclaux and Mme. Wollman's suggestion[1] that the slope is independent of the solvent and it is more conclusive in that the specimen of nitro cotton we have employed throughout is particularly homogeneous, all coming down in one fraction under the conditions of Duclaux' experiments on fractionation.

---

[1] Bull., 22, 414 (1920).

The second generalisation is that molecular weight is an important factor in a series of closely similar compounds. The lower the substance in the homologous series the better the solvent. This rule does not rest upon a very wide basis but it is illustrated within the group of five urethane and with the three formanilides, and in a comparison of acetophenone with benzophenone.

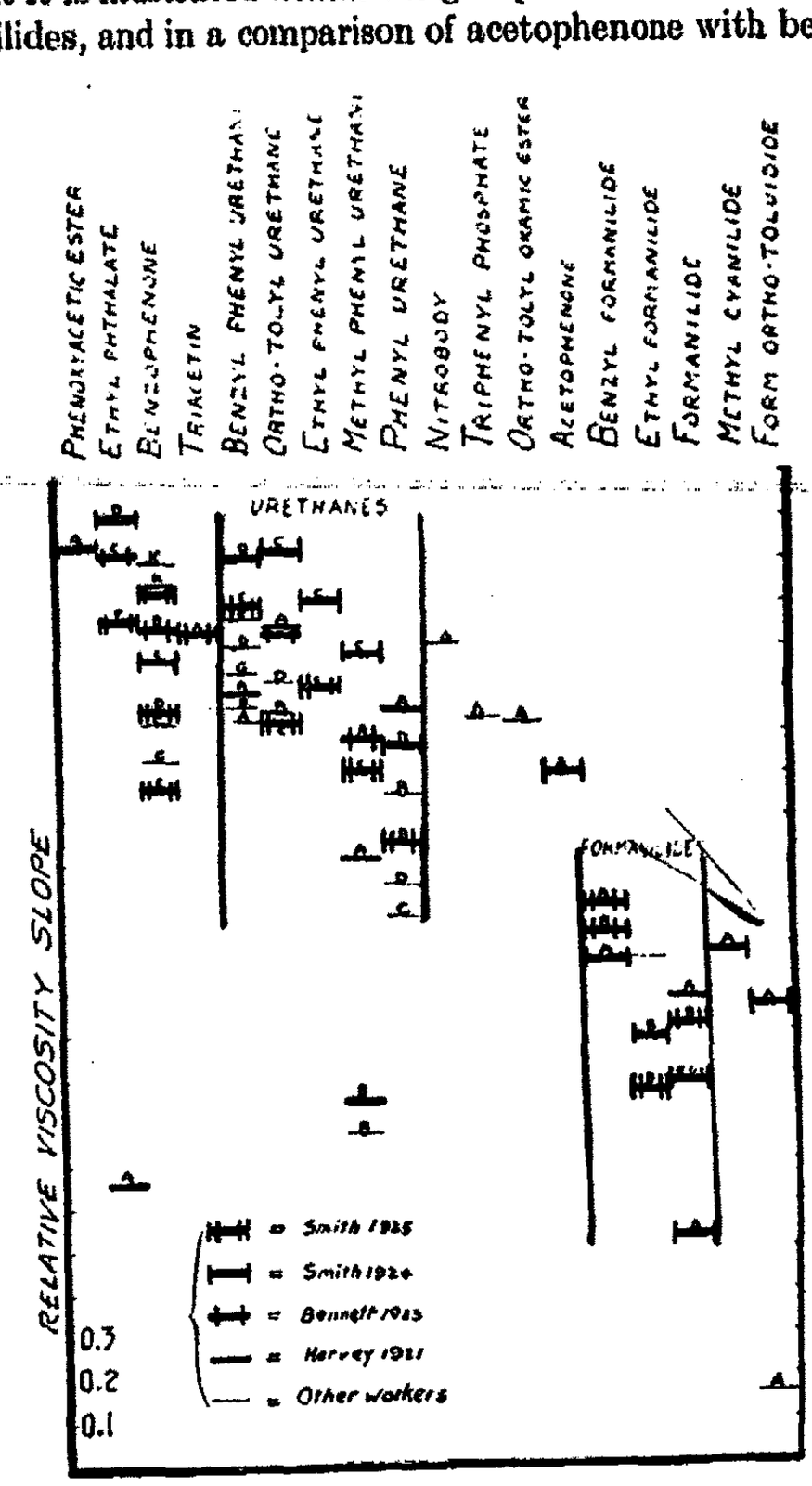



FIG. 4

Relative viscosity for unit concentration of one specimen of nitro cotton dissolved in different samples of various solvents at 55° under highly comparable conditions.

Mardles[1] has observed that the same rule holds for solutions of cellulose acetate.

It is taken for granted in this discussion that the best solvents are those which give the lowest viscosity slopes in accordance with the suggestion put

[1] J. Soc. Chem. Ind., 42, 128T (1923).

forward by Schwartz[1] and adopted by most of the succeeding workers on this subject.

The theoretical interpretation of this result is given in the following theoretical paper. The longer we have worked the more we have been impressed with the close relation between low viscosity slope and solvent power as deduced from other indications. For example, solutions with lowest viscosity slopes are found with the solvents in which the nitro cotton most quickly dissolves and in which the highest concentrations can be prepared.

A third point is that the formanilides are all much better than the urethanes and esters are fairly comparable with urethanes. Keyes[2] has pointed out that the reason why commercial esters are so much better solvents than pure esters is that they generally contain free alcohol.

It is worth while reproducing a table showing our earlier results with the impure solvents as ordinarily used and giving the comparison with these same materials and their reputation in factory tests. The fact that in certain cases there were wide divergences in the factory reputation of these materials as tested on various occasions is readily explained in the light of our later work which has brought out so clearly the connection between suitable admixture of solvents and solvent power.

TABLE XII

Relative slopes of viscosity-concentration curves compared with solvent power at 55°C. (Measurements by Harvey, Miss King and W. A. Squance with less pure materials)

| Solvent | Mean slope | Reputed solvent power |
|---|---|---|
| Form-o-toluidide | (0.1567) | Good |
| Ethyl phthalate | 0.6596 | Very good |
| Formanilide: form-o-toluidide Mixture | 0.7765 | Very good |
| Ethyl phenyl urethane | 0.8327 | Very good |
| Formanilide | 1.084 | Very good |
| Ethyl formanilide | 1.316 | Very good |
| Methyl phenyl urethane | 1.384 | Very good |
| o-Tolyl oxamic ester | 1.387 | Fair |
| Triphenyl phosphate | 1.727 | —— |
| Benzyl phenyl urethane | 1.757 | Fair |
| o-Tolyl urethane | 1.782 | Fair |
| Nitrobody | 1.897 | —— |
| Phenyl urethane | 1.960 | Poor |
| Benzophenone | 2.06 | Poor |

[1] Kolloid-Z., 12, 32-41; J. Soc. Chem. Ind., 32, 191 (1913).

[2] J. Ind. Eng. Chem., 17, 563 (1925).

(*c*) *Conclusion.*

The viscosity of solutions of nitro cotton even when calculated according to the Arrhenius formula which relates it to those of the solvents depends greatly upon the nature of the solvent, contrary to the suggestion of Duclaux and Wollman.

Low relative viscosity may be taken as a general measure of solvent power.

Increase of molecular weight with comparable compounds impairs solvent power and increases relative viscosity.

The formanilides are a much better group of solvents than the urethanes or the pure esters.

10. *Nitro cotton is only very slightly decomposed on heating in solution for long periods at very moderate temperatures.*

In every solvent we have studied at 55° or higher temperatures the viscosity of the solution of nitro cotton diminishes with time. The higher the temperature the more rapid as well as extensive is the diminution so that even a brief exposure to a high temperature such as 90° permanently diminishes the viscosity. If one portion of a solution is kept at 55° and another portion heated for a short time to 90° or if it is prepared at 90° and then kept at 55° the viscosity of the second portion is much lower than that of the first portion even after the lapse of months.

We are of the opinion that the effects we have observed are essentially due to "degradation" of the nitro cotton and not to its denitration or to nitration of the solvent at its expense. To disprove the last two alternatives several tests have been carried out from time to time.

Reid found that nitro cotton recovered from aged solutions yielded new solutions which although somewhat less viscous still aged at 55°. Squance recovered methyl phenyl urethane which had had 20% nitro cotton dissolved in it for a fortnight and tested for nitration with a negative result. Furthermore, all the solutions, including such solvents as ethyl phthalate and benzophenone behave similarly as regards ageing although many of them do not nitrate at all under ordinary conditions. Lastly, Baker's work on alcoholic solutions as well as that of Tainsh (not published) seemed to show it was a mere "physical degradation" of the nitro cotton.

(*b*) *Analysis for $NO_2$ group by Bennett.*

The most careful tests were those reported by H. B. Bennett in 1922 and 1923. To save space all details of standardization, procedure and analyses are here omitted. Three highly concentrated solutions (C, D and E) were prepared in methyl phenyl urethane at 90° and kept for a week or two at that temperature and the recovered solvents quantitatively analyzed for nitro groups by reduction with titanous sulphate. One solution (F) was kept for 4½ months at 90° in a sealed tube and when opened after this very drastic treatment it was found to be distinctly under pressure (presumably $N_2$—possibly some NO). The analytical results for this solution is given in detail.

*Results of nitration analysis.*

The time of extraction for each of the analyses below was approximately 24 hours, but the degree of extraction for solution D (24.43%) was not so high as for solution E and solution C. The extent of the nitration of the solvent was estimated as the per cent weight of available nitro cotton used up in nitrating the solvent, taking the total nitro cotton present as 100% (the sample of nitro cotton used contained 12.11% nitrogen by weight).

TABLE XIII

| Soln. | N.C. % | Age of soln. | Wt. in gms. of soln. taken. | Vol. $Ti_2(SO_4)_3$ soln. added (ccs) | Vol. from alum soln. added. | Vol. $Ti_2(SO_4)_3$ soln. used up. (ccs) | Proportion of N.C. used up in nitration. |
|---|---|---|---|---|---|---|---|
| C | 30 | 6 days | 8.75 | 99.54 | 90.52 | 3.51 | 0.38% |
| D | 25 | 8 | 10.21 | 49.72 | 45.07 | 1.90 | 0.24 |
| E | 20 | 14 | 12.11 | 64.69 | 56.53 | 4.73 | 0.71 |

Hence, in the three cases the nitro cotton which originally contained 12.10% nitrogen now contains at least 12.06%, 12.08% and 12.03% nitrogen respectively still in spite of two days at 90° and a subsequent 1 or 2 weeks at room temperature.

Solution F was prepared by shaking at 90° in a sealed tube for 3 days and stored for over 4½ months (141 days) at approximately 90°. The result was as follows.

TABLE XIV

| Soln. | % concn. of N.C. soln. | Wt. of N.C. soln. taken for extraction. | Vol. of $Ti_2(SO_4)_3$ solution added | Vol. iron alum solution added | Vol. $Ti_2(SO_4)_3$ solution used up. | Proportion of N.C. used up in nitration. |
|---|---|---|---|---|---|---|
| F | 19.92 | 17.06 | 129.20 | 47.39 | 47.92 | 1.55% |

Therefore the nitro cotton which was 12.10% is not still at least 12.10 − 0.154 = 11.95% nitrogen.

(c) *Discussion.*

The view that the nitration of any of the solvents by nitro cotton is not appreciable has been substantiated by direct test of the extent of nitration of methyl phenyl urethane under the very drastic conditions of keeping concentrated solutions at 90° for periods of one week to 4½ months. In the shorter periods much less than 1% of the available nitro groups in the nitro cotton and in the most prolonged experiments only 1.55% of the available nitro groups in the nitro cotton had combined with the solvent.

Hence, the conclusion is confidently drawn that the large amount of ageing which takes place during the first few hours and days at the very much lower temperature of 55° in all solvents alike cannot be due to denitration of the nitro cotton by the solvent.

In the experiments described in section 3 one factor was isolated; namely, the degradation of the nitro cotton itself apart from any possible interaction with solvent on heating it alone at 60°. Here the total fall of slope in a fortnight was not more than about 12% whereas in ordinary ageing experiments at the distinctly lower temperature of 55° the decrease in slope in the same period is 50% or four times greater. This is in spite of the fact that the heating of the nitro cotton alone at 60° includes both any spontaneous denitration and physical degradation of the nitro cotton itself.

*(d) Conclusion.*

It is concluded that in quite typical cases of ageing of solutions at 55° any possible effect of denitration of nitro cotton by interaction with the solvent must be inappreciable even after very long periods. The ageing effect of heating nitro cotton by itself at 60° which is in accordance with our general working hypothesis that the chief factor in the diminution of apparent viscosity is due to the disintegration of the colloidal aggregates into smaller particles through interaction with the solvent.

11. *The viscosity of solutions of nitro cotton kept at 55° for very long periods diminishes approximately proportional to the logarithm of the time.**

*(a) Summary of previous knowledge.*

Invariably, the viscosity of a solution of nitro cotton in any solvent we have used diminishes on keeping the solution at 55° and 90°. In view of the previous section this cannot be ascribed to denitration of the nitro cotton.

An approximate idea of the magnitude of ageing may be gathered from the statement that the viscosity slopes observed at one day old are reduced to about one half in three weeks and to about a quarter in three months.

Doubtless solutions or temperatures could be found where the apparent viscosity would increase with time and the solution might even set to a jelly.[1] We have probably missed this by working at so high a temperature as 55°.

The ageing or decrease in viscosity is continuous being rapid at first and apparently not reaching a limiting value even after months or perhaps years. The decrease in viscosity is greater at 90° than at 55°. Early solutions which were kept at room temperature changed to a much less extent.

Masson and McCall[2] studied nitro cotton in aqueous acetone and ether-alcohol solutions. With acetone and aqueous acetone the viscosity almost immediately assumed a maximum value from which it fell very gradually; no numerical data are given. As far as it goes this behavior agrees with that observed here.

[1] Only in one solvent, benzyl formanilide, was this diminution in viscosity interrupted. After many months at 55° during which time the viscosity fell off, such solutions set to a soft jelly. If they were then resubmitted to standard shaking for one or two days at 55° they were liquefied; but the viscosity was distinctly above the expected place on the ageing curve and they quickly set again to a jelly, the viscosity rising rapidly even during the actual measurement. The jelly did not melt upon merely raising the temperature to 90°.

[2] J. Chem. Soc., 117, 819 (1920).

Ether-alcohol behaved similarly in the case of the mixture of ether and alcohol in which nitro cellulose has least viscosity. If however the relative proportions of ether and alcohol differ widely from the optimum ratio the viscosity is not fully developed, even after 100 hours,—this in spite of very vigorous agitation followed by mechanical shaking. It would be interesting to inquire whether the sols had been completely formed in these cases.

Masson and McCall concluded that two processes occur, first the adsorption of solvent by nitro cellulose which is accompanied by the solvation of the

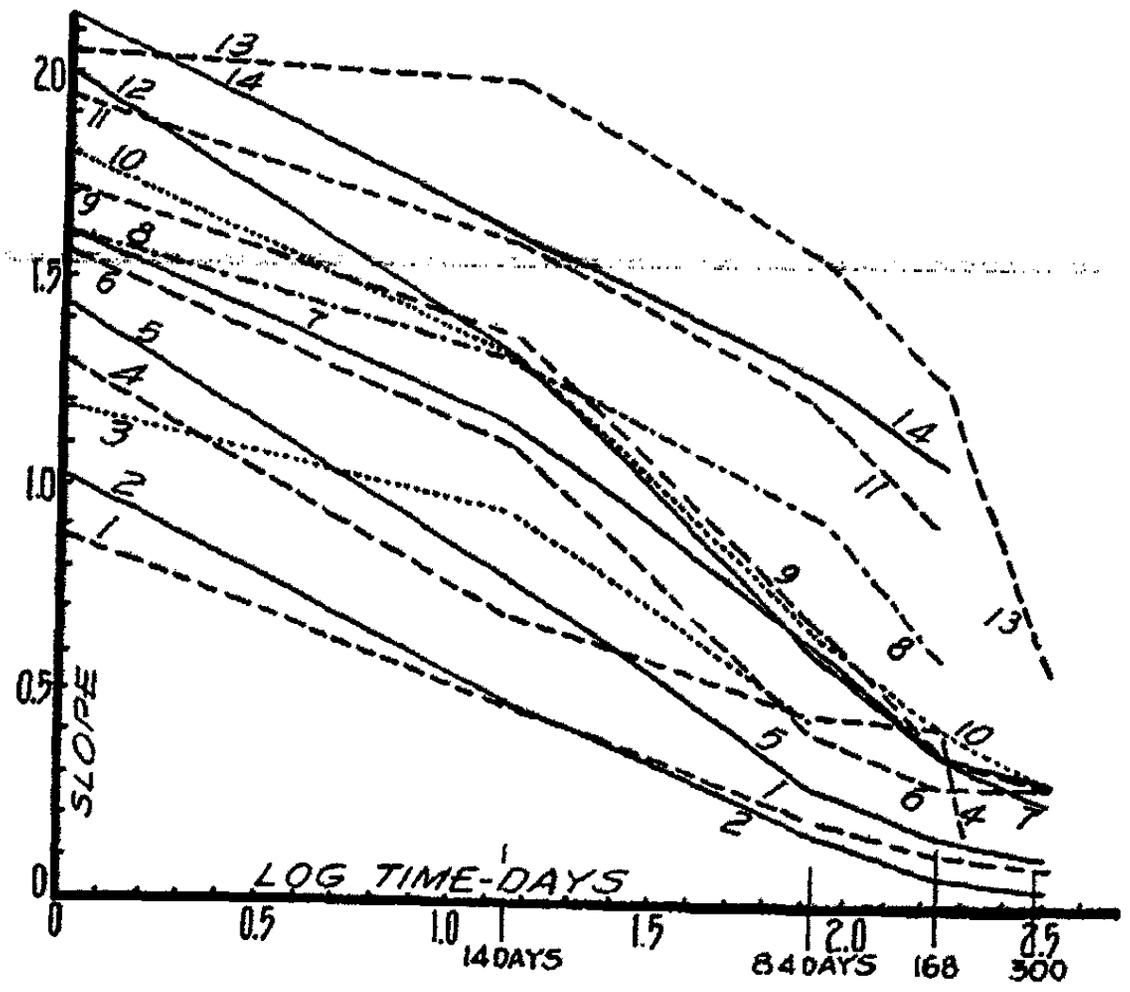



FIG. 5

Change in slope of relative viscosity of solutions of nitro cotton in various solvents measured at intervals up to a year.

Key

1. Ethyl formanilide
2. Formanilide
3. Methyl cyanilide
4. Benzyl formanilide
5. Phenyl urethane
6. Benzophenone
7. Methyl phenyl urethane
8. Acetophenone
9. Ortho tolyl urethane
10. Ethyl phenyl urethane
11. Triacetin
12. Benzyl phenyl urethane
13. Ethyl phthalate
14. Phenoxyacetic ester.

resulting gel, and secondly a change in the dispersed gel *not* necessarily accompanied by any alteration in the percentage composition of the particles, but probably to be ascribed to a change in their state of aggregation. The former process is very rapid with acetone and optimum ether-alcohol, although with other ether-alcohol mixtures the adsorption of solvent is slow. In all cases the complete disintegration of the particles or their aggregates is very slow. As we point out elsewhere, we should explain disaggregation as being

caused by solvation. Incidentally it may be mentioned that none of the preposed formulae of the viscosity concentration curve were strictly applicable.

Leysciffer[1] studied nitro cellulose (from wood) in acetone at 20°C., and found that the viscosity in acetone fell off slightly during a month, following the first measurements at the age of 15 hours. This decrease was greatest for the most viscous solutions. Schwartz had found in 1913 that viscosity in camphor-alcohol doubles in a fortnight after the first half hour, but, like Peist in 1910, who usually observed but little change, he was unable to get reproducible results, and sometimes observed a decrease and sometimes an increase.

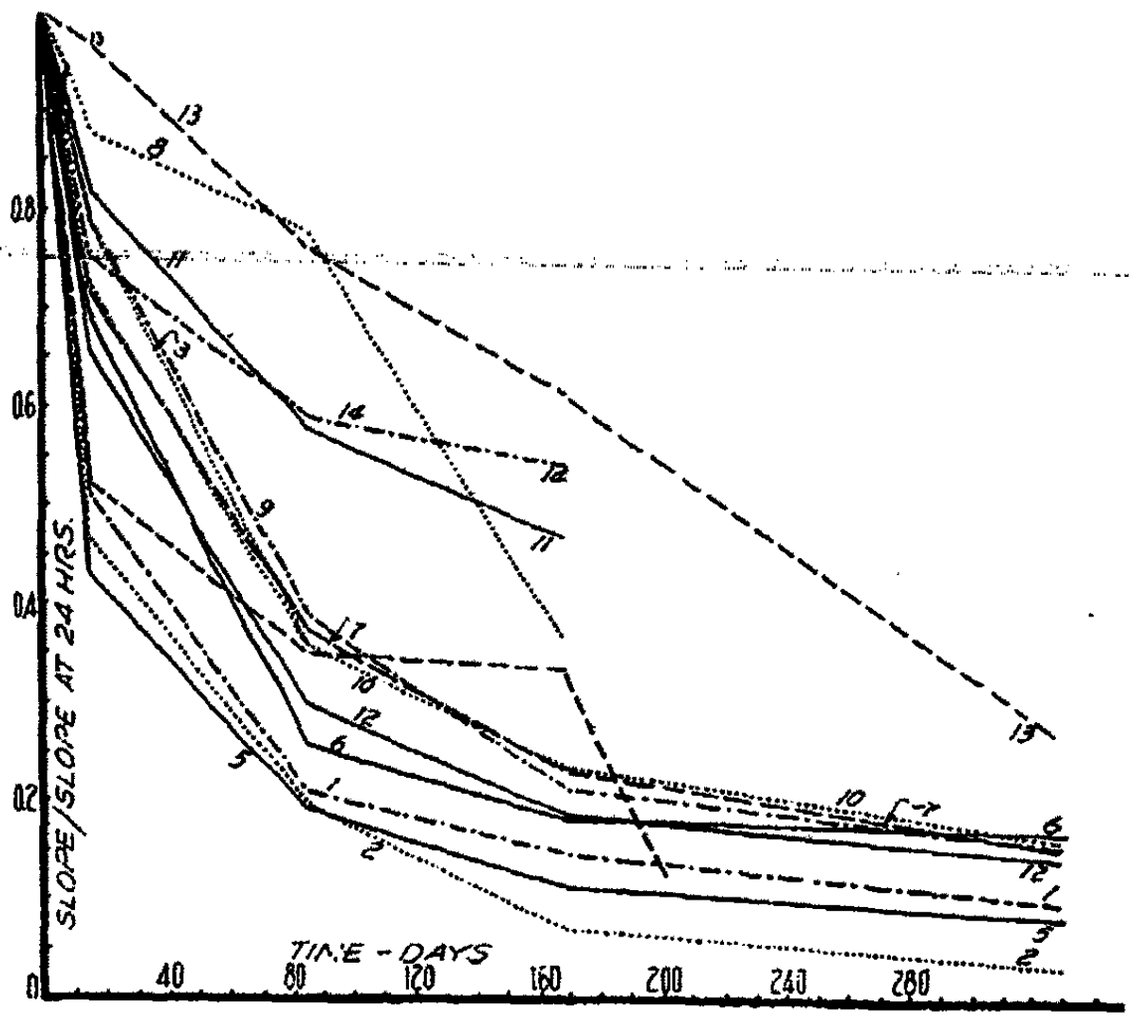



FIG. 6

Change with time in relative viscosity slope of solutions of nitro cotton taking the value at 24 hours in each case as unity.

Key

1. Ethyl formanilide
2. Formanilide
3. Methyl cyanilide
4. Benzyl formanilide
5. Phenyl urethane
6. Benzophenone
7. Methyl phenyl urethane
8. Acetophenone
9. Ortho tolyl urethane
10. Ethyl phenyl urethane
11. Triacetin
12. Benzyl phenyl urethane
13. Ethyl phthalate
14. Phenoxyacetic ester.

It is important in view of the above to note that most workers have ignored the possibility of ageing effects and that their work must be in many cases appreciably modified thereby.

(*b*) *Data up to long periods* (*one year*).

Here again most of our data are suppressed for lack of space, although series of experiments have been carried out by six of us. Typical data using

[1] Kolloidchem. Beihefte, 10, 145-178 (1918).

the latest technique may be found in the previous Table XI where the tubes were sealed and maintained at 55° in the dark.

Wholly independent duplicate determinations at age 24 hours usually agree in viscosity to within about 1% but large divergences develop after storage.

When slope is plotted against log of time for solutions of nitro cotton in a large number (14) of solvents as in Fig. 5, the general effect is a number of parallel straight lines. That is, the slopes diminish in absolute value in proportion to the log of the age of the solution and all at about the same absolute rate. The solutions showing originally the least viscosity would take about a year to approximate to the viscosity of a crystalloidal solution or to that of the solvent itself, whereas the worst solvents with the highest slopes would require about 60 years to do the same.

If all the slopes are divided by the slope for the same solution at the age of 24 hours; in other words if the initial slope is taken as unity for each solution and these relative slopes are plotted against times as in Fig. 6 it is found on examining the curves that the best solvents are those which relatively age most in a given time. Broadly speaking, the graphs maintain their relative

TABLE XV

Ageing of solutions of nitro cotton at 25°

| Solvent | Concn. | Age | Viscosity (poises) | Slope |
|---|---|---|---|---|
| Benzyl phenyl urethane (25/12/22) | 0.5288 | 1 day | 1.167 | 1.934 |
| | | 12 weeks | 1.042 | 1.841 |
| | 0.5500 | 1 day | 1.480 | 2.047 |
| | | 6 weeks | 1.404 | 2.005 |
| | 0.5288 | 1 day | 1.267 | 2.039 |
| | | 9 weeks | 1.217 | 1.968 |
| Methyl phenyl urethane (8/8/23) | 0.3761 | 1 day | 0.1422 | 1.983 |
| | | 4 days | 0.1192 | 1.781 |
| Acetone | 1.050 | 1 day | 0.01621 | |
| | | 14 days | 0.01618 | |
| | | 28 " | 0.01614 | |
| | | 120 " | 0.01572 | |
| | 1.045 | 1 day | 0.02047 | |
| | | 14 days | 0.02046 | |
| | | 28 " | 0.01999 | |
| Methyl ethyl ketone | 0.8303 | 1 day | 0.01368 | |
| | | 56 days | 0.01347 | |

position one to another so that the order of the solvents is approximately the same at every age. Furthermore, this same relative order of the absolute values of the slopes is maintained at age 168 days. This again is substantially the order of the initial values of the slopes in various solvents and is the order in which we would classify the solvents from good to bad.

12. *Ageing has a high temperature coefficient and still occurs at temperatures below the point of solidification of the solvent.*

Squance carried out measurements at 90° in which ageing is very much greater and much more rapid than at 50°. Ageing has thus a high temperature coefficient by Table XV due to Edwards at 25°, where the fall in viscosity is very slow.

Ageing still occurs when the solutions are allowed to solidify through crystallization of the solvent. When such solutions are only slightly below the melting point, the ageing may sometimes even be intensified; it is probable that in such cases only the free solvent and not that associated with the nitro cotton has crystallized. These remarks are illustrated by the data obtained by Smith, Table XVI.

TABLE XVI

Viscosity slopes of solutions of nitro cotton prepared in benzophenone (0.45%) and in o-tolyl urethane (0.36%) at 55° and measured at 55° but kept under various conditions at lower temperatures

| Treatment | Benzophenone Viscosity slope | o-Tolyl urethane Viscosity slope |
|---|---|---|
| Measured at age 24 hrs. at 55° | (1.55) | 1.66 |
| Kept undercooled at 40° for 13 days | 1.07 | 1.47 |
| Kept crystallized at 40° for 13 days | 1.48 | 1.394 |
| Soln. kept crystallized at room temperature for 13 days | 1.50 | 1.65 |

*Discussion.*

Almost invariably the viscosity of a cellulose ester changes on keeping even under constant conditions. Our work has been confined to temperatures above those at which gelatinisation of a fluid solution of nitro cotton takes place so that in all cases we observe a decrease in viscosity with age. The change in slope means a great change in viscosity so that 1% solution of nitro cotton that has been kept at 55° for a few months has a viscosity only a few per cent of its original value, a 1% solution of nitro cotton originally has a viscosity of between 7 and 100 times that of the solvent but finally it is not more than a few times that of the solvent even in the poorer solvents and in the best solvents it may exceed that of the solvent by as little as 20%.

There must be at least three aspects of the ageing process. The first is the increase in viscosity noted by other workers, but not observed in our work (even in measurements commencing at age 3½ hours), probably owing to our insistance upon obtaining homogeneous sols before measuring viscosity. This would undoubtedly be the breaking up of the finely divided suspension

of nitro cotton just sufficiently to form a true sol. The other two influences to be distinguished are the extent to which the viscosity is ultimately decreased and the rate at which the various solvents are able to effect this end. In confining the discussion to these three factors it is assumed that there is no chemical change occurring such as denitration through decomposition or nitration of the solvent.

Both viscosity and slope fall rapidly at first but apparently without reaching any definite end point. The absolute differences in slope and viscosity are greatest within the first week and least after long ageing; but the relative values of slope; that is, the ratios between slopes for various solvents are greatest after long ageing, whereas the ratios between solutions of highest and lowest absolute viscosity show no great regularity but are of the same order of magnitude throughout.

Inspection of Fig. 5 shows that the curves for slope exhibit but little confusion, there is comparatively little crossing. It seems a fair general description of the curves to say that viscosity in the solvents exhibiting the highest initial slopes (the poorer solvents) changes most but does so more slowly, in the best solvents, with the least initial slopes it changes most rapidly but has not so far to go.

It is important to note that the same behavior was observed and the same conclusions drawn for all the previous data obtained from work with less pure samples of solvent including those whose impurities made them into good solvents.

All this fits in with our interpretation that the best solvents are those which, right from the beginning, most thoroughly and quickly disintegrate the colloidal structure and reduce the aggregates to the smallest dimensions. The poorer solvents are those which are only partially successful in dissolving the bonds between the micelles of which the colloidal aggregates are built up. This distinction between the solvents persists and is even more marked at the end than it is initially. According to our view these larger loose aggregates immobilised a greater proportion of solvent and produce higher apparent viscosity. The slowness of the ageing effects we ascribe to the smallness of the residual affinity effects involved.

*Conclusion.*

Throughout all our work at 55° whether with pure or impure solvents, these solvents in which the viscosity slope was initially greatest, change most with time, but even after an indefinite period have relatively a much greater viscosity slope than the best solvents and solvent mixtures. The viscosity changes are enormous but they are in accordance with the hypothesis that the best solvents are those which most quickly and effectively resolve the colloidal aggregates into the smallest particles. The higher the temperature the greater the amount of degradation and the more quickly it takes place but apparently no definite end value is attained.

### III. The effect of Preliminary Treatment of Nitro Cotton with Acetone or Aqueous Acetone. (A method by which the viscosity of nitro cotton can be enhanced)

J. Duclaux and Mme. Wollman[1] when fractioning a commercial nitro cotton in acetone by progressive addition of water, observed that the slope of the relative viscosity for any one specimen of nitro cotton was approximately the same in various solvents. Thus the slope was 0.3 within 5% for a particular sample of nitro cotton in the following five solvents:— ethyl acetate, methyl alcohol, acetone, methyl formate, iso-butyl formate. It will be noted that all these are good solvents and should give comparable slopes. Whilst it is correct to point out the difference between the slopes caused by extreme varieties of nitro cotton according to Duclaux and Wollman, it is definitely wrong to generalize and say that the slope is independent of the solvent. With the purer solvents we have used, the range of slope is at least four-fold and with impure solvents at least 20-fold. The whole of our work consistently shows that when the relative viscosity is carefully measured under standard conditions it depends greatly upon the nature of the solvent, thus definitely disproving the suggestion of Duclaux and Wollman.

Duclaux used the Arrhenius formula, and his constant K is the viscosity slope as used in the present paper but multiplied by 100. There is no indication that he took effective measures completely to remove the acetone from the precipitated samples of nitro cotton which were under test.

Duclaux found that by this progressive fractionation he obtained a series of samples of nitro cottons whose viscosity slopes measured in acetone ranged from 3.70 down to 0.08. (Ours is about 1.3). All these fractions had the same nitrogen content and gave the same proportion of ash and differed only in the degree of colloidal dispersion. Duclaux was convinced that his separate fractions pre-existed in his original nitro cotton. However, we shall show that the very procedure of fractionation, and the manner in which it is carried out may appreciably affect the viscosity of the material obtained and may be used either to diminish or to enhance the viscosity and still more solubility. Duclaux's demonstration that all the fractions have the same ash and nitrogen content and differ only in size of particle and viscosity affords strong support for the theory of neutral colloids and the interpretation of viscosity put forward in the following paper. Duclaux found that the coarsest particles were the first to be precipitated and were those which gave the highest viscosity and the parallelism between these three properties also in accordance with the point of view here maintained.

1. *Experimental.*

From 55.3 grams of nitro cotton Duclaux obtained three fractions of 21 grams, 23.5 grams and 8 grams by adding various acetone-water mixtures to the solution of nitro cotton in acetone. R. T. Dale worked under the same quantitative conditions with Nobel's nitro cotton and practically the whole 55.3 grams precipitated out as a gelatinous first fraction. A remaining frac-

[1] Bull., 22, 414 (1920).

tion of about 1 gm. formed a milky suspension and could be separated only by using a Chamberland filter.

The precipitated nitro cotton was washed with distilled water until all the smell of acetone had vanished, and was then kept in repeated changes of distilled water. The first addition of water changed the gelatinous precipitate to a tough, white coherent solid. Finally the precipitated nitro cotton was dried in an air oven for three hours at 60° and left in a desiccator for six months. A sample of the original nitro cotton was dried for twelve hours at 60°C. Solutions could not be made under standard conditions at 55°. In ethyl phthalate it was necessary to place the solutions in the shaking machine at 88° for about 40 hours. Such solutions when measured at 55° gave a viscosity slope 11% *higher* than that of the original nitro cotton. Similarly formanilide solutions about a fortnight old at 55°, which had had 163 hours standard shaking were about 25% more viscous than similar solutions made from original nitro cotton.

Edwards recovered nitro cotton not by precipitation but merely by evaporating an acetone solution to dryness. After heating at 60° for 10 days it still showed an increase over the original weight of 0.2%. It gelatinised but did not dissolve in benzyl phenyl urethane even after shaking for 14 days at 55°. A second sample which was prepared by evaporation at room temperature required five days of shaking at 55° to dissolve (incompletely) in benzyl phenyl urethane. A third sample prepared by precipitation like Duclaux's after a fine grinding could be dissolved in benzophenone, phenyl urethane or benzyl formanilide with a couple of days shaking at 55°.

Smith prepared several samples of recovered nitro cotton by very gradual precipitation using several procedures. The third specimen was prepared by adding water drop by drop to a filtered 5% solution in acetone, the mixture being continuously agitated. The fine precipitate was dried in vacuo at room temperature for a week then at 60° for 3 hours. The various recovered nitro cottons were measured in ethyl formanilide, formanilide and phenyl urethane, the third specimen giving distinctly more viscous solutions than the original nitro cotton. Recovered nitro cotton had undergone about four days wet heating and one day's dry heating at 60°. The following table is particularly interesting because it shows the viscosities observed when these nitro cottons were dissolved in acetone, the solvent from which they had originally been precipitated.

TABLE XVII

Times of flow of solutions of 2 gm. nitro cotton in 100 ccs acetone (prepared at room temperature) shaken until solution is complete (about 3 hours) maintained for 23 hours at 55° and measured at 25°.

| Series | a | b* | c* |
|---|---|---|---|
| Recovered nitro cotton (1) | 666.8 | 679.0 | 694.6 |
| Recovered nitro cotton (2) | 802.4 | — | — |
| Recovered nitro cotton (3) | 1367.4 | 1274.6 | 1312.0 |
| Original 3 hrs. heated N. C. | 555.8 | 661.2 | 667.6 |

* In series b and c a different sample of acetone was used.

(*c*) *Discussion.*

The outstanding result is that nitro cotton recovered from solution in acetone is much more difficult to dissolve than the original nitro cotton whether the nitro cotton has been recovered by precipitation or by evaporation of the acetone. The length of time required for dissolving any one specimen of different solvents is roughly parallel with the magnitude of the usual viscosity slope and only the best solvents can dissolve recovered nitro cotton within 24 hours. This difficulty in dissolving must be largely a physical effect due to the less fine state of subdivision of the recovered as compared with the original nitro cotton. In other respects recovered nitro cotton is not very different from the original either in absolute magnitude of the viscosity slopes in the various solvents or in the diminution of viscosity with age in these solvents.

The enhanced viscosities observed in several cases particularly in acetone seem to be beyond the possible experimental error. It is puzzling that this effect is most pronounced in acetone; possibly the effect may be explained as being due to a firm re-coupling of colloidal particles or micelles which were separated in the original acetone solution. Removal of the acetone must apparently couple some of the bonds from which it has been split off, in a way somewhat analogous to the coupling one gets in such reactions as that of Fittig. Here however since residual affinity is involved it does not appear necessary that acetone has to be split from both groups simultaneously in order that they should unite. It is quite conceivable that when these coupled particles are again placed in acetone their bonds are not necessarily or immediately reloosened to allow of resolvation. It is possible too that at room temperature a nitro cotton solution may be becoming on the whole less viscous through the colloidal aggregates breaking up at certain junctions whilst simultaneously other bonds in a different part of the micelles are in process of linking up to form new but perhaps smaller colloidal aggregates.[1]

## IV. Alcohol as a Solvent for Nitro Cotton

(*c*) *Experiments at very low temperatures.*

Experiments were carried out by L. E. Smith on the gelatinizing power of alcohol. It was found that the nitro cotton containing 12.1% nitrogen was soluble at room temperature to the extent of 0.35% in 95% alcohol. Experiments were devised to find the solubility of the same nitro cotton at low temperatures in anhydrous alcohol. The alcohol was thoroughly dried and then distilled into tubes already containing the nitro cotton. Solutions of various concentrations were prepared. The tube containing the smallest quantity of nitro cotton was first cooled in a mixture of solid carbon dioxide and ether; and the nitro cotton formed a solid compact mass which could not be broken up by shaking. The other tubes were well shaken before cooling to prevent this from happening. On cooling the second tube containing approximately 0.8% nitro cotton the liquid became more viscous and dissolved the nitro cotton, forming a viscous sol which on warming to room temperature

[1] Compare the solutions of original N.C. in benzyl formanilide referred to on p. 339

set to a flowing jelly or gel. The change from sol to gel was reversible, for on cooling the gel it reverted to the sol form. Two more solutions showed the same phenomenon. The gels became more turbid as the concentration of the nitro cotton was increased. The solution containing 5% nitro cotton was a stiff very turbid gel. These gels are stable at room temperature and even after a period of 18 months still show the reverse change on cooling. They show the phenomenon of syneresis to a marked degree. It is impossible to measure the actual solubility of nitro cotton under such conditions.

Ether was also tested to see if it also exerted a solvent action on nitro cotton at low temperatures, but without success. A sample of ether which had been in contact with nitro cotton for 18 months showed that it had dissolved only 0.004% of the nitro cotton. According to Kugelmass[1] ether at low temperatures dissolves traces of nitro cotton forming suspensoids showing a blue opalescence. In the case of alcohol he reported a series of distinctly separated layers. Neither of these observations could be confirmed by Smith.

Mardles[2] states that he found with cellulose acetate on simply cooling precipitation took place in some sols. "Schützenberger[3] pointed out that the triacetate of cellulose dissolved in nitro benzene on warming whilst on cooling the solution it was precipitated in a gelatinous form. The method of observing this transition temperature of the dispersion medium from a complete solvent to a partial or non-solvent has been used to appraise the relative solvent powers of liquids for cellulose esters in a research on solvents suitable for aeronautical varnishes, the principle being that the lower this temperature, the better the solvent[4]. However, this cannot be a universal method since in alcohol and in Szegvari's experiment the temperature effect would be upside down.

(b) *Experiments with alcohol at high temperatures.*

Mardles[5] states:—"Although a liquid may be a non-solvent of a cellulose ester, at temperatures at and below its boiling point at atmospheric pressure, it often happens, for example with alcohol, benzene, methyl ethyl ketone for cellulose acetate, that it becomes a solvent at higher temperatures. Anhydrous alcohol becomes a solvent for a particular sample of cellulose acetate at 120° and industrial at 100°. Thus alcohol cannot be considered merely as a diluent, since in mixtures, especially when dissociated, it must contribute greatly to the solvent action." The validity of Mardles conclusion evidently requires re-examination in the light of our results with cellulose nitrate and alcohol at high temperatures. Nitro cotton and alcohol were sealed in a glass tube and heated to 100° for two or three hours, but no gelatinisation appeared to take place in this time. The tube was then heated at 120° for upwards of 12 hours and at the end of this time most of the nitro cotton had dissolved leaving a slight residue. The solution obtained was yellow and very mobile

[1] Rec. Trav. chim., 41, 751 (1922).
[2] J. Soc. Chem. Ind., 42, 127T (1920).
[3] Compt. rend., 68, 814 (1869).
[4] Mardles, Moses and Willstrop: Advisory Committee for Aeronautics; Reports and Memoranda, No. 568.
[5] J. Soc. Chem. Ind., 42, 128T (1920).

even when 10% of nitro cotton had gone into solution. Alcohol containing varying amounts of water also dissolved nitro cotton, but the greater the proportion of water in the mixture the greater the amount of residue and the darker the solution.

It is obvious that this solvent action is not due to unchanged alcohol alone, but partly to the products obtained by the nitration of the alcohol by the nitro cotton. The solution smelt strongly of esters. The residue was probably nitro cotton but this has not been tested.

(*c*) *Discussion.*

There are very few instances of a gel being formed from a sol on heating, and reforming a sol on cooling. Szegvari[1] thought that he had discovered the first one; namely, nitro cellulose dissolved in a mixture of amyl acetate and benzine (not benzene). This is not so striking as the present case of alcohol, where the possibilities are more limited.

Szegvari set up the *ad hoc* explanation that at lower temperatures the amyl acetate combined with nitro cellulose rather than with benzine, whereas at higher temperatures a compound was formed between amyl acetate and benzine to the exclusion of the former combination. In the present case there is no benzine to compete with the nitro cellulose.

All the experimental observations fit in well with our general working hypothesis which says nothing about association, dissociation and hypothetical combination between solvents but presupposes that certain definite chemical bonds of residual affinity have to be satisfied by combination with appropriate groups of suitable solvents in order that the micelles can be freed from each other. A mixture of suitable solvents is more likely to supply the correct groupings necessary for solvating the different portions of the nitro cellulose molecule. Alcohol by itself is a complete solvent at sufficiently low temperature, but an incomplete one at ordinary temperature owing presumably to de-solvation and relinking of certain bonds at the extremities of the constituent micelles which thereupon are relinked. This again explains the solvent action of "alcohol" at extremely high temperatures where the nitrogen content of the nitro cellulose is lowered and an ethyl nitrate appears in the solution.

To sum up, anhydrous alcohol is a complete solvent for our nitro cotton at very low temperatures but at ordinary or high temperatures admixture with a supplementary solvent such as ether or an ester is essential. The sol-gel transformation in anhydrous alcohol is completely reversible.

## V. Properties more or less parallel to Solvent Power

It is convenient to summarize the available information with regard to properties which we have found more or less parallel to solvent power[2]. Good

[1] Kolloid-Z., 34, 34 (1924).

[2] For a theoretical definition of the term "solvent power" see VIII. General Conclusion, at the end of this paper. A technical definition may be based upon the uniform appearance and case of pressing of nitro cotton gelatinized under manufacturing conditions, but this is not quite the same as the insistance that the solvent itself in sufficient quantity produces a fluid sol.

solvents unite strongly with nitro cotton, not being completely recovered either by heat or extraction; they have low melting points, relatively low viscosity, abnormally slow rate of crystallization, and their rate of crystallization is more affected by the addition of nitro cotton. The apparent viscosity of a fresh solution divided by that of the solvent is least for the best solvents steadily increasing up the worst solvents. Poor solvents require much greater time to prepare homogenous solutions, their viscosity changes most on ageing, but the change is slower. All adjustments of equilibrium with nitro cotton, such as extraction or degelatinization, seems to be slow with poor solvents, provided that they are actually capable of dissolving or gelatinizing nitro cotton. Within any homogeneous series the lower the molecular weight the greater the solvent power. Relatively small amounts of good solvents have to be added to non-solvents to give them power of dissolving nitro cotton and the best solvents stand most dilution before losing this power; however, this depends to a certain extent upon the complementary nature of the particular solvent and non-solvent chosen. The best solvents are adsorbed to the largest extent and are combined most firmly. Solvents evolve much greater heat of reaction with nitro cotton than do non-solvents. Finally, admixture with suitable complementary substances greatly enhances solvent power.

Sproxton[1] suggests from methods of measuring solvent power:—

1. First and most sensitive, apparent viscosity, which is the subject matter of the present paper.

2. Second, the so-called transition temperature; that is, the degree to which a sol can be cooled before solidification, but there is a radical objection to it because some systems show the temperature upside down, for example it is on cooling not on heating that alcohol forms sols.

3. Third, his supposedly least dependable criterion, the amount of diluent which can be added. Mardles has again made great use of this, calling it solvent power and occasionally varying the actual diluent employed. The only objection which rises from our conception and which is fully substantiated by L. E. Smith's experimental work (not included in this paper) is that the result depends upon the complementary nature of the particular diluent and solvent employed. Even the use of a perfect non-solvent if such exists, does not obviate this difficulty since it does not take into account the different kinds of chemical grouping with which various solvents unite.

4. Lastly, measurement of the amount of nitro cotton dissolved from partially soluble esters; that is, a specimen which presumably contains quite different nitro cotton, (not like the very homogeneous specimen we have used).

It is of interest to note that Mardles[2] has met several cases where criteria 1 and 3 conflict; that is, where apparent viscosity does not go parallel with "solvent power." This is only what could be expected in view of the preceding discussion.

---

[1] Trans. Faraday Soc., 16, Colloid Discussion, 78 (1921).

[2] J. Soc. Chem. Ind., 42, 210T (1923).

## VI. General Summary

1. By taking suitable proportions it is possible to obtain accurate reproducible measurements of the apparent viscosity of nitro cotton in various solvents.

2. Nevertheless, the apparent viscosity cannot be regarded as a true viscosity such as is possessed in an ordinary liquid or solution because experimentally it is found to depend distinctly upon the rate of shear and theoretically it is shown that the viscosity is so great that it must be ascribed to interference between ramifying aggregates of colloidal particles in the solution.

3. A list of the factors which influence the apparent viscosity discussed.

4. It is shown that the period of drying nitro cotton at 60° affects the viscosity of the solutions subsequently made therefrom. The most viscous solutions are those made from nitro cotton which has been heated for less than one day, and the viscosity is progressively less when the preliminary heating of the nitro cotton has been extended to weeks or months.

5. Vigorous shaking of freshly prepared solution diminishes the viscosity apparently by assisting in breaking down residual structures derived from the figures of nitro cotton.

6. The available information with regard to mixtures of liquids whether solvents or non-solvents is reviewed and extended and it is shown that in the vast majority of cases a mixture in suitable proportions is a better solvent than the individual ingredients.

7. Likewise the solvent power of a given material is greatly dependent upon adventitious impurities; the purer sample in general being the least efficient solvent.

8. It is amply demonstrated (contrary to a suggestion of Duclaux and Wollman) that the viscosity of a solution of a particular nitro cotton even when referred to that of the respective solvent depends greatly upon the solvent power of the solvent. The best solvents give the least viscous solutions. Formanilides were better than urethanes or than pure esters.

By various treatments of nitro cotton previously dissolved in acetone—the resultant viscosity of the solutions made therefrom may be affected and even increased. The recovered nitro cotton is far more difficult to dissolve.

10. The viscosity of all solutions of nitro cotton diminishes on keeping at 55° the change being roughly proportional to the logarithm of the time and the slope of the graphs such as would correspond to the viscosity of solutions in the best solvents becoming comparable with that of the solvent in about one year whereas the poorer solvents would take up to 60 years. This so-called degradation is ascribed to progressive dismemberment of the colloidal aggregates into the constituent colloidal aggregates or micelles.

11. It is shown that anhydrous alcohol is a complete solvent for propulsive soluble nitro cotton at low temperatures whereas at room temperature the sol sets to a jelly. This change being reversible indefinitely. The rather imperfect solution at very high temperatures (130°) was shown to be due to the impurities resulting from denitration and decomposition. A complete list

of all the various properties which are more or less parallel to solvent power is given.

12. The following substances have no visible effect upon nitro cotton although it is certain that they all combine with it to various extents: water, benzene, toluene, chloroform, ether, petral, tolyl carbonate, dibenzyl ether.

## VII. General Conclusions

The fundamental facts operative in the behavior of solvents and nitro cotton is direct combination between solvent and suitable complementary chemical groups in the nitro cotton. The apparent viscosity of the solutions is almost entirely due to the presence of loose ramifying aggregates of colloidal particles united by local and specific bonds of residual affinity of different kinds and degree. The best solvents are those which most effectively combine with these bonds and by themselves satisfying the residual affinities dismembers the aggregates. Hence, the best solvents yield solutions of the lowest apparent viscosities and mixtures of solvents and even "non-solvents" affording a variety of suitable chemical groups are much more efficient than a single solvent. Recoupling may take place when the proper points on the chemical particles are deprived of their chemical complements; for example, through action of a diluent. It is even possible in this way to increase the viscosity of a nitro cotton. In the transformation from a sol to a solid if the recoupling takes place without appreciable segregation (comparable with the wave length of light), transparency is not affected. In this way coherent films and transparent lacquers are produced. The above theory if correct should be applicable through out the whole subject of colloids.

We have great pleasure in acknowledging the invaluable support of Messrs. Nobel's Explosive Co., Ltd. and the unfailing interest of their scientific staff.

*Department of Physical Chemistry,*
*The University,*
*Bristol, England.*
*September, 1925.*

# ADSORPTION OF ETHYLENE AND HYDROGEN BY ZINC OXIDE, IRON OXIDE, NICKEL AND COPPER*

BY WILBUR A. LAZIER AND HOMER ADKINS

The more recent investigations on the adsorption of gases by solid catalysts have shown that adsorption precedes catalytic activity altho the latter does not necessarily accompany the former. It has been further demonstrated that any change in the extent of one of the manifestations is accompanied by a change of the other in the same direction. For example, Pease and Stewart[1] have shown that poisoning a copper catalyst with mercury or carbon monoxide or deactivating it by high temperatures, not only lowers the activity towards hydrogenation of ethylene but the adsorptive capacity for the reacting gases as well.

It has also been proposed that the course of competing reactions may be determined by the relative adsorption of the reactants or resultants of the reaction in question. The importance of correlating, when possible, data on adsorption and catalysis is thus demonstrated and there are too few examples of these two sets of data available on the same materials. Measurements of the adsorption of hydrogen and ethylene by seven catalysts have been undertaken in connection with a study of the catalytic characteristics of those contact materials previously reported.[2]

## Experimental

*Apparatus:* The apparatus used was a modified form of that described by Pease[1]. The arrangement of the various parts is shown in Fig. 1. A is the catalyst bulb which was of common glass tubing, 1 to 3 cm. in diameter and 6 to 10 cm. in length, depending upon the amount of solid material used in a determination. The bulb was heated by an electric tube furnace not shown in the figure, and was connected to the manometer, B, by means of a glass capillary tube and three-way stopcock. The manometer was equipped with a leveling bulb filled with mercury. The water-jacketed gas burette, C, was of 100 cc. capacity and was also filled with mercury as a retaining liquid. The vacuum line was placed between the gas burette and manometer, and joined these by means of a glass T, all pieces of apparatus being joined by glass seals. Well-fitting glass three-way stopcocks were used between the various parts as shown in the figure. The vacuum line included a small manometer of the closed tube type, making barometer readings unnecessary. The system was exhausted with a Cenco Hyvac pump, capable of attaining a pressure of .001 mm. of mercury although pressure readings could not be made lower than two-tenths of a millimeter. The bulb, D, was of the same capacity as the

* Contribution from the Laboratory of Organic Chemistry of the University of Wisconsin.

[1] J. Am. Chem. Soc., 47, 1329 (1925).

[2] Adkins and Lazier: J. Am. Chem. Soc., 46, 2291 (1924).

[1] J. Am. Chem. Soc., 45, 1197 (1923).

burette and was used for the storage of gas. The other apparatus shown in the figure was used for the purification of the gases used.

*Preparation and Purity of Gases:* Hydrogen was obtained by electrolysis of a 15% solution of sodium hydroxide, the electrodes being of nickel gauze. From the generator the gas was conducted through a drying tube filled with calcium chloride and phosphorus pentoxide, and then through a porcelain tube furnace containing copper heated to redness. In this manner the oxygen included in the gas by diffusion was removed by combustion, after which the

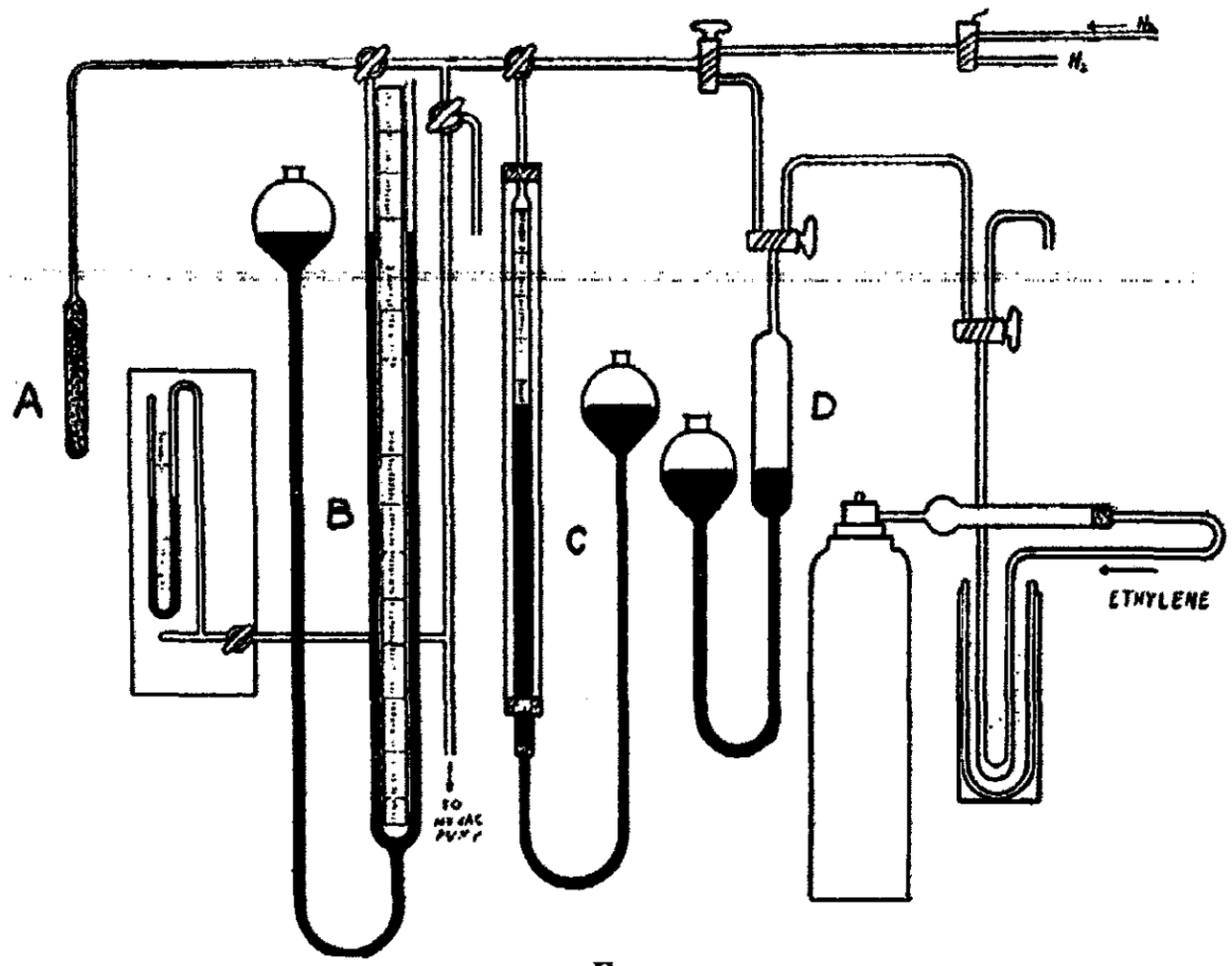



FIG. 1

Apparatus for measurements of adsorption and catalytic activity.

gas was again dried by passing over phosphorus pentoxide. In order to completely remove air from the system, the pure hydrogen was allowed to flow past the burette for 18-24 hours before the burette was filled. Commercial ethylene was purified by passing through a condensing system immersed in a freezing mixture in a Dewar flask having a temperature of about 20°C. A sample of this gas was 99.6% absorbed in bromine water. Nitrogen was prepared by the usual method of removing the oxygen from air. Carbon monoxide was obtained by allowing formic acid to drop into concentrated sulfuric acid heated to a temperature of 100°.

*Adsorbents:* Seven different adsorbents were used in this work. In each case (except where Merck's granules were used) the oxide was pressed into pellets (3 × 8 mm.) by means of a pharmaceutical tablet machine.

*Cupric Oxide* (*"Ex-nitrate"*). Two hundred grams of hydrated copper nitrate was heated in a beaker over a hot plate until the greater part of the water had been expelled and the mass was almost solid, oxides of nitrogen

being involved. The mass was cooled, placed in a Pyrex tube open at one end and heated in a furnace at 450° for 4 hours. The black powder was then thoroughly washed with water and ground in a mortar.

*Cupric Oxide* (*Merck's Granules*). Analysis showed 1.10% $Ni_2O_3$, 0.21% $Fe_2O_3$ and 0.47% $SiO_2$. The material was screened to a uniform size of 30 granules per gram.

*Ferric Oxide* (*Precipitated*). A hot solution of 100 g. of ferric chloride in 3 liters of water was treated with an excess of ammonium hydroxide. The precipitate was washed four times with three liters of hot water, after which it gave no test for chlorides so was dried at 110°.

*Nickel Oxide* ($Ni_2O_3$). Eighty mesh pumice was washed repeatedly with dilute nitric acid and finally with distilled water and then ignited 1 hour over a Bunsen flame. Three hundred grams of nickelous nitrate hexahydrate was melted and 75 g. of pumice stirred into it. This was heated over a hot plate until almost dry and then in a Pyrex tube for 5 or 6 hours at 350° to 400°. The product was found by analysis to contain 38% nickel.

*Zinc Oxide* (*Ex-hydroxide*). The hydroxide was precipitated from a solution of the sulfate by the addition of the theoretical amount of sodium hydroxide. The precipitate was washed free of sulfate and dried for 24 hours at 110°.

*Zinc Oxide* (*Ex-zinc isopropoxide*). Dry alcohol—insoluble zinc isopropoxide mixed with sodium chloride was allowed to hydrolyze in moist air. The sodium chloride was then washed out with water and the product dried at 100°.

Copper and nickel were prepared by reduction of their oxides after the bulb containing them had been sealed in place. 62.25 grams of cupric oxide, which yields 50 grams of the metal on reduction was placed in the bulb, sealed to the apparatus and reduced in a stream of dry hydrogen at 200° for 40-60 hours. After reduction was complete as shown by no gain in weight of a calcium chloride tube attached to the outlet of the bulb, the latter was sealed off with the hydrogen still flowing. 26.5 grams of nickelic oxide on pumice which analysis showed would yield 10 grams of the metal was reduced in the same manner but at a temperature of 400°.

A special bulb was devised for the reduction of the same amount of the nickel oxide by alcohol. This bulb contained a perforated core through which the alcohol vapor could penetrate the whole contents of the bulb, thus diminishing the reduction of the oxide which might take place with carbon monoxide, methane, and hydrogen, the products of the reaction of ethanol over nickel. Forty cc. of alcohol was passed through the bulb at 420° in an hour. The bulb was then sealed off.

Ten gram samples of ferric and zinc oxides were used. The greater part of the water of hydration was removed by heating the bulb, while still open at one end, in the furnace at 300°, for 2 hours before sealing on to the apparatus.

*Method.* Experiments were conducted in cycles of 24 hours, each experiment being begun in the morning and concluded on the following morning. The adsorption bulb was "degased" by exhausting and heating for 3 or 4 hours at 200° in the case of the nickel and copper and at 300° with

the oxide catalysts. Temperature control was maintained by means of a Leeds and Northrup potentiometer controller. The current was then turned off, the furnace opened, and the vacuum pump allowed to continue running during the 3 or 4 hours required to cool the contact material down to room temperature. The bulb and manometer and in turn the vacuum line were then shut off from the remainder of the apparatus. The gas burette was then opened to the exhausted tubing and a reading taken at atmospheric pressure, after which gas was admitted to the bulb from the burette. The mercury in the manometer was always adjusted in such a manner that the two columns were level at the same arbitrarily selected point near the top of the scale before volume readings were made on the gas burette. The adsorption of hydrogen by copper was found to proceed rather slowly so that frequent readings and adjustment of the mercury levels were necessary. In all cases the final readings were not made until the following morning. All adsorption determinations and volume readings were made at room temperature and atmospheric pressure. Temperatures and pressures were recorded but since the experimental error was greater than that due to such changes, these factors have been disregarded and the final results calculated from 22° and 740 mm. to 0° and 760 mm. pressure. Duplicate determinations agreeing within .5 cc. were considered satisfactory.

Assuming that nitrogen is not adsorbed, the difference between the volume of nitrogen required to fill the bulb and the volume of any other gas, gave the adsorption of the gas in question. Such an assumption is not quite valid since Benton has found that nitrogen is slightly adsorbed by some oxide catalysts. It is, however, sufficient to give comparative results.

### Data on Adsorption

The data obtained in about seventy determinations of adsorption are summarized in Table I. The values given in the Table represent the number of cc. of gas at N.T.P. adsorbed at approximately 22° and 740 mm. pressure by 100 g. of adsorbent. The measurements were made upon both 25 and 50 g. samples of copper from "Merck's Oxide", and upon one of the 50 g. samples which had been oxidized and reduced a second time. 50 g. of copper from copper "ex nitrate" was used. 10 g. samples were used in the case of the other adsorbents. In addition it was found that 100 g. of the iron oxide adsorbed 65 cc. of carbon monoxide.

TABLE I

Adsorption of Gases by Solid Catalysts

| Catalyst | Ethylene | Hydrogen |
|---|---|---|
| Copper (Merck) | 7.2 | 24.0 |
| Copper (ex nitrate) | 2.0 | 0.55 |
| Nickel (by hydrogen) | 70.0 | 84.0 |
| Nickel (by alcohol) | 205.0 | 61.0 |
| Zinc Oxide (ex hydroxide) | 57.0 | 1.8 |
| Zinc Oxide (ex isopropoxide) | 160.0 | 23.4 |
| Iron Oxide (precipitated) | 588.0 | 0.0 |

## Hydrogenation of Ethylene

Equimolecular mixtures of ethylene and hydrogen were allowed to enter the evacuated adsorption chamber, the catalyst being the same as that used for the adsorption measurements. In the case of nickel (10 g. on pumice, reduced by alcohol at 420°) and Merck's copper (50 g. reduced at 200° with hydrogen) the reaction was so rapid that it was practically (95%) completed before the first (5 min.) measurement could be made. In the case of the nickel the contraction of the gases due to reaction and adsorption was 59.0 cc. as contrasted with an adsorption of hydrogen alone of 6.1 cc. and of ethylene alone of 20.5 cc. The contraction with Merck's copper was 34.0 cc. of the mixed gases as contrasted with an adsorption of 12 cc. of hydrogen and 3.6 cc. of ethylene. Fifty g. of the copper (ex nitrate) only adsorbed or caused to react 3.6 cc. of the mixed gases after 24 hours. The hydrogen adsorption for the catalyst was 0.27 cc. of hydrogen and 1.0 cc. of ethylene when the gases were introduced separately.

## Discussion

Certain facts should be noted in connection with the results given above. The nickel, reduced through the use of alcohol, contained carbon which probably affected the amount of gases adsorbed. No means was devised to eliminate this source of error. However the adsorption values were obtained for the sake of tying them up with the measurements in catalytic activity, where carbon was also present. It was impossible to ascertain whether the nickel oxide was completely reduced before the adsorption measurements were made. However, the time of reduction was two or three times as long as previous work had indicated to be necessary, for complete reduction of nickel oxide. It is interesting to note that there was no "induction period" when nickel was used as a catalyst for the hydrogenation of ethylene. Such induction periods have been observed when the catalyst was covered with hydrogen at the beginning of the experiment. In our experiments the nickel was degased before the ethylene-hydrogen mixture was introduced. The experimental results are in accord with Palmer's explanation of the reason for the induction period, i.e. the time necessary for the replacement on the catalyst of hydrogen by ethylene.

The effect of small amounts of nickel in increasing the adsorption of gases by copper and of promoting its catalytic activity is clearly indicated by the behavior of the "copper" obtained by the reduction of Merck's copper oxide granules, as compared to the copper obtained from copper nitrate. It seems probable that the very active "copper" obtained by Taylor from "Kahlbaum's granules" may have contained nickel. (P. 102 of the First Colloid Symposium Monograph, University of Wisconsin, Madison, 1923)

It is evident from an inspection of the results of the adsorption and catalytic activity of these seven catalysts as reported in this paper and elsewhere, that there is a qualitative agreement between the two manifestations of chemical activity, as has been previously demonstrated by the extensive

work in the Princeton Laboratories. However, as pointed out by Bischoff[1] and later even more conclusively by Pease and Stewart[2], and by Russell and Taylor[3] there is apparently no quantitative relationship between total adsorption and catalytic activity.

There is not even a qualitative agreement between the relative adsorption of two gases and the relative production of these two gases in catalysis. For example, precipitated zinc oxide is more effective in dehydrogenating ethanol (as compared with dehydrating it) than is zinc oxide from zinc isopropoxide. The former is a much poorer adsorbent for hydrogen that is the latter. It seems certain that the total catalytic activity and the relative activity for different reactions is conditioned not only by adsorption but by the topography of the surface. The question as to whether the effective (for catalysis) portion of the surface is that of very unsaturated atoms[4], or is determined by the spacial relationships of certain atoms[5] will be discussed elsewhere.

## Summary

The adsorption of ethylene and hydrogen by seven catalysts has been determined. Data in addition to that already published are given as to the catalytic activity of some of these compounds. The probable effect of 1% nickel in promoting the adsorption and catalytic activity of copper has been pointed out.

*Madison, Wis.*

[1] Bischoff and Adkins: J. Am. Chem. Soc., **47**, 807 (1925).
[2] Pease and Stewart: J. Am. Chem. Soc., **47**, 1239 (1925).
[3] Russell and Taylor: J. Phys. Chem. **29**, 1325 (1925).
[4] Taylor: Proc. Roy. Soc., **108A**, 105 (1925).
[5] Adkins and Nissen: J. Am. Chem. Soc., **46**, 130 (1924).

# AQUEOUS SOLUTIONS OF SODIUM SILICATES
## PART II. TRANSPORT NUMBERS

BY R. W. HARMAN

In a previous communication[1] the results of the measurement of the electrolytic conductivity of solutions of six sodium silicates of ratios varying from 2:1 to 1:4, have been given. It was there shown that all these silicates are very good conductors in dilute solution, and that in concentrated solution the conductivity decreases as the proportion of silica in the ratio increases.

Earlier investigators such as Kohlrausch[2] and Kahlenberg and Lincoln[3] attributed the high conductivity of solutions of sodium metasilicate to complete hydrolytic dissociation. This view seemed more or less firmly established until measurements of hydroxyl ion concentration by E. M. F. methods by Bogue[4] pointed to a much lower percentage hydrolysis even in dilute solution. Bogue's measurements have been repeated and extended to other ratios and the results will be communicated in a later paper, where it is shown that his conclusions are in the main correct. The conductivity of solutions of various ratios $Na_2O$:$SiO_2$ cannot therefore be accounted for solely by hydrolytic dissociation, not even in the case of solutions of sodium meta-silicate, where the hydroxyl ion concentration is moderately high. But the ratios 1:2, 1:3, 1:4, etc., have a very low hydroxyl ion concentration, even in dilute solution, and yet their conductivity is quite high. To what is this conductivity due? The conductivity may be accounted for by the presence of a fairly mobile silicate ion, or by assuming that the silicic acid is colloidal and has adsorbed hydroxyl ions. If the latter view were correct, one would not expect the colloidal aggregate to be very mobile, and the osmotic activity of the solution would be abnormally low.

Transport experiments should throw light on this question, and by their means some knowledge could be gained of the kinds of ions and their mobilities. If silicate ions exist in solution, and it seems justifiable in view of conductivity measurements to assume that they do, then their nature must be determined.

When this work was begun, the existence of definite sodium silicates of ratios other than 1:1, i.e. $Na_2SiO_3$, was very doubtful. No conclusive evidence had been put forward to prove whether they were definite salts or merely mixtures of the metasilicate with silicic acid or caustic soda as the case may be. It was hoped that transport number experiments would produce some evidence as to whether the silica existed as colloid, simple ions, aggregates of simple ions carrying a sum total of their separate charges (i.e. ionic micelles), or as complex ions.

---

[1] Aqueous Solutions of Sodium Silicates, Part I. J. Phys. Chem., 29, 1155 (1925).
[2] Ann. Physik, (3) 47, 756 (1892).
[3] J. Phys. Chem., 2, 77 (1898).
[4] J. Am. Chem. Soc., 42, 2575 (1920).

While the results do not completely elucidate all these problems, they do yield considerable insight into the nature, complexity, and mobility of the silicate ion.

## Experimental

*Method.*

In solutions corresponding to ratios where hydrolysis has taken place there are three constituents active in carrying the electric current, viz, sodium, hydroxyl, and silicate ions. In such cases the only method likely to yield complete and reliable results is the original analytical method of Hittorf. The moving boundary method seems inapplicable to such solutions containing three kinds of ions, as the boundary formed by the more slowly moving anion would be disrupted by the quicker moving anion, even if a suitable reference substance could be found which did not coagulate or otherwise interact with the silicate solution.

This method could probably be used to determine the transport number of the sodium and the hydroxyl ions, but as the main object of these experiments was to investigate the silicate ion, the moving boundary method was deferred, though it is hoped to develop it later. Other methods of determining the transport number such as by E. M. F. measurements of cells with and without transport, or by gravity and centrifugal cells[1] are also of very doubtful or difficult application in these solutions.

By the analytical method the change in concentrations of sodium and silica at the electrodes may be determined accurately, but unfortunately it is impossible by this method to determine the transport number of the hydroxyl ion directly. The presence of hydroxyl ions and the fact that hydroxyl ions are formed as a result of the cathode reaction, not only makes the determination of the transport number more difficult, but also increases any inaccuracy in the experimental figures. However, a study of the electrode reactions shows this interference, due to the formation of hydroxyl ions, not to be so serious as might at first sight be expected.

*Apparatus.*

The apparatus shown in Fig. 1 consists of three U-tubes, the middle one about one-half the depth of the outer ones, the whole apparatus being of uniform bore throughout to avoid local heating and convection currents. It was made of resistance glass with ground-glass joints at E and F, so that the middle U-tube could be disconnected from the other two. The outer U-tubes were closed by ground-glass stoppers at A, B, C, and D, those at A and D being hollow and terminating in a tap to allow gas evolved during the experiment to escape. The electrodes of platinum were about 1.5 cm. square and were sealed in through the hollow stoppers A and D. The capacity of the apparatus was about 350 cc. During an experiment the apparatus was immersed in a water thermostat electrically heated and regulated to 25°C. ± 0.01.

The apparatus was cleaned with caustic soda and chromic acid immediately before and after use, no silicate solution ever being allowed to evaporate in it, as it would then have been most difficult to clean thoroughly.

[1] Cf. Tolman: Proc. Am. Acad., 46, 110 (1910).

A current of from 12-20 milliamps, at 55 or 110 volts was passed through the solution for from 2½ to 3 hours according to the strength of the solution. Two silver coulometers, well insulated, were included in the circuit to detect any leakage of current, and to measure the current used. These coulometers agreed within 0.01%.

At the end of an experiment, the solution was divided into five portions shown by dotted lines on the figure, A, AM, M, CM, and C of weights 100, 50, 50, 50 and 100 grams respectively. The taps at A and D being closed, the stoppers B and C were alternately removed and the portions AM and CM

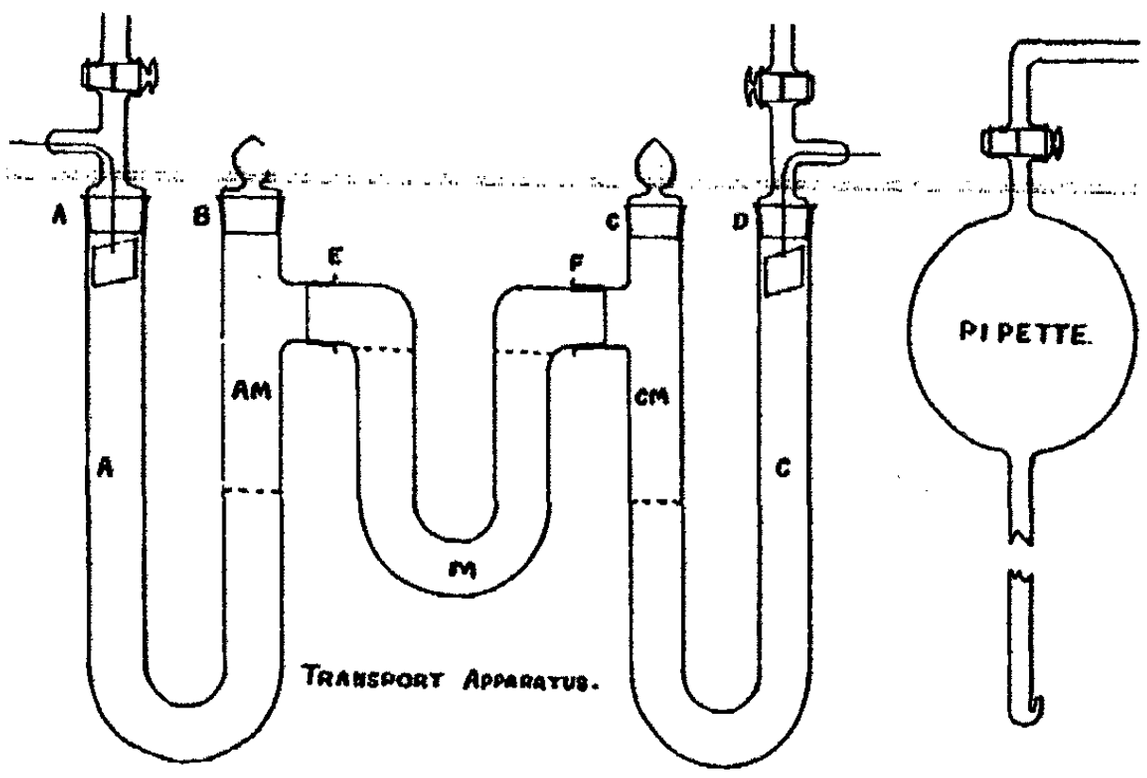



FIG. 1

withdrawn and transferred to weighed flasks by means of a pipette with an upturned tip, shown in Fig. 1. This was done while the apparatus was still in the thermostat, the tip of the pipette being kept just below the surface of the liquid which was being withdrawn. This prevented any mixing of portions A, M, and C, either by currents set up due to removal of a portion, or by shaking during removal from the thermostat. The apparatus was then taken out of the thermostat, disconnected, the joints freed from grease and portions A, M, and C transferred to weighed flasks. These five portions and a sample of the original were then set aside for analysis.

The solutions used were prepared in a manner similar to that described in Part I, on preparation and conductivity. As there, the term ratio denotes $Na_2O:SiO_2$ in equivalent proportions.

*Analysis.*

The five portions and the original solution were analysed for both sodium and silica. The procedure strictly followed in each analysis was that given by Hillebrand in his Monograph on "The Analysis of Silicate and Carbonate

Rocks", Bulletin 700 of U. S. Geological Survey, 1919. The solution was evaporated twice to complete dryness with HCl, and the silica ignited and weighed. This silica was then volatilised with HF and the residue weighed. This residue, however, was always practically negligible. The main errors to be guarded against in determining the silica are:—

(1) Incomplete removal from solution owing to an insufficient number of evaporations to dryness. Two are sufficient in the case of a simple silicate such as used here, provided each is a very complete evaporation to dryness.

(2) Failure to remove particles of silica from the evaporating dish. This error may be quite large but can easily be avoided by wiping the dish with a piece of moist filter paper which is then added to the silica to be ignited.

(3) Improper ignition. The error here may vitiate the whole experiment. It is best to begin the ignition with a bunsen flame about the size of an ordinary match flame, gradually increasing it so that the paper distils as a tar on to the crucible lid and finally disappears. If at any time the escaping gases should catch fire, the experiment is quite worthless, owing to the fine particles of silica being carried away by the draught. Finally ignite in a Meker burner till constant weight is obtained—usually half to one hour. The silica residues were always snow white.

By using these and the usual precautions, duplicate analyses for $SiO_2$ agreed within 0.01%.

The sodium was determined as NaCl, due precaution being taken to dry it thoroughly without losing any through decrepitation or volatilisation. Occasionally the water in the solution was determined by Penfield's method, but usually when needed it was found by difference.

The method of analysis outlined above was used throughout the whole of this investigation and so applies to all the other analyses mentioned in the papers on this subject. Since both electrode portions were analysed for both sodium and silica, we obtain two independent measures of the transport numbers for both the sodium and the silicate ions and thus have a valuable check on their accuracy. The middle portion M was in all cases found to be the same as the original solution within experimental error. The changes in $Na_2O$ and $SiO_2$ content of the portion AM were added to the corresponding changes in portion A to give the total change at the anode, and similarly for CM and C to get the total change at the cathode.

In expressing the results of the analyses, the sodium weighed as NaCl has always been calculated as $Na_2O$ for convenience in comparison with $SiO_2$, since the comparison of the two oxides represents a direct measure of the composition of the silicate and this is the basis of the system of nomenclature used. The change in sodium content in the electrode portions has therefore been expressed in these experiments as a change in $Na_2O$ content.

TABLE I

| No. of Expt. | Ag dep. | Portion | Analysis %$Na_2O$ | Analysis %$SiO_2$ | Total change in gms. $Na_2O$ Loss | Total change in gms. $Na_2O$ Gain | Total change in gms. $SiO_2$ Loss | Total change in gms. $SiO_2$ Gain | Transport Numbers. $N_{Na}$ | Transport Numbers. $N_{SiO_2}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | orig. | 6.331 | 5.790 | | | | | | |
| | | A | 6.313 | 5.816 | .023 | | | .017 | .22 | .166 |
| 1 | .3650 | M | 6.336 | 5.799 | | | | | | |
| | | C | 6.369 | 5.781 | | .033 | .018 | | .32 | .176 |
| | | | | | | | | | .27 | .17 |
| | | orig. | 3.080 | 2.854 | | | | | | |
| | | A | 3.051 | 2.862 | .027 | | | .008 | .36 | .13 |
| 2 | .2054 | M | 3.073 | 2.854 | | | | | | |
| | | C | 3.106 | 2.846 | | .028 | .008 | | .36 | .13 |
| | | | | | | | | | .36 | .13 |
| | | orig. | .3072 | .2918 | | | | | | |
| | | A | .2755 | .3122 | .0277 | | | .01706 | .28 | .175 |
| | | AM | .3038 | .2936 | | | | | | |
| 3 | .3488 | M | .3038 | .2920 | | | | | | |
| | | CM | .3127 | .2903 | | .0343 | .01797 | | .34 | .184 |
| | | C | .3475 | .2706 | | | | | | |
| | | | | | | | | | .31 | .18 |
| | | orig. | 3.060 | 5.940 | | | | | | |
| | | A | 3.000 | 6.060 | .0378 | | | .0690 | .48 | .90 |
| 4 | .2742 | M | 3.063 | 5.945 | | | | | | |
| | | C | 3.112 | 5.833 | | .0294 | .0672 | | .35 | .87 |
| | | | | | | | | | .42 | .88 |
| | | orig. | 1.450 | 2.850 | | | | | | |
| | | A | 1.418 | 2.916 | .0336 | | | .0566 | .36 | .63 |
| | | AM | 1.463 | 2.881 | | | | | | |
| 5 | .3238 | M | 1.455 | 2.859 | | | | | | |
| | | CM | 1.477 | 2.839 | | .0312 | .0612 | | .34 | .78 |
| | | C | 1.487 | 2.787 | | | | | | |
| | | | | | | | | | .35 | .70 |
| | | orig. | .3251 | .6342 | | | | | | |
| | | A | .2638 | .7422 | .0551 | | | .08159 | .65 | .98 |
| | | AM | .3088 | .6346 | | | | | | |
| 6 | .2690 | M | .3256 | .6339 | | | | | | |
| | | CM | .3414 | .6241 | | .2328 | .05822 | | .25 | .75 |
| | | C | .3447 | .5693 | | | | | | |
| | | | | | | | | | .45 | .87 |
| | | orig. | 2.946 | 8.356 | | | | | | |
| | | A | 2.919 | 8.482 | .0374 | | | .1096 | .47 | 1.43 |
| | | AM | 2.929 | 8.380 | | | | | | |
| 7 | .2752 | M | 2.950 | 8.360 | | | | | | |
| | | CM | 2.961 | 8.332 | | .0248 | .0989 | | .32 | 1.29 |
| | | C | 2.969 | 8.273 | | | | | | |
| | | | | | | | | | .40 | 1.36 |
| | | orig. | 1.550 | 4.325 | | | | | | |
| | | A | 1.520 | 4.535 | .0302 | | | .09759 | .45 | 1.50 |
| | | AM | 1.538 | 4.364 | | | | | | |
| 8 | | M | 1.548 | 4.329 | | | | | | |
| | | CM | 1.560 | 4.295 | | .0304 | .1046 | | .45 | 1.60 |
| | | C | 1.574 | 4.238 | | | | | | |
| | | | | | | | | | .45 | 1.55 |

TABLE I (continued)

| No. of Expt. | Ag dep. | Portion | Analysis %$Na_2O$ | Analysis %$SiO_2$ | Total change in gms. $Na_2O$ Loss | Total change in gms. $Na_2O$ Gain | Total change in gms. $SiO_2$ Loss | Total change in gms. $SiO_2$ Gain | Transport Numbers. $N_{Na}$ | Transport Numbers. $N_{SiO_3}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 9 | .1748 | orig. | 2.806 | 10.30 | | | | | | |
| | | A | 2.834 | 10.43 | .0261 | | | .110 | .52 | 2.25 |
| | | AM | 2.802 | 10.35 | | | | | | |
| | | M | 2.808 | 10.31 | | | | | | |
| | | CM | 2.813 | 10.26 | | .0275 | .117 | | .55 | 2.39 |
| | | C | 2.837 | 10.19 | | | | | | |
| | | | | | | | | | .53 | 2.32 |
| 10 | .2820 | orig. | .3560 | 1.205 | | | | | | |
| | | A | .3132 | 1.479 | .0345 | | | .2168 | .42 | 2.76 |
| | | AM | .3510 | 1.180 | | | | | | |
| | | M | .3563 | 1.207 | | | | | | |
| | | CM | .3620 | 1.238 | | .0377 | .1674 | | .46 | 2.13 |
| | | C | .3982 | 1.021 | | | | | | |
| | | | | | | | | | .44 | 2.44 |

*Calculation of Transport Numbers.*

Assuming in the first instance the presence of only $Na^+$, $OH^-$, and $SiO_3^{--}$ ions in the solutions, and setting 1 $Ag^+$ equivalent to 1 $Na^+$ and to $\frac{1}{2}$ $SiO_3^{--}$, the transport numbers of the sodium and silicate ions have been calculated thus:—

$$\text{T. N. sodium} = \frac{\text{total change in weight of } Na_2O \text{ content}}{\text{weight of } Na_2O \text{ equiv. to Ag deposited in coulometer.}}$$

$$\text{T. N. Silicate} = \frac{\text{total change in weight of } SiO_2 \text{ content}}{\text{weight of } SiO_2 \text{ equiv. to Ag deposited in coulometer.}}$$

The T. N. of the hydroxyl ion has been determined by subtracting the sum of the transport numbers of the sodium and silicate ions from unity.

This method of calculating the transport number of the silicate ion ignores the possibility of the existence of $HSiO_3^-$ ions, and also of more complex anions containing more than one mol $SiO_2$ per 2F. These points will be considered later.

*Results.*

Table I contains the results of 10 experiments on ratios 1:1, 1:2, 1:3, and 1:4 at concentrations approximately 1.0$N_w$, 0.5 $N_w$ and 0.1$N_w$. In the columns headed "analysis" are given the percentages of $Na_2O$ and $SiO_2$ found in the several portions. The next four columns give the actual loss or gain of $Na_2O$ and $SiO_2$ in grams, obtained by multiplying the percentage change by the weight in grams of the portion. The increases in the percentages of $Na_2O$ and $SiO_2$ in the portions analysed caused by the escape of hydrogen from the cathodic solution and of oxygen from the anodic solution introduce corrections which are within the limits of experimental error. The weights of the different portions were between 80–100 grams for A and C, and between 45–55 grams for M, AM, and CM, depending on the density of the solutions.

Table II contains the results collected in a more convenient form for comparison.

TABLE II

| No. of Expt. | Ratio | Approx. $N_w$ | | $n_{Na}$ | $n_{SiO_3}$ | By diff. $n_{OH} = 1-(n_{Na}+n_{SiO_3})$ |
|---|---|---|---|---|---|---|
| 1 | 1 : 1 | 2.36 | | .27 | .17 | .56 |
| 2 | 1 : 1 | 1.0 | | .36 | .13 | .51 |
| 3 | 1 : 1 | 0.10 | | .31 | .18 | .51 |
| | | | Mean | .31 | .16 | .53 |
| 4 | 1 : 2 | 1.0 | | .42 | .88 | |
| 5 | 1 : 2 | 0.5 | | .35 | .70 | |
| 6 | 1 : 2 | 0.1 | | .45 | .87 | |
| | | | Mean | .41 | .82 | |
| 7 | 1 : 3 | 1.0 | | .40 | 1.35 | |
| 8 | 1 : 3 | 0.5 | | .45 | 1.42 | |
| | | | Mean | .43 | 1.38 | |
| 9 | 1 : 4 | 1.0 | | .53 | 2.32 | |
| 10 | 1 : 4 | 0.1 | | .44 | 2.44 | |
| | | | Mean | .48 | 2.38 | |

*Accuracy of Results.*

The analyses are correct to within less than 0.1% both for $Na_2O$ and $SiO_2$, but even this high accuracy in the analysis represents a considerable error where the total change in the electrode chamber is of the order of 1%, as is the case with $Na_2O$. In the case of the silica, especially in the higher ratios, this is proportionally lower. If only one electrode portion had been analysed, this degree of accuracy would not have warranted much value being placed on the transport numbers, but since both electrode portions were analysed, we obtain two transport numbers in each case which serve as a very useful check. In the majority of the experiments it can be seen that the two transport numbers differ from the mean by about 10% for the sodium ion, and by from 2 to 5% for the silicate ion. Unfortunately the accuracy of the results does not warrant any quantitative conclusions being drawn as to the variation of the transport number with concentration, but it is sufficient to show that the transport number does not vary greatly over the range of concentrations investigated.

*Discussion of Results.*

Considering first the ratio 1:1, i.e. sodium metasilicate, it is seen that the mean of the six values of $n_{Na}$ is 0.31, of $n_{SiO_3}$ 0.16, and of $n_{OH}$ 0.53. The proportion of the current carried by the silicate ions is very small, being only about one-half that carried by the sodium ions, while over one-half the total current is carried by the hydroxyl ions. This latter result was to be expected, since E. M. F. measurements show that 10 to 30% of the silicate is hydrolysed according to the concentration, and the hydroxyl ion moves four times as fast as the sodium ion. In caustic soda $n_{Na}$ is 0.2, and $n_{OH}$ is 0.8; therefore

the present result, where $n_{OH}$ is not even double $n_{Na}$, shows that the concentration of the hydroxyl ions is not nearly equivalent to that of the sodium ions.

From the results of measurements of OH ion concentration, Na ion concentration, and total ion concentration as found from freezing point lowering, all to be communicated later, it will be seen that in ratio 1:1 the concentrations of the ions are approximately in the proportion $Na:SiO_3:OH = 8:3:2$, calculated by assuming the laws of ideal solution to be applicable. Taking the T. N. of an ion to be proportional to its mobility and to its concentration, this makes the mobility of the simple silicate ion equal to 70. The value 60 was deduced as the mobility of the silicate ion from the equivalent conductivity at infinite dilution.

The T. N. of sodium metasilicate shows no evidence whatever of any complex silicate ions or of micelle formation. If the silica is colloidal with OH ions adsorbed, such a high mobility as 70 would not be expected, as hitherto measurements have shown that such colloidal particles have a mobility approaching that of the slowest moving ions.

When we look at the results obtained with ratio 1:2, 1:3, and 1:4, we at once notice the very high transport numbers of the silicate anions. They are for ratios 1:3 and 1:4 much greater than unity. The average value for ratio 1:2 is 0.88, for ratio 1:3 1.44, and for ratio 1:4 2.38, while the T. N. of the sodium remains much the same, about 0.45 in each case.

Further, the T. N. for the silicate ion is approximately twice that of the sodium ion in ratio 1:2, three times in ratio 1:3, and four times in ratio 1:4. This high T. N. for the silicate ion at once points to the fact that the anion cannot possibly be the simple ion $SiO_3^{--}$, nor in fact should we expect it to be. These high transport numbers were obtained, it must be remembered, by assuming the anion to be the simple ion $SiO_3^{--}$.

This high T. N. may result from the following causes:—

(1) The anion may be a solvated aggregate of simple $SiO_3^{--}$ ions, carrying a charge equal to the sum of the total charges on the separate ions, or a solvated aggregate containing more than one mol $SiO_2$ per divalent charge, these aggregates splitting up on dilution.

(2) The anions may be definite ions more complex than the simple $SiO_3^{--}$ ion, i.e. definite salts of the formulae given below may exist:—$Na_2(SiO_3.SiO_2)$, $Na_2(SiO_3.2SiO_2)$ etc., which ionise to give definite divalent silicate ions of the formulae:—$(SiO_3.SiO_2)^{--}$, $(SiO_3.2SiO_2)^{--}$ etc.

Both in the case of the existence of aggregates and of definite anions, further experimental results, other than those from conductivity and transport number measurements, are required in order that their constitution may be conclusively proved. The decision as to which formation is the more probable will therefore be postponed until the results obtained by other lines of investigation have been communicated and discussed. It is evident, however, that the method of calculation already given for the transport numbers in the case of ratios 1:2, 1:3, and 1:4, is in error and must be modified to the following expression:—

$$\text{T. N. silicate ion} = \frac{\text{total change in weight of silica}}{N \times (\text{weight of } SiO_2 \text{ equiv. to Ag deposited in coulometer})}$$

where N is the number of mols $SiO_2$ per divalent charge (2F) of the anion, and the weight of "$SiO_2$ equivalent to Ag deposited" is calculated as before from the relation, 1 Ag. equivalent to $\frac{1}{2}$ $SiO_2$.

Since in ratios 1:2, 1:3, and 1:4, the T. N. previously calculated is approximately equal to the T. N. of the sodium ion multiplied by the ratio, it seems that here is no chance relationship, and since also, from the equivalent conductivity at infinite dilution, the mobility of the silicate anion or aggregate, at least in ratios 1:3 and 1:4, is approximately equal to the mobility of the sodium ion, it appears justifiable to put N equal to the molar ratio $SiO_2/Na_2O$ in the solution (average value of N).

When the transport numbers are so calculated, we get the values given in Table III, the results for sodium metasilicate being also given for comparison. The first column N contains the number of equivalents of $SiO_2$ per Faraday, i.e. the number N in the expression above.

TABLE III

| N | Ratio | $n_{Na}$ | $n_{sil.}$ | $n_{OH} = 1 - (n_{Na} + n_{sil})$ |
|---|---|---|---|---|
| 1 | 1 : 1 | .37 | .16 | .53 |
| 2 | 1 : 2 | .41 | .41 | .18 |
| 3 | 1 : 3 | .43 | .46 | .11 |
| 4 | 1 : 4 | .48 | .59 | — |

Thus calculated, we see that the values of the T. N. for the sodium and silicate ions do not total unity in ratios 1:2 and 1:3, the differences being respectively 0.18 and 0.11, which are presumably the values of the T. N. for the hydroxyl ion. This hydroxyl ion, although present in small amounts, is so much more mobile than the others that we should expect its T. N. to be something of this order, especially in ratio 1:2. In ratio 1:4, the hydroxyl ion concentration is practically negligible and from Table III its transport number is zero.

The transport numbers of the sodium and silicate ions would be approximately the same in ratios 1:2, 1:3, and 1:4, if no hydroxyl ion were present, and since the former ions are present in nearly equivalent amounts, we may conclude that their mobilities are nearly the same, probably that of the silicate ion a little higher in 1:3 and 1:4. This is in agreement with the values of mobilities calculated from conductivity experiments. The fact that the mobilities of these silicate ions are nearly all the same, even though the anion in 1:4 is more complex and so larger per charge of electricity, is probably due to hydration effects, as it has been shown that the more complex the ion the less it is isolated.

*Summary.*

1. Transport numbers of sodium silicates of ratios 1:1, 1:2, 1:3, and 1:4 at concentrations ranging from 0.1 to 2.0 $N_w$ have been measured by the Hittorf method, both electrode portions being analysed for both sodium and silica.

2. Ratio 1:1 evidently ionises to $Na^+$, $OH^-$ and $SiO_3^{--}$ ions; $n_{SiO_3}$ is small, $n_{OH}$, found by difference, is large.

3. In ratios 1:2, 1:3, and 1:4, the T. N. of the silicate ion is high, and the silicate anion contains more than 1($SiO_2$) per divalent charge; the average number of mols $SiO_2$ per divalent charge being equal to the ratio.

4. The mobility of the $SiO_3$ ion in ratio 1:1 is about 70. In ratios 1:2, 1:3, and 1:4, it is approximately equal to that of the sodium ion, thus agreeing with mobilities calculated from conductivity experiments.

5. In ratios 1:2, 1:3, and 1:4, the silicate anion is not the simple $SiO_3^{--}$ ion, but is either an aggregation of simple silicate ions with or without colloidal silica, or a definite complex silicate ion.

I wish to thank the Commissioners of the 1851 Exhibition for a research scholarship which has enabled me to carry out this work, and to express my gratitude to Professor Donnan, at whose suggestion this investigation was undertaken, for his constant kindly interest and advice.

*The William Ramsay Laboratories of*
*Inorganic and Physical Chemistry,*
*University College, London.*
*December 1, 1925.*

# THERMAL ANALYSIS OF THE SYSTEM BORON TRIFLUORIDE-HYDROGEN SULFIDE

BY ALBERT F. O. GERMANN AND HAROLD SIMMONS BOOTH

Since the discovery by Friedel[1] in 1875 of the compound $(CH_3)_2O \cdot HCl$ much interest has attached to the study of molecular combinations between gases. Practically, this discovery was less amazing than the similar discovery by Priestley a century before that gaseous ammonia combines with gaseous hydrogen chloride to form a solid, $NH_3 \cdot HCl$. But the experimental difficulties of assigning a formula to Friedel's compound were tremendously greater than those surrounding the other, which was a well-known compound, whose composition was made evident by the new method of preparation. Since the discovery of Friedel's compound, and his classic research into the nature of the compound, other methods have been developed which permit the detection and formulation of even unstable addition compounds between gases, by methods that are much simpler than those carried out by Friedel. Reference may be made, for example, to the methods used by McIntosh[2] and his co-workers, by Bagster[3] and by Baume and his co-workers[4] for determining the existence and composition of addition compounds by thermal analysis.

In the study of the properties of certain halide gases, the problem of preparing these gases in a high degree of purity confronted us. The best methods of accomplishing this involve the preparation of the desired gas

(a) in vacuo,

(b) from the purest materials,

(c) by a method involving no other volatile products,

(d) a preliminary purification of the gas from possible impurities by chemical means involving a gas absorption train,

(e) condensation of the gas to a liquid, followed by a series of careful fractional distillations, and

(f) if practicable, fractional crystallization.

In spite of all these precautions, however, some impurities are very difficult to eliminate; for example, different investigators have found it diffiult to eliminate from hydrogen chloride some impurity which imparts a rose color to the frozen gas[5]. On the other hand, Inglis[6] found, in a study of chamber gases, that on certain occasions some impurity imparted a red color to the

[1] Bull. (2) **24**, 160, 241 (1875).

[2] J. Chem. Soc., **85**, 919 (1904); Maass: J. Am. Chem. Soc., **33**, 71 (1911); **34**, 1273 (1912); etc.

[3] J. Chem. Soc., **99**, 1218 (1911).

[4] J. Chim. phys., **9**, 245 (1911); **12**, 206 (1914).

[5] Gray and Burt: J. Chem. Soc., **95**, 1640 (1909); Cardoso and Germann: J. Chim. phys., **10**, 517 (1912).

[6] J. Soc. Chem. Ind., **25**, 152 (1906).

frozen gas, usually white; on these occasions he mentions that the flue gases contained a chloride. Briner and Wroczynski[1] observed that when a mixture of hydrogen chloride and nitric oxide is cooled in liquid air, the resulting solid has a wine-red color. Germann and Phillips[2] have observed the production of a similar color with nitric oxide and boron trifluoride; and Germann has found that other halogen-containing compounds, for example phosgene, behave in the same way with nitric oxide at low temperatures, and he has used this property as the basis of a method for detecting nitric oxide in laughing gas. This red color is undoubtedly to be explained by the formation of an addition compound which halogen gases in general form with nitric oxide.

Evidently the tendency of a gas toward compound formation with a given impurity, as well as the formation of constant-boiling solutions, would enhance the difficulty of making a separation of the impurity by fractional distillation. It seemed highly desirable, therefore, to have more information, particularly at low temperatures about the affinities of the gases being studied for other gases, especially those liable to be present as a result of the method of preparation.

Boron trifluoride and phosgene were under investigation at the time these studies were carried out (1919-21), the intention being to determine the weight of the normal liter of these gases; but owing to the removal of one of us from the Morley Laboratory of Western Reserve University, where the investigations were carried out, the program was not completed, except that some preliminary measurements were made in the case of phosgene[3]. In the preliminary study of these gases, it became evident that the elimination of some of the impurities was very tedious. It seemed, therefore, worth while to determine by the methods of thermal analysis as developed by Baume the possible addition compounds formed by these gases with the impurities likely to be present.

In the case of boron trifluoride, the method of preparation involved the action of sulfuric acid on calcium fluoride and boric anhydride. Gray and Burt have shown that in the similar reaction of sulfuric acid with sodium chloride or with ammonium chloride to produce hydrogen chloride a little hydrogen sulfide was always produced; they attributed its formation to reduction of the sulfuric acid during the reaction. The possibility of hydrogen sulfide being produced in the preparation of boron trifluoride due to the presence of small amounts of reducing substances, suggested the investigation of this system.

## Preparation of Boron Trifluoride[4]

70 grams of boric anhydride were dissolved with the aid of heat in 250 cc. of concentrated sulfuric acid. Analysis showed that the boric anhydride

[1] J. Chim. phys. 9, 116 (1911).

[2] Science, 53, 145 (1921).

[3] Germann and Jersey: Science, 43, 582 (1921); Germann and Smith: Science, 57, 564 (1923).

[4] Gasselin: Ann. Chim. Phys., (7) 3, 9 (1894).

contained 10% of water. In one experiment, the effort was made to get rid of this water, by adding the calculated amount of pyro-sulfuric acid; but the gas obtained, when condensed to a solid, had a bright red color, obviously due to the same impurity, NO, which imparts a red color to solid hydrogen chloride. As the purity of the pyro-sulfuric acid used was questionable, it seemed probable that it might be the source of this impurity; in subsequent preparations, therefore, the fuming sulfuric acid was omitted, and the mixture made up of 300 cc. pure concentrated sulfuric acid, 75 grams boric anhydride, and 200 grams calcium fluoride. Prepared in this way, the gas condensed as a white solid, without a trace of pink color, and melted to a clear limpid liquid. The use of fuming sulfuric acid thus seems inadvisable.

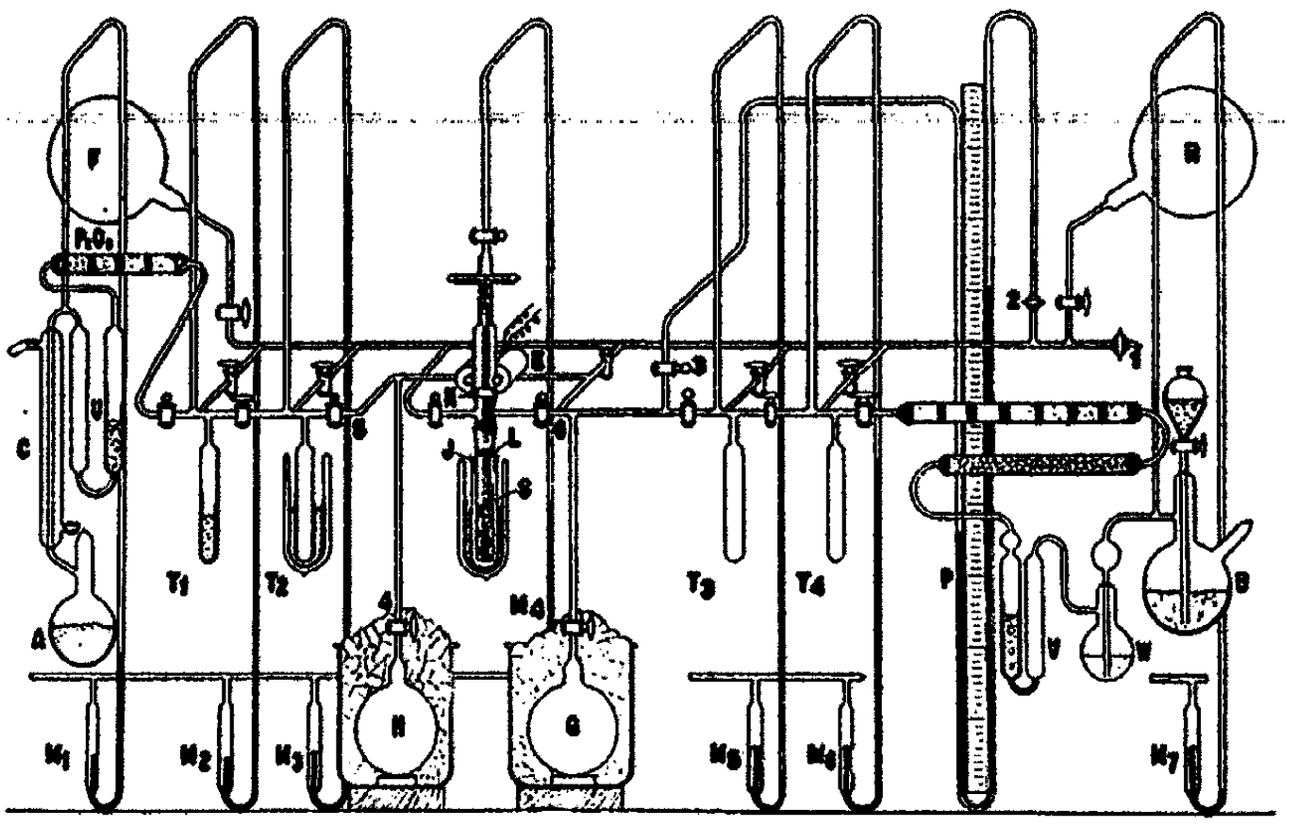



FIG. 1

After cooling the solution of boric anhydride in sulfuric acid, it was mixed with 200 grams of calcium fluoride in a large porcelain mortar, and the mixture, which warms up and froths considerably, was stirred until the gas evolution ceased. The gases given off probably consisted principally of silicon tetrafluoride. The viscous mixture was then transferred to the reaction flask labelled A at the left end of Fig. 1, which shows the arrangement of the apparatus, and the mouth of the flask was then sealed off, as shown.

Flask A communicated directly with a reflux condenser, C, and a safety manometer tube, $M_1$, with a safety wash-bottle U containing a solution of boric anhydride in sulfuric acid, made up as described above; this was followed by a tube packed with alternate layers of glass wool and phosphorus pentoxide, and by a pair of condensing and distilling tubes, $T_1$ and $T_2$, each provided with a safety manometer tube $M_2$ and $M_3$.

The reaction mixture in flask A was heated on a steam bath for an hour, while the air was pumped out of the apparatus; during this time no noticeable gas

evolution took place. Heated with a free flame, however, the reaction temperature was soon reached, and the positive heat of reaction was sufficient to maintain it. With the intervening stopcock open, and a bath of liquid air surrounding $T_1$, the gas condensed to a white solid, and melted to a clear limpid liquid. On some occasions, the liquid boron fluoride contained particles of a white solid floating around, which may have been hydrogen sulfide, as reported by Gray and Burt, or carbon dioxide, or a product of the interaction of boron fluoride with phosphorus pentoxide, a reaction that seems to take place with some readiness.

After collecting as much of the gas as was required, the reaction was interrupted by cooling flask A, and the condensed gas was subjected to a series of fractional distillations between $T_1$ and $T_2$, rejecting the first and last fractions in each distillation, and the purified product was finally stored in F, a 15 liter globe, previously evacuated and dried. When required for use, the gas was recondensed in $T_2$ with liquid air. During storage, some change occurred, evidenced by the fact that, on evaporation, a white deposit was left, which sublimed at a higher temperature; it is not clear what this was, though it may have been one of the fluorides of silicon, produced by the action of hydrogen fluoride on the glass[1]: the presence of hydrogen fluoride may be accounted for on the assumption of incomplete drying of the storage flask. A few additional fractional distillations sufficed to eliminate all traces of this impurity.

### Preparation of Hydrogen Sulfide

Hydrogen sulfide was prepared by the action of constant-boiling hydrochloric acid (minimum vapor tension) on carefully washed zinc sulfide, freshly precipitated from a solution of zinc acetate: the reaction took place in a one liter flask, B, which contained the zinc sulfide; the acid was added as needed from the dropping funnel sealed into the neck of B. The evolved gas was freed from hydrogen chloride by bubbling it through a suspension of freshly precipitated aluminium hydroxide in water contained in the safety wash bottle W, and through the gas bubbler V, containing water, dried by contact with anhydrous calcium chloride and phosphorus pentoxide, and finally condensed in tube $T_4$ in a bath of carbon dioxide snow and acetone. The safety manometer, $M_7$, interposed between the reaction flask B and the wash bottle W, is essential, as any clogging of tubes in W or in the drying tubes might give rise to serious consequences.

Cardoso[2] has very ably discussed the impurities accompanying hydrogen sulfide, which is difficult to obtain perfectly pure, and has devised elaborate precautions for their elimination. For our purposes the product obtained after three fractional distillations was of sufficient purity, and was stored in the globe marked R until required, when it was condensed in $T_3$.

[1] See Germann and Booth: J. Phys. Chem. 21, 83 (1917).

[2] Gazz., 51 I, 153 (1921).

## The Freezing Point Measurements

The central portion of the apparatus was devoted to the measurement of the gases, the preparation of the solutions, and to the measurement of the freezing points. The details are similar to those described by Baume[1]. The gases were measured volumetrically in the calibrated flasks H and G, packed in cracked ice to maintain constant temperature. The pressure of the gas was measured on the baro-manometer P, one side of which could be evacuated by opening the stopcocks 2 and 1 leading to the vacuum apparatus, thus making the readings independent of atmospheric pressure. To measure a quantity of boron fluoride, for example, stopcock 4 of flask H, and stopcock 3 leading to the manometer were opened, and boron trifluoride was allowed to evaporate through stopcock 5 into the evacuated space thus made available, until the pressure reached a little more than one atmosphere. 5 was closed, and the pressure read and recorded; 4 was then closed, and the dead space between it and the manometer evacuated by liquid air condensation of the gas it contained into $T_2$, by opening 5 for a few moments. H then contained a known volume of gas under a known pressure, P′, at a known temperature, 0°. The dead space between the mercury of the pressure manometer and the stopcock of the measuring flask contained the same gas at a pressure P″, equal to its vapor tension at the temperature of the cooling bath used (liquid air or liquid nitrogen, sometimes liquid oxygen). The gas in H was then transferred to the freezing point tube L by liquid air condensation, opening 4 and 6 for the purpose; when no further condensation occurred, 6 was closed, and the pressure P″ was read on the manometer P; the weight W of the gas condensed in L was then (neglecting the small correction for the deviation of the gas from Boyle's law)

$$W = \frac{L\,V\,(P'-P'')}{1000 \times 760} = \frac{L\,V\,P^{\circ}}{1000 \times 760}$$

where L is the weight of the normal liter of the gas, V is the volume of the measuring flask in cc., and $P^{\circ}$ is the pressure. Since, however, the molecular composition of the solution was required, rather than the composition by weight, the mass of the gas used was not actually needed. Assuming the perfect gas law, we have

$$\frac{M_g}{M_h} = c\,\frac{P_g^{\circ}}{P_h^{\circ}}$$

where $M_g$ and $M_h$ are the number of moles of the two gases measured in G and in H, $P_g^{\circ}$ and $P_h^{\circ}$ the pressures of the two gases, and c the ratio of the volumes of the two flasks,

$$V_h = c\,V_g.$$

Correcting for the deviation of the two gases from the perfect gas laws, we have

[1] J. Chim. phys. 9, 245, (1911); 12, 206, 216, 225, 242, 250, 256, 270, 276 (1914).

$$\frac{M_g}{M_h} = c\,\frac{P_g^\circ + \frac{P_g^\circ}{760}\,A_g']_\circ^1}{P_h^\circ + \frac{P_h^\circ}{760}\,A_h']_\circ^1} = c\,\frac{P_g^\circ\,(760 + A_g']_\circ^1)}{P_h^\circ\,(760 + A_h']_\circ^1)}$$

where $A_g']_\circ^1$ and $A_h']_\circ^1$ are the compressibilities of the gases in G and H between zero and one atmosphere. The mole fraction Xg of the gas in G is given by

$$X_g = \frac{M_g}{M_h + M_g} = \frac{c\,P_g^\circ\,(760 + A_g']_\circ^1)}{P_h\,(760 + A_h']_\circ^1) + c\,P_g^\circ\,(760 + A_g']_\circ^1)}$$

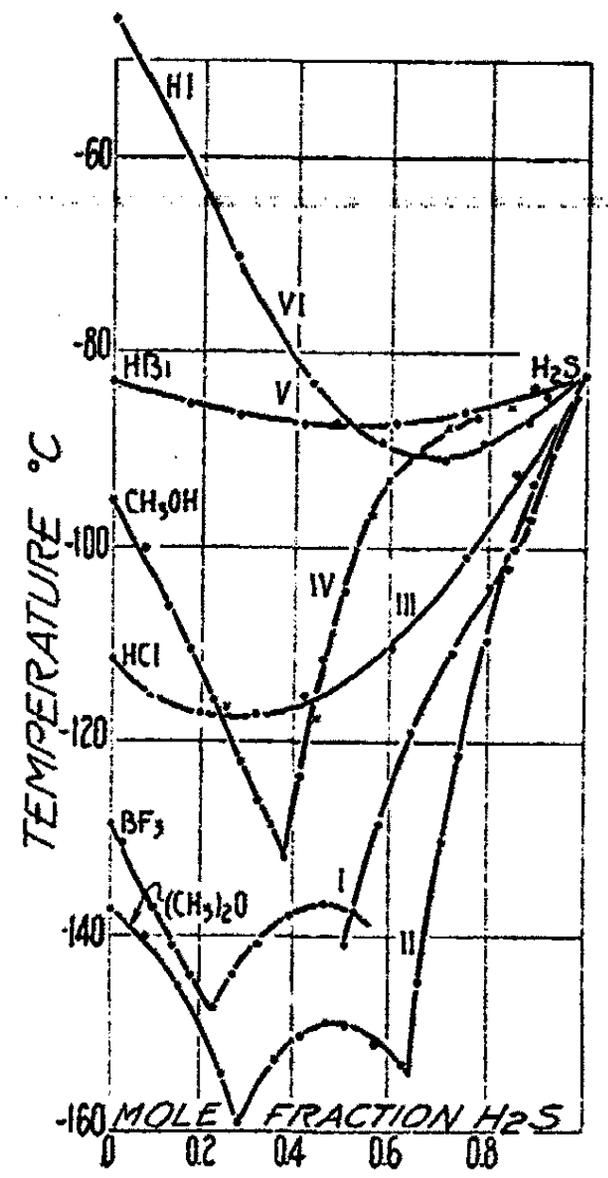



FIG. 2

The corrective factors are small and may be neglected in most cases, especially if the gases are in approximately corresponding states at $\sigma^\circ$ and one atmosphere. In this case the calculation takes the simple form

$$X_g = \frac{M_g}{M_h + M_g} = \frac{c\,P_g^\circ}{P_h^\circ + cP_g^\circ}$$

The volumes of the two globes were 893.53cc. for G, and 896.50cc. for H.

Enough gas was condensed in L to cover the bulb of the thermometer; then the freezing point was determined, using as cooling agent a bath of liquid air, separated from the freezing tube by an air jacket J, containing a few pieces of anhydrous calcium chloride to prevent the formation of hoar frost in the annular space between the jacket and the freezing tube. The liquefied gas was stirred by the vertical motion of a spiral glass stirrer S, actuated by the attraction of an electromagnet E for a soft iron collar K attached to the top of the stirrer; the electromagnet worked intermittently, having an electrically connected metronome in the circuit.

A small amount of the second gas was then measured into the freezing point tube, and the freezing point observed again, and so on until the solution was approximately equimolar with respect to the two components. A similar routine, beginning with the second gas, and adding small amounts of the first, gave the data for the other half of the freezing point curve.

The thermometer employed was a liquid propane thermometer, constructed by Mr. Pierre E. Haynes, Director of the Linde Air Products Research Laboratory, of Buffalo, N. Y., and presented by him. The correction

curve for the emergent column was prepared by observing the freezing points of a number of pure liquids, chosen so as to give points at intervals along the scale. The corrected temperatures are probably accurate to one or two degrees. However, for our purposes, relative rather than absolute temperatures were required, so that an error from this source would not impair the validity of conclusions bearing on the chemical affinities of the substances studied.

In Table I are the data with which the curve in Fig. 2 was constructed.

TABLE I

| $P^o_g$ $H_2S$ mm. | $P^o_h$ $BF_3$ mm. | Mol. Frac. $H_2S$ | Average Temp. F. P. °C. | $P^o_g$ $H_2S$ mm. | $P^o_h$ $BF_3$ mm. | Mol. Frac. $H_2S$ | Average Temp. F.P. °C |
|---|---|---|---|---|---|---|---|
| 3170.0 | 0.0 | 1.000 | − 82 | 108.6 | 2350.3 | .044 | −135 |
| " | 44.3 | .987 | − 84½ | 156.2 | " | .063 | −132 |
| " | 35.7 | .974 | − 86½ | 200.8 | " | .079 | −137 |
| " | 250.5 | .927 | − 90½ | 247.3 | " | .095 | −137 |
| " | 329.3 | .907 | − 93½ | 290.9 | " | .110 | −139 |
| " | 415.4 | .884 | − 97 | 332.6 | " | .124 | −139 |
| " | 518.1 | .860 | −100 | 370.3 | " | .136 | −141 |
| " | 639.3 | .833 | −102 | 421.0 | " | .152 | −143 |
| " | 780.1 | .803 | −104 | 501.3 | " | .176 | −144 |
| " | 976.4 | .765 | −106½ | 594.9 | " | .202 | −146 |
| " | 1170.7 | .731 | −111 | 689.2 | " | .227 | −147½ |
| " | 1361.8 | .700 | −113 | 781.6 | " | .250 | −146 |
| " | 1542.1 | .674 | −116 | 885.0 | " | .274 | −144 |
| " | 1761.4 | .644 | −119 | 1008.5 | " | .301 | −142 |
| " | 2025.2 | .611 | −125 | 762.3 | 1558.5 | .329 | −141 |
| " | 2291.9 | .581 | −128½ | 879.0 | " | .361 | −139½ |
| " | 2540.3 | .556 | −133 | 1013.1 | " | .395 | −138 |
| " | 2808.4 | .531 | −137½ | 1173.8 | " | .430 | −137½ |
| " | 3059.7 | .510 | −141 | 1347.0 | " | .464 | −136 |
| 0.0 | 2350.3 | .000 | −128½ | 1524.9 | " | .495 | −137 |
| 39.1 | " | .016 | −131 | 1947.6 | " | .556 | −130 |
| 75.0 | " | .031 | −130½ | | | | |

For purposes of comparison, the data relative to other systems containing hydrogen sulfide as one component have been plotted along with the curve for the system here studied. These include systems of hydrogen sulfide with hydrogen iodide and with hydrogen bromide, by Bagster[1]; hydrogen sulfide with hydrogen chloride, by Baume and Georgitses[2]; and hydrogen sulfide with methyl alcohol and with methyl ether by Baume and Perrot[3].

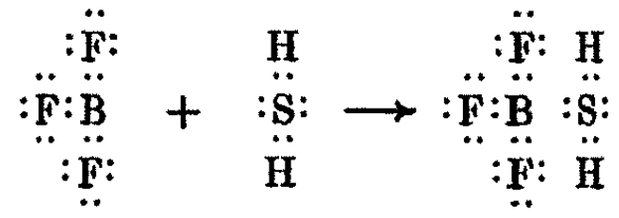
[1] J. Chem. Soc., 99, 1218 (1911).
[2] J. Chim. phys., 12, 250 (1914).
[3] J. Chim. phys., 12, 225 (1914).

## Discussion

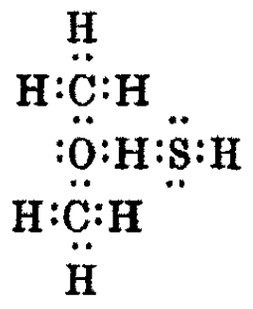
The system boron fluoride-hydrogen sulfide (see curve 1) presents a maximum at $-137°$, with a solution containing equimolecular quantities of the two gases, showing the existence of the compound $BF_3 . H_2S$. This compound is considerably dissociated at the melting point, as shown by the fact that addition of either of the products of dissociation to the compound has little effect on the freezing point[1], yielding a well rounded maximum. The curve shows two eutectics, one on either side of the maximum, one at $-148°$ with 22% of hydrogen sulfide, the other at $-140°$ approximately, with 53% of hydrogen sulfide.

The form of the curve at $-99°$ with $87\frac{1}{2}$% of hydrogen sulfide indicates that this is the transition point of a crystalline addition compound, whose formula seems to be $BF_3 . 7H_2S$, and which dissociates into boron fluoride and hydrogen sulfide at this temperature.

Comparing with the diagrams for the other systems that have been recorded in the literature, it appears that boron fluoride has more affinity for hydrogen sulfide than have any of the other substances. Methyl ether, which is noted for the readiness with which it yields oxonium compounds, yields a diagram that is almost identical with that for boron fluoride, except that there is no indication of a higher hydrosulfide. If we assume with Lewis[2] that boron fluoride possesses three electron pairs in the valence shell of boron, we can easily represent graphically the structure of the first compound as one in which a lone electron pair of hydrogen sulfide is attracted to the boron atom in such a way as to complete its octet:—



Boron fluoride is known to form compounds with the ethers[3], in which the union may be represented in the same way, oxygen occupying the place of sulfur, and methyl groups the places of the hydrogen atoms; but in the addition compound between methyl ether and hydrogen sulfide, the hydrogen bond[4] evidently serves as the linkage between oxygen and sulfur, since the octet of each is complete:



[1] Kremann: Monatshefte, 25, 1215 (1904).
[2] "Valence and the Structure of Atoms and Molecules", p. 98 (1923).
[3] Gasselin: Ann. Chim. Phys., (7) 3, 28, 48 (1894).
[4] Latimer and Rodebush: J. Am. Chem. Soc., 42, 1431 (1920); Huggins: J. Phys. Chem., 26, 614 (1922).

Judging from the form of the maxima, the sulfhydride of boron fluoride and that of methyl ether are dissociated at their respective melting points to about the same extent, indicating that the two types of linkages, that between sulfur and boron on the one hand, and that between sulfur and oxygen via hydrogen on the other, are about equally strong, neglecting the difference in the temperature.

Any attempt to account for the non-formation of molecular compounds between hydrogen sulfide and the hydrohalogens and methyl alcohol would require a comprehensive analysis of all the known addition compounds of these substances, as well as of other similar ones. For example, why should the mere replacement of a methyl group in methyl ether by a hydrogen atom render the attraction of the oxygen atom for hydrogen sulfide inoperative? Is the temperature at which the alcohol-hydrosulfide eutectic separates so high that the addition compound is completely dissociated? That halogen atoms may unite with sulfur by means of the hydrogen bond is evidenced by the compound $BF_3 . 7H_2S$; why do the halogen atoms in hydrogen chloride, hydrogen bromide and hydrogen iodide not yield addition compounds? It is true that Pollitzer[1] found the solubility of hydrogen sulfide in aqueous hydrogen iodide greater than in pure water (100% greater in 7N − HI, and 15% greater in 10 N − HCl), which has been interpreted as evidence of compound formation[2], but other evidence given by Pollitzer would seem to indicate that some other explanation would fit the facts better.

The experimental work described here was performed in 1920 at the Morley Chemical Laboratory of Western Reserve University. The liquid air used was supplied by the Linde Air Products Co., to whom we desire to express our appreciation.

## Summary

The freezing point curve of the system boron trifluoride—hydrogen sulfide, has been investigated, and has been found to contain two eutectics, a maximum corresponding to $BF_3 . H_2S$, with freezing point −137°, and a transition point of a compound $BF_3 . 7H_2S$ at −99°.

Judging from the flatness of the curve at the maximum, the compound, $BF_3 . H_2S$, is considerably dissociated, so that there should be little difficulty separating $H_2S$ as an impurity from $BF_3$ by fractional distillation.

*Laboratory Products Company, Cleveland, Ohio,*
*and*
*Western Reserve University, Cleveland, Ohio.*

---

[1] Z. anorg. Chem., **64**, 121 (1909).
[2] Lewis and Randall: "Thermodynamics", p. 106 (1923).

# OLD AGE AND DEATH FROM A CHEMICAL POINT OF VIEW

BY N. R. DHAR

In two previous papers[1] we have discussed the question of ageing of sols and gels. As life processes are mainly due to catalysts and colloids, I shall endeavor to explain the phenomena of old age and of death, which have been described by Metchnikoff as the most mysterious of natural phenomena, from a purely chemical point of view.

When a lump of sugar is left in air at the ordinary temperature, no oxidation of the sugar takes place; but when the same lump is taken into the animal body it is burnt readily with evolution of carbon dioxide and water, supplying heat to the animal body. We now know definitely that the oxidation of sugar in the animal body is accelerated by the enzymes, which are always present in the animal system. The activity of these enzymes really controls the velocity of the oxidation of food materials in the animal body.

We have repeatedly observed that the chemical reactivity of a freshly precipitated substance is much greater than that of a substance prepared long ago. Thus when ferric hydroxide, chromic hydroxide, etc., are freshly precipitated, they dissolve very readily even in dilute HCl; whilst the same substances prepared in a similar manner and placed at the ordinary temperature in a flask even in contact with water lose much of their chemical reactivity and do not dissolve in dilute hydrochloric acid; even concentrated hydrochloric acid dissolves these old samples of hydroxides with difficulty. The adsorptive power of these substances decreases considerably on ageing. Moreover we have shown that the catalytic decomposition of hydrogen peroxide due to the presence of manganese dioxide is much greater when it is freshly precipitated than when the same weight of an old sample of manganese dioxide is used. The generation of oxygen is much greater in the same time with a fresh sample of manganese dioxide than with an old sample.

It is well known that the percentage of water which enters into the composition of the animal body decreases with the age of the animal in question as will be shown in the following lines:—

A three-months' human fetus contains 94 percent water; at birth the water content is from 69 to 66 percent; in adult life 58 percent. It is held that in old age, the water content decreases; turgescence in general, and of the skin in particular, is obviously lost. With ageing there occurs shrinking.

From our experience on gels and sols we know that ageing of a sol is always associated with its dehydration.

We shall now utilize these results in the explanation of old age and death from a purely chemical point of view. We have already mentioned that the speed of the oxidation of food materials is essentially dependent on the activity of the catalysts inside the animal body, provided a sufficient supply of food

[1] Dhar: Zeit. Elektrochem. **31**, 266 (1925); J. Phys. Chem. **29**, 435 (1925).

and air are available for the animal body. Now just as a freshly precipitated manganese dioxide is more reactive as a catalyst in the decomposition of $H_2O_2$, similarly enzymes or other catalysts in the body of a child or a young man are likely to be more reactive than the enzymes or catalysts in the system of an old man. Consequently the amount of oxidation per unit weight of the body of a young person should be much greater than that obtainable in the case of an old person. As the animal or the individual grows older and older the amount of oxidation per unit weight of its body grows less and less as the enzymes and the activators in its body become more and more aged and inactive. It is well known that a certain minimum quantity of heat is necessary for the maintenance of the body temperature of about 37.4°C. When the system can not generate this minimum quantity of heat it breaks down and death follows. As time goes on the activity of the enzymes and other catalysts in the body becomes less and less and after a time a certain stage arrives in which the catalyst is unable to accelerate the oxidation of food materials by oxygen of the air to such an extent that the minimum quantity of heat required for the maintenance of the body temperature is obtainable. At this stage death is likely to occur.

It also follows from the general dynamical principle that the free energy of a system tends to decrease.

We have repeatedly observed that a freshly precipitated sample of $Fe(OH)_3$, $Cr(OH)_3$, hydrated manganese dioxide, etc., loses its chemical reactivity more readily when kept at a higher temperature even in contact with water than when kept at a low temperature in contact with water. We have observed that the amount of adsorption of arsenious acid by a definite weight of $Fe(OH)_3$ kept at a temperature of 50° even in contact with water is much less than the adsorption of the same substance by the same weight of $Fe(OH)_3$ kept in contact with water at 25°; in other words, the decrease in the chemical activity of these substances or of ageing of these substances is more marked and more rapid when the substances are kept at higher temperatures than when kept at ordinary temperature. It follows consequently that $MnO_2$ will lose its catalytic activity towards the decomposition of $H_2O_2$ more readily when freshly precipitated $MnO_2$ is kept at a higher temperature than when kept at ordinary temperature and this is corroborated by experiments. It seems probable therefore that the life period of the enzymes and other catalysts in the human or animal body should decrease more readily if the human being or the animal has to live at a higher temperature than his body temperature. It follows therefore that the fall in the velocity and amount of oxidation of food materials in the animal body will be more marked with time when the animal lives in a warmer climate than when the animal has to live in a colder climate, because the catalysts lose their activity more readily at higher temperatures than at lower temperatures, though the amount of oxidation in a warm country will be larger in the beginning than in a cooler country. Moreover as the catalyst has to oxidize a greater quantity of food material at a higher temperature in an unit of time, its activity should decrease more rapidly.

Consequently it appears that old age and death would take place more quickly in warmer climates than in colder climates, under otherwise identical conditions, especially with cold blooded animals. Krehl and Soetbeer[1] have compared the heat production of animals from temperate climates (Lacerta, Rana) with tropical forms (Alligator, Uromastix) and found higher figures for the former than for the latter at identical temperatures.

TABLE I

Heat Production of Different Animals

| | Weight in Grms. | Cal. per Kg. and hour. at 25.3° | Cal. per Kg. and hour. at 37.° |
|---|---|---|---|
| Lacerta | 110 | 0.8 | 1.5 |
| Rana | 600 | 0.5 | 0.95 |
| Alligator | 1380 | 0.3 | 0.47 |
| Uromastix | 1250 | 0.26 | 0.4 |

Statistics show that the average longevity of human beings in tropical countries is much less than the average longevity of human beings in colder countries, as in tropical countries for some time of the year, the outside temperature is higher than the body temperature.

There is some direct experimental evidence available on this question from the work of Loeb and Northrop[2], Table II.

TABLE II

Effect of Temperature on Duration of Life of Drosophila (fly)—a cold-blooded insect.

| Temperature °C | Total Duration of Life from egg to death. |
|---|---|
| 10 ..... | 177.5 days |
| 15 ..... | 123.9 " |
| 20 ..... | 54.3 " |
| 25 ..... | 38.5 " |
| 30 ..... | 21.15 " |

From this table it is seen that at the lowest temperature the duration of life is longest, and at the highest temperature shortest. Cold slows up the rate of living for the fly. Heat hastens it. One gathers from the account which Loeb and Northrop give of the work, that at low temperature the flies are sluggish and inactive and perhaps live a long time because they live slowly. At high temperatures, on the other hand, the fly is very active and lives its life through quickly at the pace that kills. This relation is more easily applicable to cold-blooded animals. In the case of warm-blooded animals the relation is more complicated because of the so-called chemical heat regulation, as will be shown in the subsequent paper.

[1] Pflüger's Archiv, **77**, 611 (1899).
[2] J. Biol. Chem., **32**, 103 (1917).

The activity of the catalysts or the body cells is usually associated with its surface energy. In course of time the surface energy of all systems tends to decrease. Consequently the activity of the cells or enzymes is likely to decrease because of the fall of their surface energy with time; hence their catalytic activity is likely to decrease with time. It is quite possible for the membranes or tissues in the body which consist mainly of cells or protoplasms become hardened in course of time due to their partial coagulation and dehydration. It should be emphasized that dehydration and decrease of surface energy play a very important rôle in the catalytic activity of tissues, membranes, enzymes, and cells.

There are several biological facts in support of the above views. In investigations made upon isolated organs, it has been shown that a certain minimum metabolism involving respiratory exchange is inseparable from the life of every organ and will persist when the organ is doing no work whatever so long as the ability to do work remains.

Comparative experiments on the standard metabolism at different ages have been made on man by Magnus-Levy and Falk (1899). The older experiments of Tigerstedt and Sondén (1895) were also made on man, but the standard conditions were not rigorously observed. The general results of Tigerstedt and Sondén's experiments were very similar to those of Magnus-Levy and Falk.

Calculated per unit weight (kilogram) the metabolism of growing individuals is much larger than of adults, and in old age there is a distinct decrease. Adult individuals belonging to the same species, but of different size, have a larger gas-exchange per kilogram, the smaller their size, while it has been shown that when the metabolism is calculated per unit surface (square metre) about the same figure is obtained for all sizes. A comparison between young and adult human beings must therefore be instituted on the basis of surface instead of weight, as there are large differences in size. When this is done, Magnus-Levy and Falk find that the differences, though of course diminished, are not abolished as Table III shows.

TABLE III

Standard Metabolism of Males of Different Age

| Age, years. | Weight, Kg. | Surface Sq. M. | Per square metre and minute Oxygen c.c. | $CO_2$ c.c. |
|---|---|---|---|---|
| 2.5–11 | 11.5–26.5 | 0.627–1.094 | 175–154 | 501–122 |
| 10 –16 | 30.6–57.5 | 1.205–1.834 | 159–132 | 133–109 |
| 22 –56 | 43.2–88.3 | 1.516–2.441 | 129–111 | 105–82 |
| 64 –78 | 47.8–69.3 | 1.628–2.077 | 103–87 | 86–63 |

Magnus-Levy and Falk have also made experiments on three subjects of approximately the same weight and height (and consequently the same surface) but vary different age. They obtained the results given in Table IV;

TABLE IV

Standard Metabolism of Persons with Same Surface

| Age, year's. | Weight, Kg. | $O_2$ per minute c.c. | $O_2$ per Kg. relative figures. |
|---|---|---|---|
| 15 | 43.7 | 217 | 110 |
| 24 | 43.2 | 196 | 100 |
| 71 | 47.8 | 163 | 75 |

but individuals of the same age and stature may also have very different standard metabolisms. Consequently, these experimental results support the view that old age is associated with marked decrease of the catalytic activity of the body enzymes and consequently in old age there is a marked decrease of metabolism. Death, according to this point of view, follows when the amount of oxidation in the body is just less than the minimum necessary to keep up the body temperature.

## Summary

1. The chemical reactivity and adsorptive power of freshly precipitated substances are greater than those of substances prepared long ago.

2. The catalytic decomposition of hydrogen peroxide due to the presence of manganese dioxide is much greater when it is freshly precipitated than when the same weight of an old sample of manganese dioxide is used.

3. Old age is associated with marked decrease in the catalytic activity of the body enzymes and consequently in old age there is a marked decrease of metabolism.

4. A certain minimum quantity of heat is necessary for the maintenance of the body temperature. When the amount of oxidation in the body is just less than the minimum necessary to keep up the body temperature, death is likely to follow.

5. Animal life is assumed to depend essentially on the catalytic activity of the enzymes in the animal body.

*Chemical Laboratory,*
*Allahabad University,*
*Allahabad, India.*
*June 9, 1925.*

# STRUCTURAL COLORS IN INSECTS. I

BY CLYDE W. MASON[1]

## Introduction

On looking over the literature on insect colors, one finds a very striking lack of agreement on many points; the nature of various colors thought to be due to structural conditions has been the subject of a great many conflicting papers. The situation is hopeful, in that most people do not need to be convinced that structural colors are of widespread occurrence in the insect world, but in many instances there has been an unfortunate tendency to assume that all these colors are to be explained on the same basis.

Actually, to determine the relationship of the structural features to the color phenomena observed in any given case requires more than a cursory inspection, particularly since pigmental and structural colors are combined in many instances and mutually influence the appearance observed.

In a study[2] of structural colors in feathers the main criteria for the identification of different types of color were assembled, and their application to a number of typical cases was illustrated. The present paper is an attempt to carry out a similar study in the case of a sufficient variety of insect color types to show how such criteria may be applied to any given specimen. It is not the aim of the writer to present a mass of information regarding a large number of different insects, or to assume the position of referee in all disputed cases. Such material, where it does appear, is incidental to the main purpose of this investigation, namely the development of reliable and simple methods for distinguishing between pigment colors and the different types of structural colors, when present in insects, either singly or in combination. It is hoped that such methods may be applied by entomologists to any cases which are of particular interest. The speciments used in the present work (furnished through the kindness of Dr. W. T. M. Forbes, of the Entomological Department at Cornell) were chosen irrespective of genus or species, the aim being to secure as great a variety of types of color as possible—in other words, to "sample" the collection on the basis of color phenomena rather than entomological relationships, though, naturally, representatives of different orders are present in the assortment which was studied.

Such an effort is by no means original with the writer. Many other workers[3] have made extensive studies with more or less the same purpose in mind, but some of their findings are none too conclusive, and have placed

[1] The investigation upon which this article was based was supported by a grant to Messrs. Bancroft, Chamot and Merritt from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Mason: J. Phys. Chem., 27, 201, 401 (1923).

[3] Hagen: Proc. Am. Acad., 17, (1881-82); Coste: Entomologist, 23, 24, (1890-91); Tower: Dec. Pub. Univ. Chicago, 10, 33 (1903); Mallock: Proc. Roy. Soc., 85A, 598 (1911); Biedermann: Handbuch vergl. Physiol., 3, I, 2, 1657 (1914); Onslow: Phil. Trans., 211B, 1 (1921); Suffert: Z. Morphol. Okol. Tiere, 1 II, 172 (1924).

emphasis on the specimen rather than the method, so a somewhat different line of attack is perhaps not out of order. Much that appears in the following pages is not new, but inasmuch as it either confirms or contradicts earlier observations, its inclusion seems justified, particularly since it must be taken into consideration in any conclusions which may be drawn.

### Distinction between Structural and Pigment Colors

To decide whether structure or pigment is the cause of a given color phenomenon, a number of tests are useful. Obviously, if some specialized structure functions in accordance with certain optical principles to produce color, the chemical nature of the tissue in which this structure is present will be of negligible importance, except in so far as it may render the physical structure susceptible to alteration by chemical reagents; but any treatment which alters the nature of the *optical system* will produce a modification of the color. On the other hand, if the color is due to selective absorption or reflection of certain of the constituents of white light by a pigment, it will be very little affected by alterations in its physical condition, but will be susceptible to any chemical treatment which alters its inherent nature.

In accordance with the above principles, a structural color should satisfy most of the following general criteria:

Hue altered by pressure, distortion, swelling or shrinking.

Color destroyed if system is made optically homogeneous by permeating with a liquid of the same index of refraction as that of the tissue, and color restored on removal of this liquid.

Color not destroyed by bleaching, or affected by chemical reagents unless these swell, shrink or destroy the tissue.

No pigment, except possibly black or brown, extractable by solvents or revealed by chemical tests.

All constituents of the incident white light accounted for, either in the reflected, transmitted, or scattered light.

Similar color phenomena duplicable with colorless substances in similar physical condition.

Iridescence of some sort generally exhibited.

The converse of the above will serve to characterize pigment colors, and usually the distinction can be made even more positive by further tests regarding the particular sort of pigment or structure concerned. Structural conditions may modify the appearance of pigmented tissues, while the lustre of the surface, or the presence of over- or under-lying colored tissues may also have considerable influence; a given pigment may exhibit different tints or shades, or even apparently slightly different hues, depending on whether it is present in a fine or course state of subdivision, or in combination with white. In most cases, even where the type of color is established, study under a Greenough-type binocular microscope at moderate magnifications will show the relative importance of these different factors in a most striking manner.

For instance, there is probably about the same amount of pigmentation in all the black beetles, but those which have highly lustrous surfaces appear much blacker than those which have their integument dulled and roughened by age and exposure. Supplying the "glaze" by means of a film of oil or varnish gives a deep lustrous black in such cases. However, even such glossy black is not as dark as the black of certain butterflies. These latter do not even show "highlights", yet their pigment is probably no more dense than that of the beetles. Their dark scales, naturally of little lustre and with numerous interstices between them, serve to "entrap" the light, and give a much darker shade for a given amount of pigment (just as velvet appears darker than satin dyed with the same dye). This appearance is particularly marked if one views the butterfly's wing from the tip, that is, looking down into the shadows between the scales.

It is highly probable that the browns and blacks are due to a melanin pigment, as they are in birds and mammals, the color present depending not only on the amount of pigment present but also upon its condition, black being found with granular pigmentation and brown with more or less perfectly diffuse pigmentation (pigment in solution rather than suspension in the tissue).

By permeating the tissue with a colorless liquid of nearly the same index of refraction (say 1.55-1.6 for chitinous material) the effect of any structures associated with the pigment to be studied is minimized, and the true absorption color may be observed by transmitted light.

Besides the ordinary colors which depend upon absorption of light, certain others have been ascribed to pigments: white, which depends on the power of scattering light, and certain cases of iridescent colorings, which are said to be due to pigments showing selective reflection. The latter will be considered in connection with the discussion of other iridescent colors with which they are most likely to be confused.

### White in Insects

White depends for its perception on a rather high intensity of reflected or refracted colorless light reaching the eye of the observer without the perception of transparency or vitreous or metallic lustre. This will be the case whenever the surface by which such light is reflected or refracted to the eye are so small as not to be readily resolved as separate by the means of observation employed. Obviously, the finer the surfaces, the more perfect the "scattering" of light and the whiter the object. White objects, because of their power to scatter light in all directions, transmit light very imperfectly, and are more or less opaque, even though the actual material composing them is transparent (e.g.: snow and ice; foam or fog and water; sand and rock crystal; blanc fixe and barite; chalk and Iceland spar; "Rayon" and "Cellophane", and so on). The colorless metals appear white by reflection from irregular surfaces but in the case of all other colorless substances, refraction also plays a part in scattering the light to produce white, and the elimination of the reflection and refraction at their numerous small bounding surfaces results in transparency, with no

whiteness. Since this reflection and refraction by transparent materials depend upon the relative indices of refraction of the substance and the medium surrounding it, it is obvious that if the latter can be varied, (as it can in two-phase systems when at least one phase is fluid) the white may be completely destroyed, by rendering the system *optically homogeneous*. So whenever we have practically colorless chitin in such form as to present many more or less unordered reflecting surfaces, we shall observe whiteness. Nearly all of the whites of insects are to be explained on this basis, as proved by the fact that when the air in contact with the chitin is replaced by a liquid of index of refraction near 1.55 they are rendered colorless and transparent, while if the liquid is either of greater or less index of refraction the destruction of the white is not so complete. On removal of the permeating liquid, the original whiteness is restored, proving that no white "pigment" has been dissolved out.

The above procedure may readily be followed under the microscope, and the connection between air as a permeating medium, and the whiteness is very evident by reflected light or dark field illumination. The increase in transparency as the liquid penetrates the interstices of the structure is very striking, and corresponds to the familiar process of "clearing" tissue for microscopic study. By means of the "Becke test" (given in any text-book of petrography) one can select from a series of liquids one which matches the index of refraction of the chitin almost perfectly, and thus render it almost completely invisible, even by dark field illumination. The scales of white butterflies and moths illustrate this very nicely.

The question as to whether the whites of insects are due to pigment or to structure is merely one of definition. All white materials, whether commonly thought of as pigments or not, owe their whiteness to the reasons given above, and white paint is just as much a structural white as snow. We are ordinarily in the habit of thinking of pigments as something distinct from the substance which is pigmented by them, and from this point of view there are very few white pigments in nature. Generally the tissue in question is its own white pigment, and the white cannot be removed without destroying the structure on which it depends.

Certain butterflies, notably the *Pieridae* are said to owe their whiteness to a definite pigment (uric acid) which is present in their scales as an excretion from one stage of their development.[1] Although uric acid is white, and might well serve as a pigment when finely divided, it plays a very minor part in producing the white of butterfly scales, for these may be extracted with solvents for uric acid (such as dilute alkalies) but on washing and drying their white appears undiminished. The scales become transparent on penetration with liquids of $n$ = 1.55-1.6. Assuming that any uric acid is present in the free state, and not in solid solution in the chitin, it might be expected to appear white when finely divided, but the ribbed and reticulated structure of the scales accomplishes this so well that whether uric acid is present or not is of little importance, as far as their whiteness is concerned.

[1] Hopkins: Phil. Trans., **186**, 661 (1896).

The belief that the chalky whites of butterflies, particularly the Pieridae, are due to pigment is common; but the more lustrous whites, such as those of *Euproctis* are ordinarily admitted to be air-filled cavities in the scales. Actually both sorts have hollow scales, as do insects in general; both are rendered transparent by permeation with liquids of $n = 1.55$-$1.6$., and there is no question but that, whatever may be the chemical composition of the scale in both cases, the white is due to essentially the same causes, namely, the scattering of light by reflection and refraction by the minute structures of the scales.

### Lustrous Whites

The question of lustre is closely related to that of color, and may best be discussed in connection with white, for we have all types illustrated by colorless insects. White butterfly wings exhibit lustres ranging from chalky to micaceous, silvery, or pearly, and these are of necessity to be explained on the basis of the structures present, since the constituents of the wings are essentially the same in all these cases.

Chalky or matte lustre is characterized by the absence of high lights, and by practically uniform scattering of light in all directions. This requires a random arrangement of the surfaces which reflect and refract the light. Although the scales of butterflies are arranged systematically on the wing membrane like shingles on a roof, this is not of importance in the case of the chalky whites, for the individual scales serve to scatter light in all directions, whatever their arrangement may be; a single scale appears just as white as do a group of scales. The overlapping of the scales on the wing contributes little to their whiteness, because of the high degree of opacity of the white. Such scales, under the microscope, show more or less regular longitudinal striations, boldly defined, and probably due to deep corrugations in the surface of the scale, or to longitudinal partitions in it, or to both. Besides these, fine transverse markings are present, which, although unordered in their pattern, add materially to the opacity and whiteness. On permeating with a liquid of $n = 1.55$-$1.6$ the markings and outline of the scale become almost invisible. The above multiplicity of fine structural details furnishes reflecting and refracting surfaces to scatter the maximum amount of light in all directions, and to give the minimum of sheen.

Intermediate between the matte whites and the pearly or silvery whites is that shown by *Euproctis*. Here a distinct sheen is observable, when the line of vision is that direction along which light would be reflected by the surfaces of the scales. In other positions the wing appears matte white, tho not so bright or opaque as in the case of the typical chalky whites; single scales appear very much more transparent and scatter less light than when grouped on the wing, where under the Greenough they are seen to overlap considerably; this overlapping adds to their reflecting power, for if a blackened scalpel is inserted under the free edge of the scales they permit it to be seen thru them very clearly. With high powers, the individual scales are seen to be striated longitudinally, but these markings are very much less distinct than in the scales of the *Pieridae*, and constitute the only surfaces for scattering light, the

finer reticulations being absent. The whole appearance is that of considerable transparency, even without a permeating liquid; when the scales are filled with liquid of $n$ = 1.55-1.6 they are barely visible under the microscope, and the entire wing is rendered so transparent that one may easily read thru it, even when the liquid chosen does not match the index of refraction of the scales very perfectly. In the above case, the white is due to a certain amount of scattering by the finer structures of the scales but we have here also the necessary structure for the production of pearly lustre, namely, the superposed transparent reflecting surfaces presented by the scales as they lie on the wing. This is the situation which is present in all cases of pearly lustre, such as mother-of-pearl, ground mica, crystallized $CdI_2$, or a pile of glass plates[1], and it is of considerable importance also in the production of metallic lustre[2].

The essential difference between matte whites and pearly whites depends on the amount of random scattering which the presence of minute structures in the scales may cause.

When the lamellae which produce pearly lustre are almost perfectly plane and transparent, and there is a minimum of diffuse scattering of the light, we have very perfect and typical pearly lustre, which may under favorable circumstances verge into true metallic lustre. This is exhibited by *Helicopus cupido* and by the common "Silverspot" (*Argynnis*). The name of the latter is very appropriate, for the spots, though not as metallic as burnished silver, strikingly resemble matte silver. They do not scatter light well, and only along the line of direct reflection do they appear bright. Even in this position they do not send as much light to the eye as do the chalky white scales. Microscopic study of the scales shows longitudinal striations and a distinctly transparent appearance. There is some scattering of the light which falls across the striations, but on the whole a rather glassy appearance is noted by reflected light.

The pearly areas of *Helicopis cupido* are similar in appearance to those of the "Silverspot", but are even more highly lustrous and show distinct though pale iridescent colorings, which strongly resemble those of mother-of-pearl. The overlapping, transparency, and lack of light-scattering power or whiteness are even more pronounced; microscopically the scales show only very faint striations and appear to be little more than a transparent envelope with thin walls nearly in contact, all of which constitutes a system for the production of pearly or metallic lustre by superposed laminae, more perfect than that of *Euproctis* because of the almost complete transparency and absence of diffusion of the light. However, even here the whiteness and reflecting power at the most favorable angle are rather less than in the matte whites.

Leydig[3] has ascribed the pearly lustre of *Argynnis* to the fine structure of the scales, without specifying how this is related to the general phenomenon

[1] Bancroft and Allen: J. Phys. Chem., **28**, 546 (1924); 29, 564 (1925).

[2] "Silver" patterns on the wall paper are made with ground mica; a roll of waxed paper is pearly, while a roll of colorless, transparent "cellophane" (sheet viscose) is hardly to be distinguished from a polished steel rod.

[3] Arch. Mikr. Anat., **12**, 536 (1876).

of pearliness, and Biedermann[1] while disagreeing with him on details, apparently also failed to recognize that superposed, more or less transparent lamellae were in themselves sufficient to account for all the observed lustre. Süffert[2] also places undue emphasis on the minute structural details of the scales, and considers their high reflecting power to be due to the longitudinal ridges of the upper lamella, which serve by two refractions and one total reflection to send the light back along the original direction, in somewhat the same manner as does ribbed glass. He admits that such a structure must be highly perfect if it is to function as indicated, but apparently does not appreciate the possibility of the high lustre being accounted for by any less complex system.

Microscopic study of scales of *Argynnis*, with transmitted and with vertical illumination reveals a structure that is closely similar to that described by Süffert: a ribbed upper lamella, a fairly smooth lower lamella, an interior space with fairly plane surfaces and a relatively small amount of spongy or columnar material in this cavity. Slow permeation by viscous liquids aids in the interpretation of these appearances, and helps to isolate their several effects; for instance, the iridescent colors seen by axial reflected light are observed only when the interior of the scale is empty, irrespective of whether the lamellae are in contact with liquid outside. The dry scale is apparently the same viewed either side up. If the scales are covered by a cover glass, and a viscous liquid is allowed to surround them, one notices that the reflecting power of unwetted scales is apparently no greater than that of the air spaces between the slide and the cover glass. Also, if one compares the reflecting power of the scales on the wing with that of a single thin film of glass, the latter is much more brilliant, yet when we consider that the scales consist of two lamellae, separated by an air space, and that they overlap so that they are two deep on the wing, it is evident that we might expect an even higher degree of reflection from the four films of chitin thus functioning as reflectors.

Actually it appears that the high lustre of the pearly scales is *in spite of* rather than because of their fine structure. The latter plays its part in diffusing the light, so that the metallic appearance is visible over a wider angle, and in producing certain color phenomena, but acts to cut down the efficiency of the multiple-film system for producing metallic or pearly lustre; this loss in specularity of reflection is accompanied by an increased appearance of whiteness, and greater opacity of the scales.

The delicate iridescent colorings, the cause of which will be discussed later, enhance the resemblance to pearl, and possibly give the illusion of even greater lustre.

### Non-Porous Whites

In addition to the ordinary sort of structural whites in which the minute surfaces are in contact with air, another type may occur in which the structure is non-porous, and possesses no air-filled spaces. The reflection and refraction

[1] Handbuch vergl. Physiol., 3, I, 2, 1932 (1914).
[2] loc. cit. p. 287. Z. Morphol. Okol. Tiere, 1 II, 172 (1924).

which are the cause of the scattering of the light take place at surfaces bounding two tissue materials of different refractive indices, and their perfection will be governed by the amount of this difference. Such a system is optically the same as a porous white rendered partially transparent by a liquid of index of refraction fairly near that of the tissue but not matching it; examples are common: marble, vitrified porcelain, ivory, pearl, paraffin wax, etc.

Obviously, any attempt to destroy the white by rendering it transparent by means of a permeating liquid cannot be successful, for there are no interstices to be filled. The only possibility would be in some way to render the indices of refraction of the various structures identical, which would involve chemical alteration, hydration or some similar treatment.

The non-porous whites are of very little importance in the insect world, and are mentioned merely for the sake of completeness; the "air whites" may definitely be said to be the only important cause of whiteness in insects. In most cases whites of this sort are more or less transparent, and of little scattering power; in insects this is particularly true, because the various kinds of material which make up the tissues have almost the same index of refraction; in no case is the difference in the indices nearly as great as the difference between one of them and that of air. Wing membranes, when bare of scales, and occasionally veins may give a weak white, but these play a very small part in the whiteness of the insect as a whole.

### Influence of Structure on Coloration

Where a color pigment is combined with white it is usually dissolved or dispersed in the tissue itself, so that we have to deal with a more or less colored and transparent substance, which is in a state of subdivision corresponding to that existing in the whites. Unless the tissue is very heavily pigmented and rendered almost opaque, such fine structure will reflect a large part of the incident light; what light does actually enter the colored tissue will be refracted and reflected out again, without traversing more than a very short distance in the tissue. Thus there will be little absorption, although the scattering of the light takes place just as in the unpigmented tissues and as a result we have the hue of the pigment with a large admixture of white, giving a tint much lighter than the tissues would exhibit if the fine structure were absent. Many common materials illustrate this great difference in tint dependent upon their fineness; beer and its foam, vulcanized rubber and its dust, the "streak" of colored minerals, taffy before and after pulling, butter and cream, coarse and fine copper sulphate, and so on. It follows that, since structural conditions cause a very much lighter tint than shown by the colored substance in mass, the best way to observe the true hue and tint is by eliminating reflection and refraction as completely as possible. This is accomplished by rendering the system *optically homogeneous* by bringing a liquid of the proper index of refraction in contact with all the minute surfaces, just as is done when whites are rendered transparent.

The above treatment is particularly useful in studying the hue, concentration, uniformity, and state of aggregation of pigments in the scales of butter-

flies and moths, and one may rest assured that any color observed by transmitted light under these circumstances is due to pigmentation and not to any structural effect.

To the naked eye, permeation with liquids darkens the tint considerably and increases the transparency of the scales and of the wing as a whole. This behavior has many familiar analogues; wet and dry watercolors, grease or water spots on wood, colored fabrics, and papers, etc., mud and dust; copper sulphate may be powdered so fine as to be almost white, but its deep-blue is restored by wetting with a liquid of the proper index of refraction.

Where pigmentation is combined with some specialized structure other than that capable of producing ordinary white, a number of effects are possible. Hairs and scales play a considerable part in modifying the tint and lustre of the pigment. The deep blacks and browns of some of the bees are closely analogous to the rich shades of velvet or plush; the hairs standing on end have their surfaces in position to reflect a minimum of light, and if they are even moderately pigmented appear in a very much darker shade than if they are lying more or less flat, (as in crushed velvet).

If the scales are all practically in the same plane, they present an excellent reflecting surface to light which falls along their length; this corresponds to the structure of satin, and, like it, may exhibit a very high lustre.

*Ornithoptera poseidon* exhibits two types of black which illustrate the influence of structure on pigment coloration. The deep velvety black which occupies most of the non-iridescent portion of the wing is due to the heavily pigmented, overlapping, convex scales, of low reflecting power, and with only a small portion of their curved surfaces in position to reflect light at any given angle. The brownish black areas just in front of the rear iridescent border of the upper sides of the forewings are markedly different in appearance; the scales are very much narrower and more numerous, stand erect, are sharply curved at the upper end and less heavily pigmented. They overlap very little, and permit the light colored wing membrane to be seen between them; under the microscope the appearance resembles that of open-weave Brussels carpet. Individually they show more reflecting power than do the scales from the deep black portions, and on the wing this is more pronounced because of the greater number of minute surfaces presented by the finer scales, and because of the partial visibility of the wing membrane between them.

It has been pointed out that relatively transparent, smooth, overlapping scales may show a pearly to metallic sheen; if these are colored this effect is greatly enhanced, and may be of typical metallic lustre[1]. The wings of *Chrysophanus virgaureae* and their members of this family have the appearance of tarnished brass, but their scales are as described above, with the addition of a yellow orange pigment. Dyeing the silvery scales of *Helicopus cupido* or

[1] A pile of three to five sheets of yellow gelatine has a metallic lustre equal to that of polished brass, and corresponding appearances may be obtained with other colors. Crystallized lead oxide looks golden; anhydrous chromium sesquichloride is a metallic purple; ground phlogopite resembles bronze; the goldfish is golden rather than yellow because of his scales.

*Argynnis* or the pearly ones of *Euproctis* with dilute Bismarck brown gives them a golden appearance. This metallic appearance of relatively smooth, transparent scales is observed irrespective of whether their color is due to pigment or to structure, and *Urania*, *Morpho*, *Apatura*, in fact most of the brilliantly lustrous and iridescent butterflies may be cited as examples, without discussing the nature of their coloring at present[1].

Biedermann[2] has discussed in considerable detail the relationship of the form and surface of insect scales to the color phenomena which they exhibit collectively on the wing of the insect. Convex, concave, warped, or stepped surfaces, or unusual inclinations of the scales may prevent their color (pigment or structural) from being seen except in certain directions.

The blue-green bars on the upper surface of the wings of *Apatura* (*Chlorippe*) *seraphina* are composed of scales which are strongly convex and form minute cylindrical surfaces, the axes of which are cross-wise of the scales. Some part of such surfaces is in position specularly to reflect light to the eye of the observer almost irrespective of the position of the wing as a whole, and the color bands may be seen from any position. The remainder of the upper surface of the wing appears dull brown, except in certain positions, where it is purple to blue-green, so that as the wing is inclined this brilliant color flashes out, only to disappear as suddenly with further inclination of the wing. Study with the Greenough-type binocular microscope permits this behavior to be observed at moderate magnifications with highly realistic stereoscopic effect, so that interpretation of appearances is greatly simplified. It is found that the scales in these brown to blue areas are not particularly convex but are markedly inclined to the surface of the wing, so that the tip is considerably higher than the base, and the plane of the scale makes an angle of about 30° with the plane of the wing. The reflection from these scales is specular, and as a consequence they appear bright only when the angle of incidence of the illuminating beam and the angle of reflection along the line of vision are equal[3]. These two factors combine to render the reflection color visible when one looks "along the grain" of the wing, while if the line of vision falls "against the grain" there is no reflection, and the effect is that of the brown pigmentation, the shade of which is darker because the scales are seen endwise and the interstices beneath them serve to "entrap" the light. All this may be checked varying the plane of the scales ("ruffling them up" or flattening them down) with respect to the plane of the wing, and study of single scales is also of value.

Essentially the same situation exists in *Apatura ilia*, and it is of interest to note that even the scales in the white bands possess the same blue reflections, which may be enhanced by dyeing them with a brown or black dye so that the

[1] In discussing the influence of the form of the scales on the color exhibited by them, Onslow mentions the importance of flat, smooth surfaces in the production of metallic appearances. Phil. Trans., **211B**, 5 (1921).

[2] Handbuch vergl. Physiol., **3**, I, **2**, 1657 (1914).

[3] It should be remembered that if the plane of the scale makes an angle of 30° with that of the wing, a vertical illuminating beam will be reflected at an angle of $2 \times 30°$ from the normal to the surface of the wing. (A change of $n$ degrees in the plane of the reflector causes a change of $2n$ degrees in the direction of the reflected ray.)

white is eliminated. *Ancyluris meliboeus*, *Acraea sp.*, *Callicore eluina*, *Zephyrus quercus*, and numerous other butterflies show a bluish over-sheen or "bloom", in addition to their ordinary pigment coloring (commonly melanin brown).

## Tyndall Blues in Insects

The ability of a finely divided transparent substance to scatter light increases with increasing fineness until the order of magnitude of the particles is near the wave-length of light; for finer material the action is selective, and the particles scatter the short wave-lengths of white light, while permitting the longer wave-lengths to pass through unaffected. Such a system appears turbid blue to white from positions out of the line of the directly transmitted light and turbid yellow to red in this latter direction. Tyndall[1] first explained this phenomenon, and it has been recognized in a great number of common objects; the sky, blue eyes, smoke, "opal" glass, skimmed milk, blue feathers, very fine precipitates, collodion jelly, sublimates on charcoal in blowpipe analysis, etc.

The properties of Tyndall blues have been discussed at some length in a previous paper[2], and only the main criteria for their recognition need be summarized here: 1—Minute structure, of dimensions less than 0.5$\mu$, of different index of refraction from that of the surrounding medium. 2—Blue to bluish white scattered; brown to red, orange, or yellow by transmitted light. 3—Scattered light more or less polarized; vibrations in a plane perpendicular to the direction of the incident beam.

To observe the scattered light, it is desirable that the illuminating beam should fall more or less tangentially on the tissue under examination, and if any surface irregularities are present, the scattering of light by these should be eliminated as completely as possible, preferably by immersion in a liquid of the same index of refraction as that of the tissue. Dark field illumination is very satisfactory for the examination of Tyndall blues, but the polarization is not readily observed unless the light is unidirectional. A cap nicol prism above the eyepiece, with or without a "Selenite plate" serves to determine the polarization of the scattered light. By transmitted light with critical illumination and an objective of at least N.A. = 0.85 a thin layer of the material should show fine stippling, the individual particles being about 0.3$\mu$ to 0.5$\mu$ between centers. These may also be observed by reflected light under favorable circumstances. The color of the tissue is, of course, yellow to orange or brown, by transmitted light, unless dark pigment underlies the blue structure, and this may readily be noted. A dark background for the blue cuts off any stray light from below, so that only the scattered light is observed.

Biedermann[3] mentions Schatz as having ascribed the metallic blue of the *Morphos* to a turbid layer over a dark background and points out that the

[1] Phil. Mag., (4), **37**, 385 (1869).
[2] Mason: J. Phys. Chem., **27**, 215 (1923).
[3] Handbuch vergl. Physiol., **3**, I, 2, 1970 (1914).

lustre and brilliancy of the color are inconsistent with the thickness of the structure where they are assumed to originate, while the change of hue with changing angle of incidence is certainly different from the behavior of Tyndall blues. Needless to say, no evidence structural or optical, has been found to support Schatz's supposition with respect to the metallic blues.

In *Enallagmae* the blue of the abdomen lies over a dark layer, to which it is closely adherent, but it is possible to dissect away the underlying pigmented tissue, and to study the blue layer by itself. The criteria given above are all satisfied, although the polarization is not very distinct. In all probability this case of Tyndall blue is due to fine particles enclosed in a chitinous material, for the color is not destroyed by prolonged soaking in permeating liquids, and pressure has little effect on the blue, tho if pores were present they should be partially closed by this treatment.

*Mesothemis simplicicollis* is typical of dragon flies which develop a "bloom" with maturity; the color of the body of this insect is really only a very grayish blue, but it eonstitutes an example of Tyndall blue where air is in contact with the surfaces which scatter the light.

This "bloom" or efflorescence may be removed by scraping, leaving exposed the black or brown integument which serves as a dark background for the blue. The scrapings are in such a fine state of subdivision that they appear almost opaque by transmitted light and scatter light very effectively. However, their microscopic structure is indefinite and too coarse to give better than a grayish blue.

When the "bloom" is wetted by a liquid of index of refraction near 1.5 it becomes completely transparent and invisible and the dark pigmented tissue beneath it is perfectly visible. On removal of the liquid the original appearance is restored.

A somewhat similar "bloom" is found on the wings of *Libellula pulchella* ("Ten Spot"), in the form of white cloudy spots, which shade to whitish blue at their edges. This is a Tyndall blue, the white portion of the spot being due to a coarsening of the structure. Microscopic examination shows the spots to consist of a very fine granular coating on the wing membrane; this may be scraped off readily, and is rendered completely invisible by wetting with liquids of $n = 1.5$. Removal of the liquid restores the original appearance.

It is noteworthy that while all non-metallic blues in feathers are Tyndall blues, in insects examples are few, and most blues are due to other causes.

Of the possible specimens suggested by Dr. Forbes, only one was found to possess a blue pigment: the hairs of *Xylocopa Caerulea* are a clear blue by transmitted light, and show no evidence, structural or optical, of any but pigment coloration. The color change brought about by treatment with acids is undoubtedly of the nature of an indicator effect, more or less perfectly reversible by alkalies.

The conclusions of this paper are as follows:

1. All whites of insects are structural.

2. Pearly and metallic lustre are due to superposed transparent parallel laminae.

3. Tyndall blue occurs in a few insects.

4. Blue pigments do not appear to be present in insects.

5. Structural conditions may modify the appearance of pigment colors very markedly.

*Laboratory of Chemical Microscopy*
*Cornell University.*

# THE ELECTROLYSIS OF ACID SOLUTIONS OF COPPER SULPHATE. II. CONSTANT CURRENTS

BY J. T. BURT-GERRANS

The experimental work of Mr. L. V. Redman[1] having shewn general agreement between certain predictions of the mathematical theory[2] of changes of concentration at the electrode, and the behavior of acid solutions of copper sulphate on electrolysis, it remained to enquire whether the want of sharper agreement was due to inaccuracy in the fundamental assumption of the theory (viz: that the diffusion constant of copper is independent of its concentration in the electrolyte employed) or was due to insufficient approximation in the laboratory to the ideal experimental conditions postulated by the equations. The present paper gives an account of experiments on the electrolysis at 18.0°C of acid solutions of copper sulphate with constant current, which were undertaken to answer this question.

## I. THE ELECTROLYTIC CELL

*Exclusion of air:*—Mr. Redman himself had discovered one source of error in the apparatus used by him, viz: the action of air-saturated electrolyte on the copper electrodes. I therefore carried out all electrolyses in an atmosphere of carbon dioxide, after first freeing the electrolyte from air by evacuation. A large quantity of stock solution, containing 15.45 g. of copper per litre, was prepared by dissolving recrystallized (hydrated) copper sulphate in maximum-conducting sulphuric acid (30.5% acid by weight, about 7.6 normal); this was diluted with the same acid to the desired concentration before each experiment, and freed from air by evacuation in a thick-walled glass bottle standing in the thermostat. Carbon dioxide was then bubbled in for two minutes, the solution evacuated again, treated with the gas for two minutes as before, evacuated once more, then left for at least two hours in the thermostat in a slow current of the gas, which was obtained from a cylinder, and was washed with water and passed through sulphuric acid on its way to the electrolyte.

A few minutes before the electrolysis the electrolyte was transferred (by gravity, through rubber tubing) into the electrolytic cell (which had been standing ready for at least half an hour in the thermostat) and was protected again by the gas; two portions of 100 cc. each were removed at this stage for analysis, and two more after the electrolyses were completed, unless the four analyses agreed the experiment was rejected. The copper was determined electrolytically in a King's electrolytic outfit[3]; the solutions were almost neutralized with ammonia, and sodium nitrate was added to secure a good deposit.

---

[1] L. V. Redman: J. Phys. Chem., 29, 1548 (1925).

[2] T. R. Rosebrugh and W. Lash Miller: J. Phys. Chem., 14, 816-884 (1910). Equations from this paper are indicated by "R & M".

[3] Chem. and Met. Eng., 21, 25 (1919).

*Precautions to secure uniform thickness of film.*—In his apparatus Mr. Redman secured a uniform electrolytic field by the use of two stationary non-conducting horizontal plates, one at the top and the other at the bottom of the (perpendicular) rotating cathode. It seemed quite possible that the friction of the electrolyte against these plates might affect the thickness of the "diffusion film" of liquid adhering to the cathode, by making it thinner near the

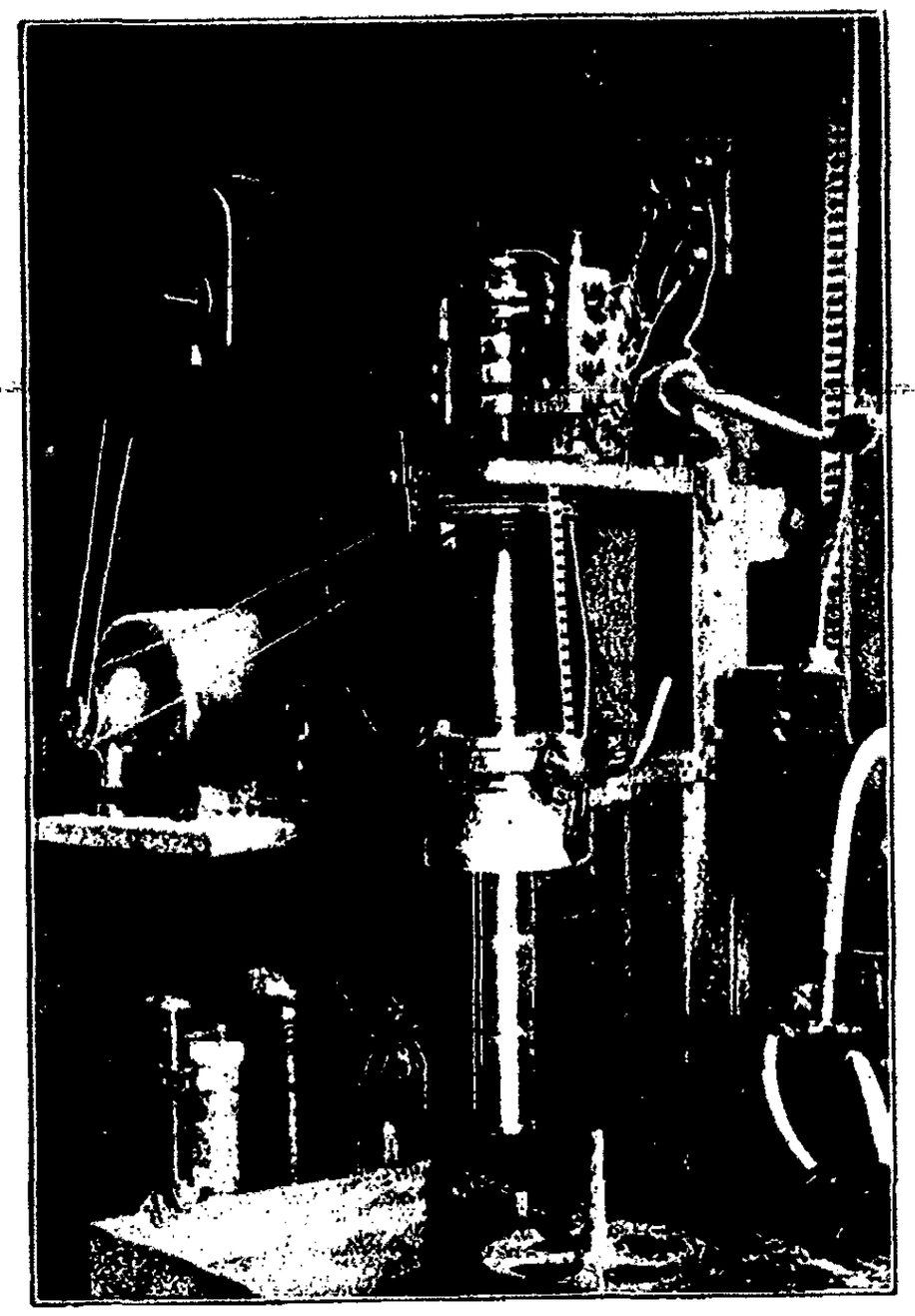


FIG. 1

ends of the cathode than near the middle; while the equations of the "mathematical theory" are based on the assumption that the film is of equal thickness throughout. I therefore reconstructed the cell, and provided three cathodes on the same shaft, (Fig. 1), separated from each other only by thin discs of insulating material ("Redmanol"); the three cathodes were of the same diameter (4.60 cm) and height (6.40 cm), and each was provided with its own rheostat so that the same number of amperes could be sent through each, but only the central cathode was connected to the oscillograph. The "current" recorded in the tables is that through the central cathode, and reached it by a mercury cup on the top of the shaft; the currents for the other two were led

in through brushes. The cathode shaft runs on a double-faced cone-bearing just above the cathodes and on a ball-bearing below the brushes. The common anode, which also serves as cell, is a drawn copper cylinder 10.2 cm internal diameter and 21 cm high, which screws into a flange on the casing of the lower bearing of the cathode shaft; it is provided with a delivery tube for filling the cell and with an overflow pipe to ensure that the electrolyte is always at the same level. The whole is mounted on a lathe bed set vertically, so that it can be lowered into the bath, whose temperature is held within 0.1°C by an electrically controlled thermostat.

Stationary horizontal insulating plates were employed, as in Redman's apparatus, one close to the top of the upper cathode and one close to the bottom of the lower cathode; with this arrangement the uniform electrolytic field was retained, but the plates were at such a distance from the central cathode that there seemed little danger of their affecting the thickness of its adherent film.

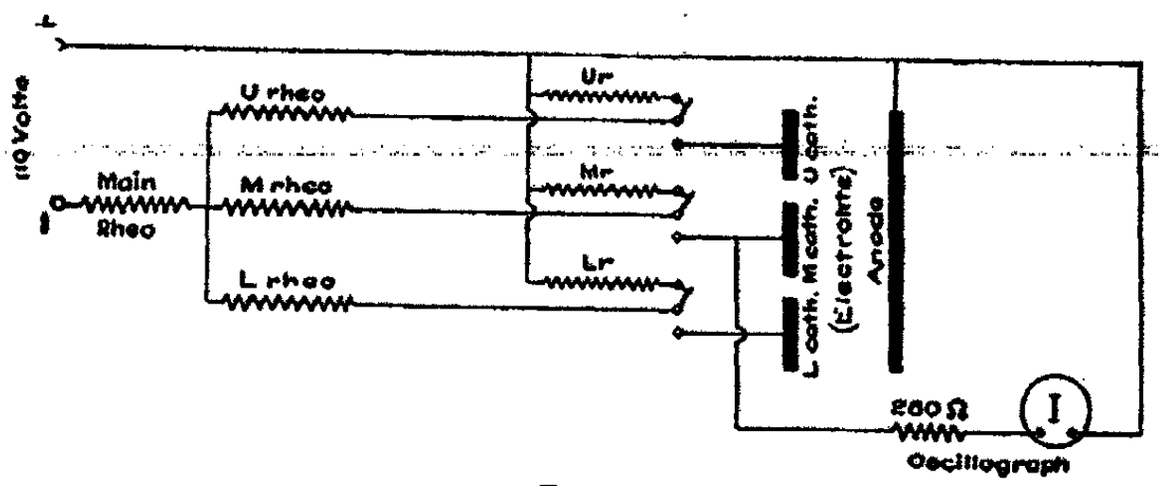



FIG. 2

## II. THE CIRCUITS

*Rearrangement of circuits.* Redman's tuning-fork method of calibrating the time axis on the film, and of recording the rate of rotation of the cathode shaft, was retained; but the short-circuiting bar used to protect the cell while the current was being adjusted was found to leak a little, and was replaced by an automatic device which threw the cell completely out of circuit and replaced it by an equivalent resistance, except while the oscillograph shutter was open and the record was actually being made.

Three exposures were needed for each film, one to record the line of zero voltage, one for the voltage-calibration line, and one for the voltage-time curve taken during the electrolysis. For each of these special electrical connections were required, which were made by amalgamated copper contacts mounted on wooden blocks and dipping in the cups of a 48-cup mercury switchboard. The actual electrolytic circuit was kept away from this board for fear of accidental leaks; therefore, before each exposure a number of well insulated knife-switches had to be opened or closed by hand, but for each operation the mercury switchboard kept a red light burning near each switch, and this was extinguished only when the switch was moved to the proper posi-

tion for the operation in hand. This arrangement much facilitated the manipulation of what, in the end, became a very complicated piece of apparatus.

Without going into details of the mercury switchboard, signal lights, safety devices, adjustable contacts geared to the oscillograph drum, etc., etc., the main electrical circuits will now be described in simplified form, then the results obtained, and finally the computations.

*The electrolysis circuit.* (Fig. 2). The three "cell-resistances" *Ur*, *Mr*, and *Lr* were adjusted once for all to be equal to the resistance through the electrolytic cell and leads *via* the upper, middle, and lower cathode respectively. Except while the oscillograph shutter was open, contacts were maintained between *Ur* and the "upper rheostat", *Mr* and the "middle rheostat", and *Lr* and the "lower rheostat"; these three rheostats were adjusted until the same current flowed through each of the three "cell resistances", by means of an ammeter, not shewn in the figure, which could be switched into series with each of the three rheostats in turn. This adjustment once made, the elec-

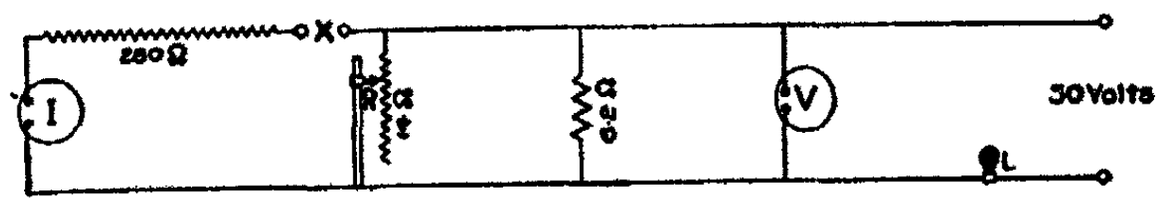



FIG. 3

trolysis-current could be varied by means of the "main rheostat", though before each electrolysis the equality of the three currents was checked; the source was a large 110 volt storage battery. When the oscillograph opened its shutter, the relays described below connected the upper cathode, instead of the upper cell-resistance, to the upper rheostat, and the same with the other two, thus sending the current through the cell; and oscillograph element No. 1 recorded the potential-difference between the anode and the middle cathode. When the shutter closed, the former connections were automatically restored.

To avoid induction, carbon lamp rheostats were used throughout, fine adjustment being effected by a slide wire rheostat in series with one of the lamps; the resistance of these lamps had a high temperature coefficient, but as the current flowed through them continuously this did not matter. The "cell resistances" were of manganin, wound non-inductively, and the leads to and from the cell, and from one connection to another, ran side by side in pairs. The ammeter used was a Weston Model 45 (150 divisions full scale) provided with suitable shunts; they were calibrated against a copper coulometer, and also by means of a potentiometer and standard ohm; for each electrolysis-current the appropriate shunt was used, so that the reading on the instrument was never less than 100 divisions of the scale.

*The voltage-calibration circuit.* (Fig. 3). The 32 c.p. carbon lamp *L* allowed about 0.32 amperes to flow from the 50 volt storage battery; thus with no resistance in the slide-wire rheostat *R* the voltmeter shewed about two volts; this was reduced to the desired value by means of *R* and recorded. When the

oscillograph shutter opened, contact was automatically made at $X$, and a line was photographed whose height corresponded to the recorded voltage, as the resistance of 280 ohms in series with the oscillograph element I prevented any drop in voltage when contact was made at $X$. When the shutter closed again, the connection at $X$ was automatically broken.

To keep the second element of the oscillograph from drawing a horizontal line while the calibration-voltage line was being photographed, a circuit was arranged which sent sufficient current through that element to throw the light spot off the paper from the moment before the shutter opened until just after it closed again.

The voltmeter was a Weston Model 45 with 500 ohms internal resistance, in a series with which was 4500 ohms; the combination was calibrated by the potentiometer, each division corresponded to 0.0206 volts.

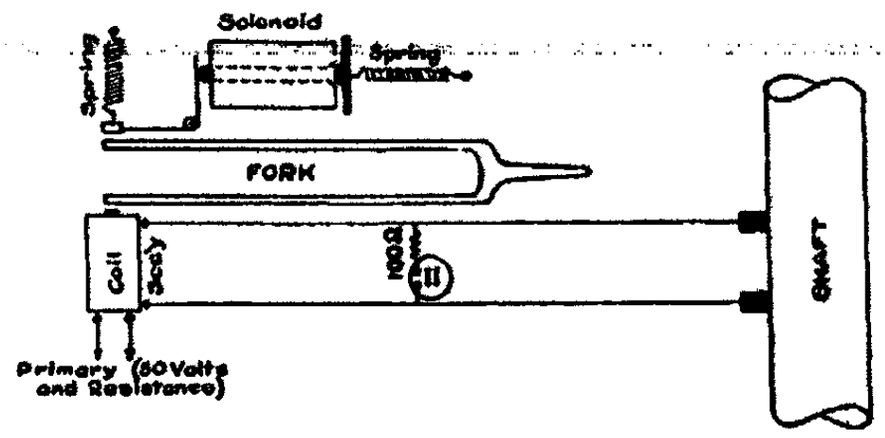



FIG. 4

The oscillograph was the Siemens-Halske two-element instrument used by Redman; a current of 4 milamperes through the element gave a deflection of 45 millimeters on the photographic paper; on most of the oscillograms the deflections ran from 15 to 30 mm.

*The tuning-fork circuit.* (Fig. 4). A constant current of about one ampere from a storage battery passed through the primary of a small induction coil, the secondary winding of which (7 ohms) was in series with the second element (II) of the oscillograph; the latter was short-circuited for a moment during each revolution of the cathodes, by means of a brass contact attached to the cathode shaft. When the tuning fork was struck (hammer and solenoid) its vibrations induced a sinusoidal current in the secondary of the coil; the resulting wavy line on the photographic paper served to calibrate the time axis, and its interruptions recorded the speed of rotation of the cathodes. To get a nice curve, free from the evanescent distortions which follow the hammer blow, the fork had to be struck about one second before the shutter opened; this was attended to by a contact wheel geared to the oscillograph drum which rotated once for every four revolutions of the drum.

*Relay circuits.* (Fig. 5). A system of three 20-ohm telegraph relays was used to make the contacts indicated in Fig. 5; the primary of each of them was connected to a dry cell through a resistance so adjusted that the current from the dry cell was insufficient to pull the armature of the relay up to the

magnet, but was sufficient to hold it there (against the pull of the relay spring) if a surge of current from some other source had once brought it close; these dry-cell circuits are omitted in the figure.

In the normal state of the relays, with their tongues held away from their magnets by the springs (as in Fig. 5), contact was made in the secondary circuit of Relay II but not in either of the others. When the oscillograph shutter opened, a surge of current from the "opening magnet" of the oscillograph (special connections to which were made for this purpose) excited the magnet of Relay I, which thereupon closed the circuit through the secondary of Relay II to the "electrolysis-magnet"; this circuit remained closed (because of the dry cell on the primary of Relay I) until the "closing-magnet" of the oscillograph was excited and closed the shutter. A surge of current from

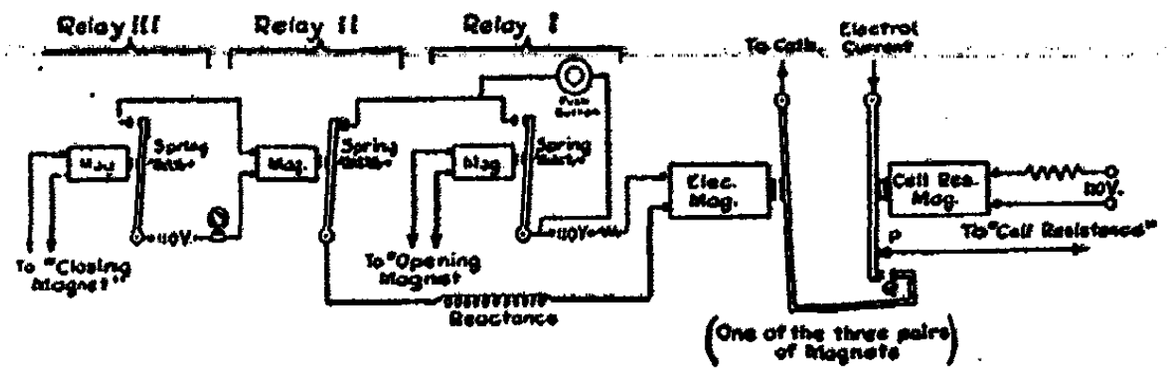



FIG. 5

this "closing-magnet" passed through the primary of Relay III and thus closed the circuit through the secondary of that relay, activated the magnet of Relay II and broke the electrolysis-magnet circuit. To set the relays ready for use again, it is only necessary to break the dry cell circuits for a moment; the tongues are thereupon pulled away from the magnets, and remain away when the dry cell circuits are completed again.

The "cell-resistance magnet" is supplied with current sufficient to attract its armature and hold it firmly against the contact $P$; the electrolysis-current then passes via armature and $P$ to the cell-resistance (Fig. 2). When the "electrolysis-magnet" is excited, however, it not only makes the contact at $Q$, which sends the current through the cathode, but being much stronger than the "cell resistance magnet" it pulls back the armature of the latter and breaks the circuit through $P$; as, for a moment, the cell-resistance is in parallel with the cell, the contact at $P$ breaks without a spark. There is a "cell-resistance magnet" and an "electrolysis-magnet" for each of the three cathodes; the three electrolysis-magnets are connected in series, and operated from the same relays. In order that the moment at which electrolysis begins might be recorded accurately, a reactance coil was inserted in the circuit leading from the relays to the electrolysis-magnets; this delays the action of these magnets a little, so that the time-voltage curve begins with a short horizontal portion on the zero-voltage line, and rises perpendicularly when the current passes through the cell.

### III. MANIPULATIONS TO SECURE A TIME-VOLTAGE CURVE

While the electrolyte was being freed from air, photographic paper was placed on the oscillograph drum, switches were closed to supply current to the oscillograph magnets and motor, fork-hammer, signals, relays, voltage circuit, etc.; the "calibration-voltage" block was put on the mercury switchboard, circuits corrected until the red lights went out, the arc lamp adjusted, voltage set and read, and the switch thrown which permits the oscillograph to open its shutter and record the calibration-voltage line. The oscillograph handles were reset, the current to the calibration-voltage circuit broken, and the zero-voltage line secured.

The electrolyte was then transferred to the cell, the cathode-shaft motor set going, and its speed read on an electric speed-counter and adjusted by means of a rheostat in series with the armature of the motor. The cell thermometer was read, and the temperature of the electrolyte recorded.

The "D. C. electrolysis" block was then put on the mercury switchboard, red lights put out, "relay jack" closed (to complete the dry-cell circuits), and at a signal from the oscillograph the "fork jack" closed, which made it possible for the machine to operate the tuning-fork hammer; immediately after the blow, the "operating jack" was closed, and after waiting a second for the fork to assume steady vibrations, the oscillograph opened its shutter, sent the current through the cell, and photographed the time-voltage curve and the time-calibration curve simultaneously; it then closed its shutter, and the relays stopped the electrolysis.

After two or at most three electrolyses the electrolyte was removed, taking samples for analysis, and the cathodes cleaned. This precaution was necessary because during part of the time of each electrolysis hydrogen was being liberated together with the copper, and the powdery deposit formed under these conditions must obviously affect the thickness of the diffusion film. Under conditions of current, concentration, temperature, and speed of rotation such that comparatively little of this deposit was formed, five time-voltage curves (recorded one under the other on the same photographic paper) which were obtained from five successive electrolyses made without cleaning the cathodes, proved to be almost identical; but under less favorable conditions, there was a distinct difference between the first and the last curve; and in the final determinations, those recorded below, the cathodes were cleaned after every two electrolyses.

Fig. 6 shews one of the time-voltage curves obtained as just described.[1] *AB* is the zero-voltage line, *CD* is the voltage-calibration line, *EF* is the time-voltage curve. Each revolution of the cathodes required 19.5 "waves" of 1/128 second, i.e. the shaft revolved once in 0.152 seconds. The point marked with an arrow, where the curve shews a point of inflexion, was taken to indicate the moment at which the concentration of copper at the cathode

[1] The actual oscillograms were all 21 cm long and 9 cm wide.

reached zero; this is 84.5 "waves", or 0.660 seconds, after the point at which electrolysis began; in Table II this determination would be recorded as $\vartheta = 0.660$.

### IV. LIMITING-CURRENT DETERMINATIONS

When the "limiting-current block" was put on the mercury switchboard, it made contacts to the "push-button" as shewn in Fig. 5; when this button was pressed, it completed the secondary circuit of Relay I and, therefore, sent the electrolysis current through the cell; when the pressure was removed, the current flowed through the cell-resistances again. The block also arranged to have the potential difference between the anode and the middle cathode shewn on the calibration voltmeter.

The current was first adjusted to an amperage somewhat lower than that of the estimated limiting-current, this current was recorded; the button was

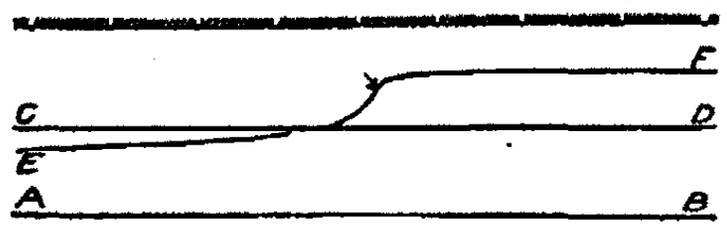



Fig. 6

then pressed, and the potential difference read and recorded. These operations were repeated with successively greater currents, and the observed voltages plotted against the currents; the point at which the curve shewed a sudden increase in steepness gave an approximate value of the limiting-current under the known conditions of concentration, temperature, and rate of rotation of the cathodes. This preliminary determination, however, involved repeated electrolyses, each lasting several seconds, so that the cathodes became covered with a deposit which affected the thickness of the diffusion film; to obtain the definitive value of the limiting-current, therefore, the cathodes were cleaned and a few voltage determinations made with currents closely below and above the provisionally determined value of the limiting current; to cut down the duration of each electrolysis, a lens was held over the voltmeter near the expected reading, and the button was pressed just long enough for the reading to be taken. Thus the final value for the limiting-current was obtained before the cathode surfaces were spoilt; immediately after the last voltage reading a switch was closed which caused the oscillograph to record the speed of rotation of the cathodes, the cell thermometer was read, and a portion of the electrolyte was removed for analysis.

#### Results of the Limiting-current Determinations

Fig. 7 shews that, within the limits of experimental error, the limiting current is connected with the concentration of the electrolyte and the rate of rotation of the cathode by the relation

(*Lim. current*) × (*sec. per rev.*) $^{0.77}$ = 0.0790 × (*g. Cu per L.*) (1)

which is the equation to the curve drawn on the figure; the lowest concentration used in these experiments was 0.46 grams of copper per litre and the highest was 4.0 grams.

The form of this relation is that used by Brunner[1], the exponent 0.77 signifies that doubling the peripheral speed of the cathode increases the limiting current to 1.71 times its original value; the theory accounts for this by assuming that the adherent film has been reduced to 1.0/1.71 = 0.59 of its original thickness. Forty unpublished determinations by Redman (18°C, 1.0 to 6.0 g Cu per L) are in good agreement with the exponent 0.55; that is, with Redman's apparatus, doubling the speed of rotation reduced the thickness to two-thirds. The peripherical velocities and the form and dimensions of the cathode in Redman's experiments were almost exactly the same as in mine;

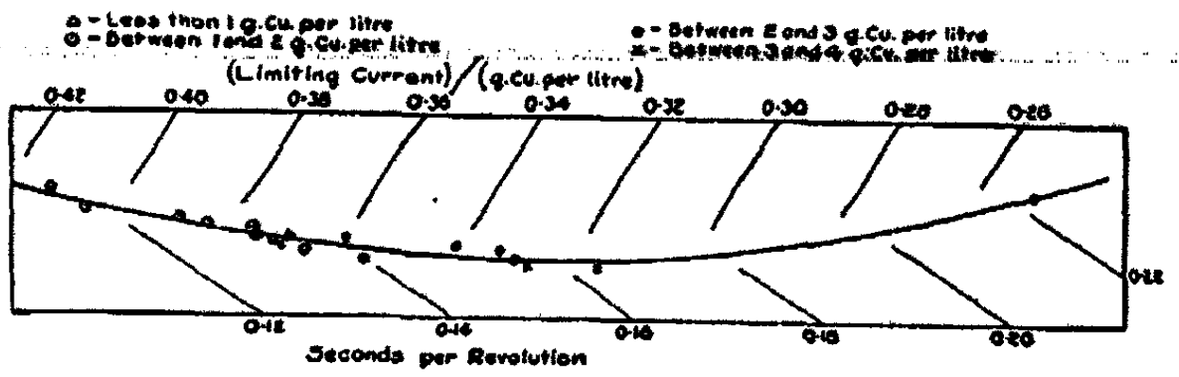



FIG. 7

but in his, the stationary plates were close to the ends of the rotating electrode, while in my three-cathode cell they were 6.5 cm distant from the middle cathode (for which the limiting currents were obtained).

To test the effect of the position of these stationary plates, two thin circular plates of Redmanol were cut to fit across the cell and perforated in the centres so that they would just slip over the cathodes. These plates were attached by three rods of the same material (at their outer edges, near the anode) to the upper and to the lower stationary plate respectively, so that the central cathode revolved in a cell of its own with stationary plates close to its upper and lower ends. With this arrangement the limiting current was greater (i.e., the film was thinner) than when the plates were at a distance from the central cathode, and the effect of changing the speed of the cathodes was less. The four experiments of Table I fit the equation

(*Lim. current*) × (*sec. per rev.*) $^{0.41}$ = 0.206 × (*g.p.L.*) (2)

TABLE I

1.950 g copper per litre, 18°C.

| Sec. per rev. | Limiting current (amp.) obs. | calc. by Eq. (1) | calc. by Eq. (2) |
|---|---|---|---|
| 0.172 | 0.825 | 0.599 | 0.823 |
| 156 | 860 | 643 | 861 |
| 131 | 911 | 737 | 924 |
| 117 | 967 | 803 | 968 |

[1] Z. physik. Chem., 47, 56 (1904).

In view of these results, it is obviously illegitimate to assume that there is a diffusion film of uniform thickness over the whole surface of a rotating electrode, unless the latter is kept well away from the stationary ends of the electrolytic cell.

### A. COMPUTATIONS OF $k$ AND $l$ FROM THE LIMITING-CURRENTS AND THE TIME-VOLTAGE CURVES.

From the assumptions (*i*) that the diffusion constant $k$ is independent of the concentration of copper in the electrolyte, (*ii*) that the diffusion film is of uniform thickness $l$ cm, (*iii*) that in these strongly acid solutions there is no electrolytic migration of the copper, and (*iv*) that the jump in voltage used to determine the limiting-current occurs when the concentration of copper at the cathode is brought to zero, there follows that the limiting current[1] ($-I'$ amperes), the concentration[2] of copper in the body of the electrolyte ($z_0$), and the area of the cathode ($A$ sq. cm.), are connected by the equation

$$I' = 96500\, A\, z_0\, k/l = 96500 \times 92.5 \times (g.\ p.\ L) \times k/(31800 \times l) \quad (3)$$

$$\text{whence } k/l = 0.003562 \times I'/(\text{g. p. L.}) \quad (4)$$

Expressing the limiting-current in terms of concentration and speed of rotation (Eq 1) this gives

$$k/l = 0.0002815/(sec.\ per\ rev.)^{0.77} \quad (5)$$

The quantity $\vartheta$ (the interval in seconds between the beginning of electrolysis and the first liberation of hydrogen) which is determined experimentally by means of the time-voltage curve as explained above, is related to the electrolysis current ($-I$ amp.) by the equation

$$-96500\, A\, k\, z_0 = I\, l\, (1 - 8/\pi^2\, \Sigma e^{-m^2 a\vartheta}/m^2 \text{ [R \& M 16]} \quad (6)$$

where $m$ is written as an abbreviation for $2n+1$, $a$ for $\pi^2 k/4l^2$ and $\Sigma$ for $\sum_{n=1}^{\infty}$.

The two equations (4) and (6) thus furnish two independent relations between $k$, $l$, $I'$, and $\vartheta$, so that from a time-voltage curve and the value of $I'$ for the same experimental conditions (which may be found from Eq. 1), both $k$ and $l$ may be computed. If the electrolysis-current be twice the limiting-current, or greater, $k$ can be computed from the time-voltage curve alone, for in that case Eq. (6) may be replaced by

$$I'/I = 0.718352\sqrt{a\vartheta} \quad \text{[R \& M 22a}^3\text{]} \quad (7)$$

$$\text{whence } k = 1.616 \times 10^{-5}\, I^2\vartheta/(g.\ p.\ L.)^2 \quad (8)$$

But if the electrolysis-current be less than twice the limiting-current, Eq. (6) becomes

---

[1] The convention adopted in the "mathematical theory" and followed here, is that a current is reckoned positive if it *increases* the concentration-at-the-electrode of the substance whose diffusion-constant is represented by $k$. At the cathode in solutions of copper sulphate, the current *decreases* the concentration of copper; the "limiting-current" as defined above thus corresponds to $-I'$ of the equations, and the electrolysis current to $-I$.

[2] The number of equivalents of copper in one cubic centimetre of the solution taken for electrolysis is represented by $z_0$; the number of grams of copper in a litre of the same solution by $(g.\ p.\ L)$; thus $(g.\ p.\ L) = 31800\, z_0$.

[3] Since, when $z = 0$, $(z\text{-}z_0)/Cl = I'/I$; see R. & M., Eq. 24.

$$I'/I = 1 - 8e^{-a\vartheta}/\pi^2 e^{-a\vartheta} \quad [\text{R \& M } 17] \qquad (9)$$

and both time-voltage curve and limiting-current determination are needed.

The actual computations are most conveniently carried out by means of a table giving *log* $(I'/z_0)$ for different rates of revolution of the cathode, and a second table giving *log at* for different values of log $I'/I$.

## VI. RESULTS OF THE COMPUTATIONS

1. When the electrolysis-current is twice the limiting-current or greater, the theory predicts that the time needed to bring the concentration of copper at the electrode to zero will be independent of the rate of rotation of the cathode. This follows at once from equation (7) by substituting for $I'$ its value from equation (4) and for $a$ its value, $\pi^2 k/4l^2$; the expression for $\vartheta$ so

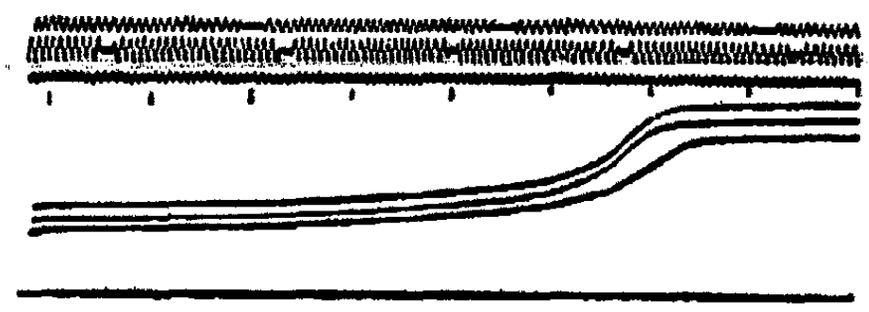


FIG. 8

obtained, viz $\vartheta = factor \times (g.\ p.\ L.)^2 \times k/I^2$, does not contain $l$ and is therefore independent of the rate of rotation of the electrode (see Eq. 5).

Figure 8 gives the time-voltage curves for three electrolyses carried out one immediately after the other, with the same electrolyte (*g. p. L.* = 1.910) and the same current ($-I$ = 1.180); the cathode speeds were 0.280, 0.184, and 0.110 seconds per revolution respectively[1]. From these data, the values of $I'/I$, viz 0.341, 0.471, and 0.700, were computed. The values of $\vartheta$ read from the oscillogram are 0.644, 0.648 and 0.700 seconds respectively—the first two equal, within the limits of error of the experiments, and the third greater, as predicted.

2. Table II gives the experimental data for 42 time-voltage curves, and the value of $k$ computed from each; the determinations are arranged in order of increasing $I'/I$ in the table, and the values of $k$ are plotted against copper-concentration in Fig. 9. In neither case is there positive evidence of a trend in the values of $k$, although the graph hints at a decrease with increasing concentrations; all the determinations lie around $k = 4.0 \times 10^{-6}$. Rejecting the three extreme values (one below and two above the mean), the remaining thirty-nine give $k = (4.00 \pm 0.07) \times 10^{-6}$; thus the dispersion, or "probable error" is one and three-quarters percent of the mean value, 19 of the determinations shew less.

An error of one percent in the copper-determination or in the electrolysis-current would introduce an error of two percent in $k$; an error of one percent

[1] The interruptions on the third tuning fork curve, which are quite distinct on the original oscillogram, have their positions indicated by pen marks in this reproduction.

TABLE II

| Film No. | (*g. p. l.*) | *Sec. p. r.* | $-I$ | $I'/I$ | $a\vartheta$ | $\vartheta$ | $10^6k$ |
|---|---|---|---|---|---|---|---|
| 293 | 2.556 | 0.146 | 2.667 | 0.334 | 0.216 | 0.227 | 3.98 |
| 302 (a) | 1.910 | 0.280 | 1.180 | 0.341 | 0.225 | 0.644 | 3.98 |
| 183 | 1.600 | 0.138 | 1.583 | 0.367 | 0.261 | 0.261 | 4.13 |
| 487 | 0.460 | 0.141 | 0.416 | 0.395 | 0.302 | 0.316 | 4.18 |
| 128 | 3.795 | 0.150 | 3.077 | 0.420 | 0.342 | 0.383 | 4.07 |
| 175 | 1.200 | 0.139 | 1.032 | 0.420 | 0.342 | 0.323 | 3.68 |
| 182 | 1.600 | 0.133 | 1.410 | 0.424 | 0.349 | 0.316 | 3.97 |
| 130 | 3.875 | 0.144 | 3.185 | 0.428 | 0.355 | 0.348 | 3.80 |
| 424 | 3.440 | 0.133 | 2.968 | 0.433 | 0.363 | 0.336 | 4.04 |
| 129 | 3.875 | 0.144 | 3.137 | 0.433 | 0.363 | 0.356 | 3.79 |
| 132 | 3.875 | 0.141 | 3.198 | 0.433 | 0.363 | 0.348 | 8.83 |
| 126 | 3.795 | 0.149 | 2.983 | 0.436 | 0.368 | 0.398 | 3.97 |
| 127 | 3.795 | 0.141 | 2.983 | 0.455 | 0.401 | 0.391 | 3.90 |
| 301(b) | 2.244 | 0.223 | 0.204 | 0.468 | 0.424 | 0.844 | 3.92 |
| 302(b) | 1.910 | 0.184 | 1.180 | 0.471 | 0.430 | 0.648 | 4.00 |
| 173 | 1.200 | 0.121 | 1.020 | 0.472 | 0.432 | 0.350 | 4.10 |
| 291 | 2.556 | 0.142 | 1.930 | 0.472 | 0.432 | 0.445 | 4.07 |
| 486 | 0.460 | 0.139 | 0.356 | 0.501 | 0.486 | 0.481 | 4.04 |
| 440 | 3.924 | 0.131 | 2.900 | 0.512 | 0.507 | 0.453 | 4.00 |
| 422 | 3.440 | 0.131 | 2.488 | 0.523 | 0.530 | 0.480 | 4.05 |
| 98 | 1.566 | 0.141 | 1.061 | 0.528 | 0.541 | 0.571 | 4.22 |
| 100 | 1.578 | 0.139 | 1.061 | 0.536 | 0.558 | 0.547 | 4.00 |
| 439 | 3.924 | 0.133 | 2.730 | 0.537 | 0.560 | 0.523 | 4.08 |
| 99 | 1.572 | 0.138 | 1.061 | 0.538 | 0.562 | 0.555 | 4.08 |
| 289 | 1.460 | 0.140 | 0.975 | 0.538 | 0.562 | 0.578 | 4.15 |
| 181 | 1.600 | 0.133 | 1.085 | 0.551 | 0.591 | 0.522 | 3.86 |
| 96 | 1.550 | 0.134 | 1.012 | 0.569 | 0.632 | 0.584 | 4.00 |
| 421 | 3.440 | 0.133 | 2.185 | 0.589 | 0.681 | 0.630 | 4.04 |
| 176 | 1.200 | 0.121 | 0.804 | 0.599 | 0.704 | 0.562 | 4.04 |
| 655 | 2.400 | 0.151 | 1.462 | 0.599 | 0.704 | 0.789 | 3.99 |
| 664 | 2.802 | 0.147 | 1.592 | 0.610 | 0.732 | 0.773 | 3.96 |
| 296 | 3.332 | 0.143 | 1.925 | 0.612 | 0.737 | 0.750 | 3.98 |
| 670 | 2.753 | 0.139 | 1.543 | 0.645 | 0.826 | 0.851 | 4.21 |
| 285 | 1.460 | 0.143 | 0.796 | 0.649 | 0.837 | 0.848 | 3.96 |
| 423 | 3.440 | 0.131 | 1.990 | 0.654 | 0.851 | 0.725 | 3.81 |

TABLE II (continued)

| Film No. | (g. p. l.) | Sec. p. r. | $-I$ | $l'/l$ | $a\vartheta$ | $\vartheta$ | $10^5k$ |
|---|---|---|---|---|---|---|---|
| 650 | 2.050 | 0.134 | 1.136 | 0.671 | 0.901 | 0.852 | 4.07 |
| 680 | 1.708 | 0.127 | 0.952 | 0.695 | 0.977 | 0.832 | 4.00 |
| 663 | 2.802 | 0.137 | 1.465 | 0.699 | 0.991 | 0.990 | 3.80 |
| 302 (c) | 1.910 | 0.110 | 1.180 | 0.700 | 0.994 | 0.700 | 4.13 |
| 694 | 1.378 | 0.133 | 0.726 | 0.710 | 1.028 | 0.963 | 4.10 |
| 679 | 1.708 | 0.125 | 0.921 | 0.727 | 1.088 | 0.922 | 4.08 |
| 301 (a) | 2.244 | 0.111 | 1.204 | 0.801 | 1.405 | 0.977 | 4.01 |

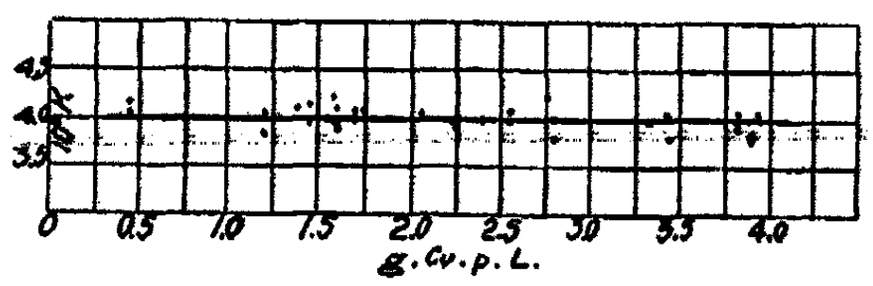



FIG. 9

in reading $\vartheta$ would cause an error of one percent in $k$; an error of one percent in the rate of rotation of the cathode might cause an error of 1.2 percent in $k$. A few determinations made at varying temperatures shew that an error of 0.1°C in the temperature of the electrolyte (which affects $l$ as well as $k$) would cause an error of 0.6% in $k$. Thus it seems justified to adopt the value $k = 4.0 \times 10^{-5}$ as the diffusion constant of copper in 7.6 normal sulphuric acid at 18°C, for concentrations from 0.5 to 4.0 grams per litre; and to conclude that the predictions of the mathematical theory for electrolysis with constant currents are borne out by the experiments within the limits of experimental error.

3. To test the theory under unfavorable experimental conditions, two electrolyses were carried out with very slow rotation of the cathode, five with the cathode stationary, and four in a rectangular glass cell with flat copper electrodes 6.5 cm × 7.5 cm, which fitted closely to the sides of the cell and were 2.0 cm apart; Eq. (8) was used to calculate $k$. The results are given in Table III; they agree with the others as well as could be expected, when the probability of accidental motion of the liquid is taken into consideration.

## VII. EFFECT OF VARIATION OF $l$ ALONG THE CATHODE

The very noticeable increase of the limiting-current brought about by placing stationary plates close to the two ends of the middle cathode (pg.404), must be due to their action in retarding the circular motion of the electrolyte, which would increase the friction at the surface of the revolving cathode, and, therefore, decrease the thickness of the adherent liquid film; it follows that when the plates are close to the ends of the cathode, the film must be thinner at its ends than at its middle.

TABLE III

| No. | *g. p. l.* | *Sec. per rev.* | $-I$ | $\theta$ | $10^4k$ |
|---|---|---|---|---|---|
| 371 | 1.938 | 0.582 | 1.379 | 0.516 | 4.22 |
| 372 | 1.938 | 0.781 | 1.408 | 0.488 | 4.17 |
| 382 | 1.868 | stationary | 1.073 | 0.688 | 3.67 |
| 354 | 1.868 | " | 1.110 | 0.656 | 3.75 |
| 363 | 1.868 | " | 1.197 | 0.590 | 3.92 |
| 360 | 1.868 | " | 1.404 | 0.477 | 4.36 |
| 361 | 1.868 | " | 1.486 | 0.406 | 4.15 |
| 366 | 1.838 | flat cell | 1.023 | 0.219 | 3.92 |
| 365 | 1.838 | " | 1.038 | 0.219 | 4.04 |
| 364 | 1.838 | " | 1.195 | 0.149 | 3.64 |
| 363 | 1.838 | " | 1.337 | 0.125 | 3.83 |

The theory of electrolysis when the thickness of the film is different at different points of the electrode was not dealt with in the paper on "mathematical theory", and it cannot be treated quantitatively unless the distribution of the different thicknesses along the electrode is known. It would seem that some theory of this distribution should be found in treatises on hydrodynamics, but I have not been able to find one; and in what follows have restricted myself to a rough qualitative treatment of the problem.

Consider the surface of the vertical cathode to be divided into a number of infinitesimal horizontal strips, each passing completely around the cathode, and each of the area $A_1$; since the strips are parallel to the plates, the film will have the same thickness opposite every part of the same strip, its thickness will be least for the end strips, will increase towards the middle, and will be the same for pairs of strips situated symmetrically with respect to the middle of the cathode. The suffix $_1$ is used to indicate the middle strip, and $_2$ one of the end strips; thus, $l_1 > l_2$.

At any moment during electrolysis the whole surface of the cathode mus be at the same electrical potential; the $i.r$ drop from anode to cathode is the same for each strip; and if it be assumed that the rest of the potential difference (viz: concentration-voltage and overvoltage) depends merely on the concentration of copper in the electrolyte at the surface of the cathode, it follows that at any moment during electrolysis the concentration must be the same opposite every strip. This hypothesis is in accordance with experimental results obtained by Mr. A. R. Gordon, a preliminary account of which has already been published[1].

From the beginning of the electrolysis until $a_2.t = 0.5$ (at which moment $at$ for every other strip[2] will be less than 0.5), the rate of fall of concentration at the cathode is independent of $l$ and is proportional to the current density (R & M 22); hence in order to maintain the same concentration opposite every strip, the current density must have the value $-I/A$ at every point on the

[1] W. Lash Miller: Franklin Institute, Centenary Publications, September, (1924).
[2] $at = \pi^2 kt/4l^2$

cathode until $a_2.t = 0.5$; and if the concentration of copper falls to zero before that moment, it is obvious that the variation in $l$ along the cathode can have no effect on the value of $\vartheta$. From then on, however, the current-density at the end strips must be appreciably greater than that at any other strip (including the middle strip) where the film is thicker than at the end strip; but as the electrolysis-current is maintained at constant intensity, this means that from $a_2.t = 0.5$ on, the current-density at the middle strip must fall, and that at the end strips increase. Equations have been developed for following the concentration changes at the cathode when the current-density changes with the time according to any given law, but as the distribution of $l$ is not known, they cannot be made use of.

Two propositions, however, can be established:

(*i*) There must be some constant current-density, $-B_1/A_1$ amperes per cm.$^2$, less than $-I/A$ (the actual current density at the middle strip when $t = 0$) but greater than the actual current density at the middle strip when $t = \vartheta$, which, if maintained at the middle strip from $t = 0$ to $t = \vartheta$, would just bring the concentration at the strip to zero at the moment $t = \vartheta$. Thus

$$B_1 A/I A_1 < 1.0 \qquad (10)$$

(*ii*) The limiting-currents for each strip, viz: $-I_1$, $-I_2$, etc., are related to $-I'$, the limiting-current for the cathode as a whole, by the equations:

$$I_1' . l_1/A_1 = I_2' . l_2/A_1 = \ldots = I' . L/A; \text{ whence } I'/I_1' = l_1 A/L . A_1 \qquad (11)$$

This follows from Eq. (6), since by definition the limiting currents make $z = 0$ at the electrode, when $t = \infty$. In this equation, $L$ is the fictitious film thickness introduced by making the false assumption that the film is of uniform thickness throughout.

By means of equations (10) and (11), a lower limit to the value of $l_1/L$ may be obtained from the data of Table IV, as follows:—Each value of $k$ given in this Table was computed by looking up the value of $at$ that corresponds to the fraction $I'/I$ and multiplying it by $4L^2/\pi^2\vartheta$; the true value of $k$ would be found by looking up the value of $at$ that corresponds to the fraction $I'_1/B_1$ and multiplying it by $4l^2_1/\pi^2\vartheta$. Near $at = 0.8$ (an average value for Table IV) the ratio of these two values of $at$ is close to the 2.2 power of the ratio of the two fractions; hence

$$\frac{k\ (table)}{k\ (true)} = \left(\frac{I' \cdot B_1}{I \cdot I_1'}\right)^{2.2} \cdot \left(\frac{L}{l_1}\right)^2 = \left(\frac{B_1 \cdot A \cdot l_1}{I \cdot A_1 \cdot L}\right)^{2.2} \cdot \left(\frac{L}{l_1}\right)^2 = \left(\frac{B_1 \cdot A}{I \cdot A_1}\right)^{2.2} \cdot \left(\frac{l_1}{L}\right)^{0.2} \qquad (12)$$

so that, by Eq. (10), $(l_1/L)^{0.2}$ must be at least equal to the ratio of the values of $k$.

While the results of Table IV differ rather widely, due to the difficulty of fitting the plates in exactly the same positions after each electrolysis, yet every experiment with rotating cathode gives a higher value of $k$ than the three with cathode stationary; the average with rotating cathode is $4.14 \times 10^{-6}$, with

stationary[1] cathode $3.83 \times 10^{-6}$, and the quotient 1.08. Using this quotient for want of a better, (and remembering that $B_1 A/l A_1$ is less than unity) Eq. (12) gives 1.47 as the minimum value of $l_1/L$; as $L$ (calculated by Eqs. 2 and 4) runs from $2.3 \times 10^{-3}$ to $2.7 \times 10^{-3}$, this would make the film at the middle of the cathode a little thicker than in the experiments of Table II; and as it seems unlikely that the friction of the plates could actually *increase* $l$ at any point of the rotating electrode, it may be concluded that the thickness of the film at the centre of the cathode is the same whether the plates are close to its ends, or are separated by the lengths of the upper and lower electrodes.

TABLE IV

| No. | *g. p. l.* | *Sec. per rev.* | $-l$ | $l'/l$ | $a\vartheta$ | $\vartheta$ | $10^6 k$ |
|---|---|---|---|---|---|---|---|
| 88 | 1.950 | 0.126 | 1.508 | 0.623 | 0.766 | 0.414 | 3.92 |
| 89 | " | 0.121 | 1.522 | 0.627 | 0.776 | 0.445 | 4.30 |
| 87 | " | 0.129 | 1.393 | 0.666 | 0.887 | 0.516 | 4.13 |
| 90 | " | 0.121 | 1.379 | 0.692 | 0.967 | 0.547 | 4.24 |
| 81 | " | 0.172 | 1.173 | 0.703 | 1.004 | 0.724 | 4.04 |
| 79 | " | 0.148 | 1.173 | 0.749 | 1.172 | 0.801 | 4.35 |
| 86 | " | 0.131 | 1.223 | 0.756 | 1.201 | 0.711 | 4.16 |
| 92 | " | 0.124 | 1.237 | 0.764 | 1.234 | 0.648 | 3.86 |
| 80 | " | 0.164 | 1.095 | 0.769 | 1.256 | 0.989 | 4.18 |
| 91 | " | 0.123 | 1.166 | 0.813 | 1.464 | 0.844 | 4.26 |
| 85 | " | 0.126 | 1.137 | 0.826 | 1.538 | 0.883 | 4.17 |
| 82 | " | stationary | 0.981 | ..... | ..... | 0.922 | 3.78 |
| 83 | " | " | 1.138 | ..... | ..... | 0.703 | 3.88 |
| 84 | " | " | 1.202 | ..... | ..... | 0.625 | 3.84 |

Thus, although the experiments of Table IV are obviously not accurate enough for individual computation, they serve to shew that the disturbing influence of the stationary plates does not extend far along the cathode, and that when the plates are removed to the ends of the cell, as in the experiments of Table II, the film may be regarded as of uniform thickness throughout.

### VIII. EFFECT OF AN UNSYMMETRICAL ELECTROLYTIC FIELD

The first and second experiments of Table V were made exactly as those of Table II; in the third and fourth no current was sent through the upper and lower electrodes. Owing to the low *i.r* drop through the electrolyte, and to the high polarization from the very first moment of electrolysis, one would expect the current to distribute itself fairly uniformly over the cathode, in spite of the fact that the anode was three times as high. The results bear out this conclusion, and shew that the provision of additional cathodes is not so im-

[1] This value is lower than the average of the more reliable determinations of Table II; but it seems better to compare values which were obtained during the same series of determinations and which, therefore, may be assumed to be affected with the same constant experimental errors. Substitution of the value $k = 4.0 \times 10^{-6}$ does not alter the final conclusion.

portant as it is to keep the working cathode away from the ends of the cell. A further experiment, in which current was sent through all three cathodes, but the upper cathode (instead of the middle cathode) was connected to the oscillograph, gave $k = 4.38 \times 10^{-6}$; while a duplicate in which the middle cathode was connected gave $4.18 \times 10^{-6}$, shewing again that it is more necessary to keep the hydrostatic field uniform than the electric.

TABLE V

| No. | *g. p. l.* | *Sec. per rev.* | $-I$ | $I'/I$ | $a\delta$ | $\vartheta$ | $10^6k$ |
|---|---|---|---|---|---|---|---|
| 71 | 2.552 | 0.133 | 1.236 | 0.772 | 1.269 | 1.172 | 4.04 |
| 72 | " | " | " | " | " | 1.164 | 4.01 |
| 73 | " | " | " | " | " | 1.195 | 4.12 |
| 74 | " | " | " | " | " | 1.191 | 4.10 |

## Summary

The paper describes apparatus and circuits for recording the potential difference over an electrolytic cell during the first second or so of an electrolysis, and for calibrating the oscillographic record with respect to the time and to voltage. The electrolyses described were carried out at 18.0°C. with solutions of copper sulphate in maximum-conducting sulphuric acid.

To secure uniform fluid friction over the whole surface of the revolving cathode, the latter was mounted on a vertical shaft between two auxiliary electrodes of the same dimensions; to secure a uniform electrolytic field, the three electrodes were supplied with currents of the same intensity; only the central cathode was connected to the oscillograph.

The rate of revolution of the cathode-shaft was recorded on the oscillogram, and an empirical relation was established between the limiting-current, the rate of revolution, and the concentration of the electrolyte.

From this relation, if the diffusion-constant of the copper be known, the equations of "The mathematical theory of the changes of concentration at the electrode" can predict the time that must elapse before hydrogen will be liberated by a known current passing through a solution of known concentration into a cathode revolving at a known rate. Assuming $k = 4.0 \times 10^{-6}$, these predictions agree with the time intervals recorded by the oscillograph within the limits of experimental error. Results of electrolyses between flat copper electrodes were also in accordance with the predictions.

The effect of unequal friction between the electrolyte and different parts of the same cathode surface is discussed, and evidence adduced that errors from this source have been avoided in the apparatus employed.

The apparatus described has grown out of that employed by Mr. L. V. Redman in this laboratory in 1907-10; it has been rebuilt, tested, and re

modelled many times since then. I wish to express my obligations to Professor W. Lash Miller under whose direction this series of investigations has been carried out, to Mr. L. V. Redman from whom I received my first instruction in the technique of these measurements, to Mr. H. A. G. Willoughby, Mr. A. D. Hone and Mr. H. R. Brant, who worked with me in constructing and improving the complicated apparatus, to Dr. S. Dushman for assistance in the earlier measurements and to Mr. A. R. Gordon for cooperation in the final determinations.

*The University of Toronto,*
*Electrochemical Laboratory,*
*December, 1925.*

# THE EFFECT OF ULTRA-VIOLET LIGHT ON THE OXIDATION OF SODIUM SULFITE BY ATMOSPHERIC OXYGEN*

BY RALPH B. MASON AND J. H. MATHEWS

Dilute solutions of sodium sulfite are readily oxidized by atmospheric oxygen. The rate of this reaction is quite dependent on the presence of minute traces of foreign substances, which may either retard[1] or speed up the reaction[2].

Under the influence of violet light sulfurous acid[3] is changed to sulfuric acid. Loew[4] exposed sealed tubes containing dilute solutions of sulfates, sulfites, sulfurous acid and sulfuric acid to the bright summer sun for three months. The sulfurous acid remained clear for two months, but after that sulfur was deposited and sulfuric acid formed. The other solutions remained unchanged. Sodium sulfite solutions are oxidized more rapidly in ultra violet than in ordinary light. Mathews and Weeks[5] have investigated the effect of certain negative catalysts upon the rate of this photochemical reaction.

Several theories have been advanced as to why certain oxidations proceed more rapidly in ultra-violet light than in ordinary light. Some contend that ozone or hydrogen peroxide is formed from the oxygen and this in turn oxidizes the substance. Chlopin's[6] experiments show that the ordinary moist air of a room, after subjection for a few minutes to the action of ultra-violet light, contains traces of ozone, hydrogen peroxide, and nitrogen trioxide. Others think that the oxygen is ionized by the action of light and that this ionized oxygen is more active than ordinary oxygen. In their work on activated air, Bredig and Pemsel[7] exposed oxygen to ultra-violet light, X-rays, uranium rays, and phosphorus one-fourth second before it was passed into a solution of sodium sulfite and found no increase in the rate of the reaction.

The purpose of the work to be described was to determine, if possible, the effect of the ultra-violet light alone on the oxidation of sodium sulfite solutions when certain catalysts were present. Early experiments indicated clearly that the reaction was mainly a "dark reaction". The term "dark reaction" is used here and elsewhere to indicate the reaction that takes place in the diffused light of the laboratory. The rate of the reaction is no slower in absolute darkness. The difference between the rate of the total reaction and the rate of the reaction in the dark was taken as the rate of the light reaction. Absorption spectrograms were made for all reacting substances, products and catalysts.

---

*Contribution from the laboratory of physical chemistry, of the University of Wisconsin.

[1] Bigelow: Z. physik. Chem., **26**, 493 (1898).

[2] Titoff: Z. physik. Chem., **45**, 641 (1903).

[3] Eder: "Photographie bei künstlichem Licht," 332.

[4] Am. J. Sci., (2) **49**, 368 (1870).

[5] J. Am. Chem. Soc., **39**, 635 (1917).

[6] J. Russ. Phys. Chem. Soc., **43**, 554-561 (1911).

[7] Eder's Jahrbuch Phot., 1900, 541.

## Preparation of Materials

*Sodium Sulfite.* Sodium sulfite was prepared by three different methods, Since there was no difference in behavior between these samples, and Merck's blue label sulfite, the latter was used in the final experiments.

*Water.* The water used was distilled from an alkaline permanganate solution then from barium hydroxide in an all-metal still, provided with a trap and a block tin condenser. It had a conductivity of 2 to $2.4 \times 10^{-6}$ mhos at 25°C.

*Catalysts.* The phenol was purified by recrystallizing three times. The copper sulfate, hydroquinone and sugar were recrystallized from conductivity water. No attempt was made to purify the quinine sulfate.

*Source of Ultra-violet Light.* A quartz mercury vapor lamp was used in the preliminary experiments as a source of ultra-violet light but was later replaced by the cadmium spark which could be brought closer to the reaction flasks, thus giving a greater intensity of ultra-violet and one much easier to control. The alternating current of the laboratory was stepped up through a one K.W. transformer and passed between two cadmium electrodes 5 mm. in diameter and 4 mm. apart. A variable resistance, inserted in the primary circuit, was used to keep the current constant at 3.5 amperes. In parallel with the secondary circuit were four large glass plate condensers in series. This equipment gave an intense, fat spark and the reaction was more rapid than with the mercury vapor lamp.

*Reaction Flasks.* The spherical transparent quartz reaction flasks were placed equidistant from the source of ultra-violet light, the distance from the light to each flask being equal to the focal length of the flask when filled with water.

*Temperature Control.* Since the oxidation of sodium sulfite is not a pure photochemical reaction but one which also takes place in the dark, it was necessary to keep the temperature more constant than for a pure photochemical reaction. By means of a small gear pump the water from the thermostat (kept at 25°) was forced into a reservoir above the reaction flasks and was then distributed in a thin film over the outer surface of the flasks from hollow, perforated block tin collars. The variations of temperature in the reaction flasks were less than .1°C from 25°C.

*Air.* The air from the pressure line in the laboratory was purified by passing through soda lime, sulfuric acid, sodium hydroxide and conductivity water. It was then passed into a five gallon bottle which acted as a buffer to small fluctuations in pressure. The flow of air through the reaction flasks was controlled by two very fine needle valves and the rate of flow measured by flow meters[1]. The rate of flow was 60 liters per hour, except as otherwise stated. The air was forced through small glass tubes and bubbled up through the solutions in the quartz reaction flasks. These tubes were made by cutting a long tube in the middle and grinding the ends. With tubes so prepared the

[1] Benton: J. Ind. Eng. Chem., 11, 623 (1919).

rates of the reactions in the two flasks were equal for a given volume of air per minute. Experiment showed that the shape and size of the bubble influenced the rate of the reaction, hence the necessity of delivering the air in exactly the same manner to both flasks.

In order to keep the solutions well mixed, mechanical stirrers were first used but it was found later that the bubbling of the air through the solutions caused sufficient mixing.

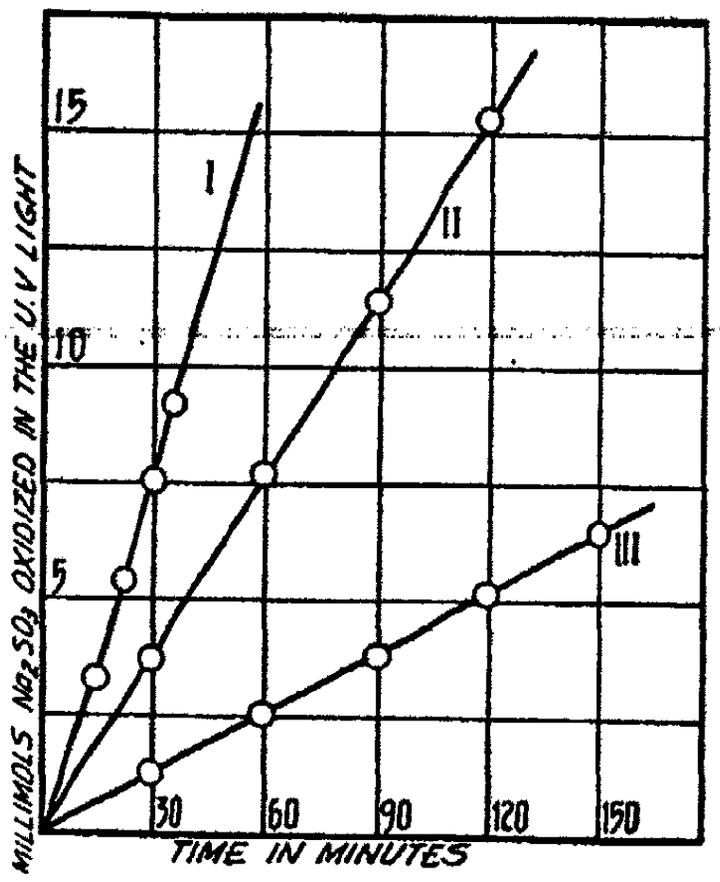



FIG. 1

I. 30 Liters pure $O_2$ per hour
II. 60 Liters air per hour
III. 30 Liters air per hour
Temperature 30°C

A large size Krüss spectrograph containing quartz lenses and prism was used for making the absorption spectrograms. The ends of the absorption cell were transparent plates (optical flats) of quartz. Each solution used was placed in the absorption cell and exposed for fifteen seconds and a graph was made from the spectrograms for the absorption of the solution for varying lengths of the cell (10, 30, 60, and 100 mm.).

*Procedure.* For each determination an approximately .1 molar solution of the purified sodium sulfite was prepared. 150 cc of this solution were introduced into each of the quartz flasks. The flasks were placed equidistant from the cadmium spark and the time of starting the spark noted. At intervals of 20 to 30 min. 5 cc portions were withdrawn from the flasks by means of a pipette and run into an excess of a .03 N solution of sodium thiosulfate. The two flasks were first standardized against each other in the laboratory light.

The flow of air was varied very slightly until the rate of reaction in the two flasks was the same. It was possible to duplicate these runs, that is, keep the

rate of reaction in the two flasks equal but it was impossible to duplicate from day to day the total time required for a run. This would vary from four to five minutes in a three hour run, so flask No. 1 was used as a control. Spectrograms showed that a thick glass plate cut out all the ultra-violet light. The rate of reaction behind a thick glass plate was no faster than in total darkness, hence the difference in the rate of reaction in the flask in ultra-violet light and the rate of reaction in the flask shielded from the ultra-violet light was considered to be due to the ultra-violet light alone.

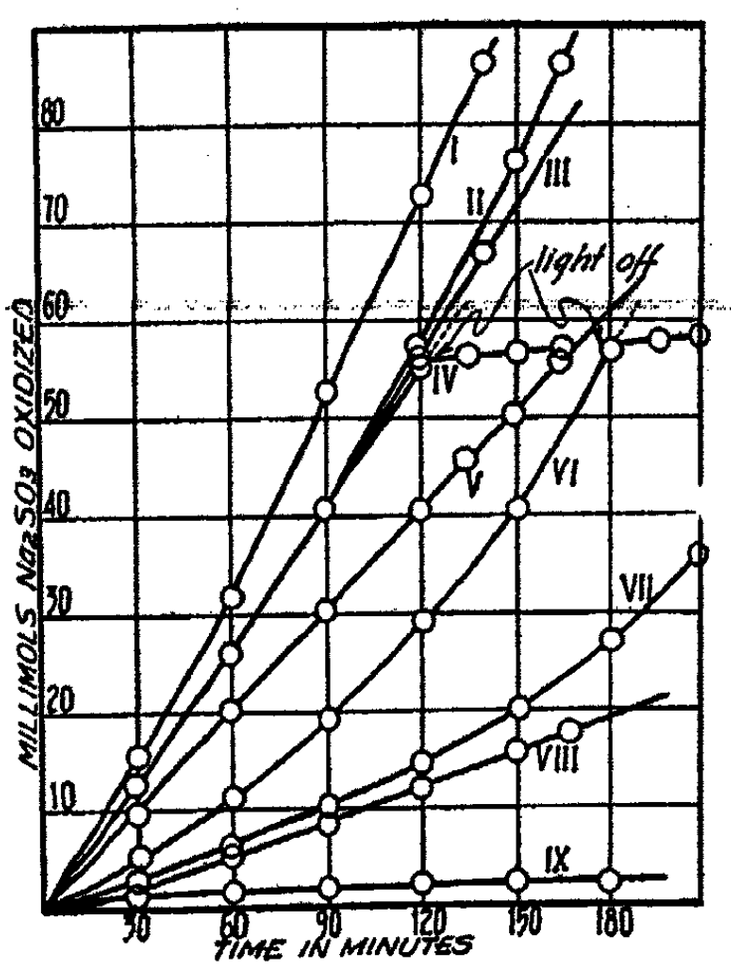



FIG. 2

I. Control
II. $CuSO_4$ in Light and Dark
III. Control in dark
IV. Rubber in light
V. Rubber in dark
VI. .001 Hydroquinone in light
VII. .002N Hydroquinone in light
VIII. Rubber catalyst made in U. V. light and used in the dark
IX. .001N and .002N Hydroquinone in dark

The rate of oxidation in the dark at 0°C is not much slower than the rate of oxidation at 30°C (1:1.32). This is due no doubt to the fact that oxygen is more soluble at 0° than at 30°.

Pure $CO_2$ bubbled through the solution stopped both the dark and light reactions. Increasing the rate of flow of air through the solution increased the rate of oxidation. The rate of oxidation in the light was more than doubled when the rate of flow was sixty liters per hour instead of thirty liters (See Fig. 1). Pure oxygen speeded up the rate of reaction.

In the preliminary experiments it was observed, after a run was nearly completed and the ultra-violet light turned off, that the rate of oxidation in

the flask previously exposed to the ultra-violet light was many times slower than the rate of oxidation in the other flask. This phenomenon indicated the building up of a strong negative catalyst by the light, which had little influence on the light reaction but a powerful influence on the dark reaction. After a long search, the rubber stoppers in the trap of the condenser were found to be the cause of this peculiar behavior. Water prepared in a still having no rubber stoppers did not show this phenonemon. A well-washed rubber stopper placed in conductivity water and boiled for a few minutes would dissolve enough to act as a catalyst. The break in the curve (Fig. 2) indicates the point where the light was turned off. If there was no rubber constituent in the solution

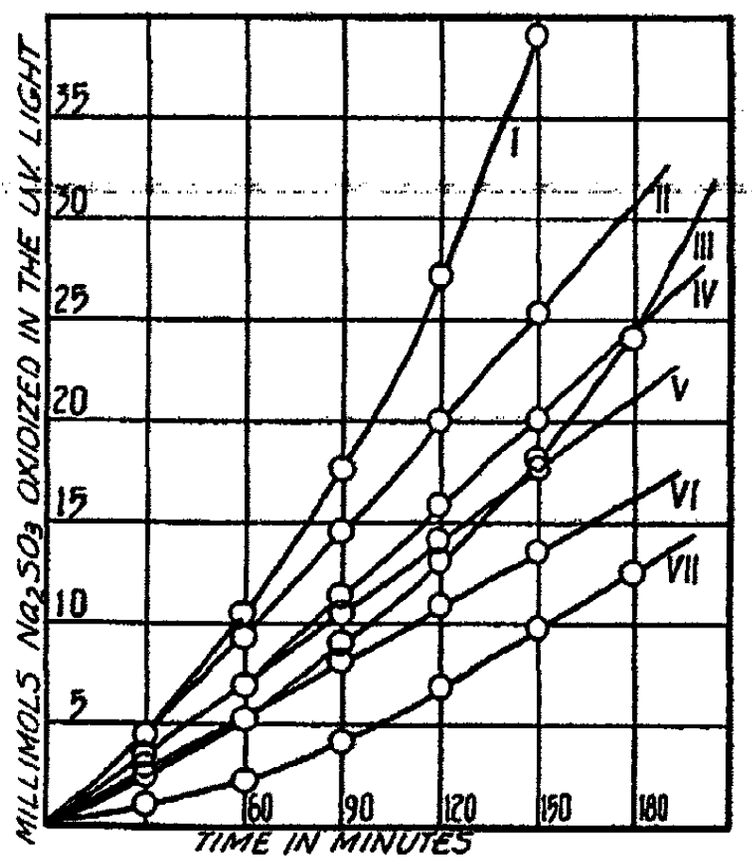



FIG. 3

I. .001 N Hydroquinone
II. .001 N Phenol
III. .002 N Hydroquinone
IV. Control
V. Rubber and pure gum
VI. Sugar
VII. .001 N Quinine Sulphate

the rate would have been the same as in the flask not exposed to the light. Pure gum rubber acted in the same manner as the rubber stopper, indicating that it was the rubber and not the substances used to vulcanize the rubber which caused this behavior. Water containing traces of rubber showed a banded absorption in the ultra-violet region, with a slight transmission around 2300 Å (Fig. 4).

The effects of different catalysts on the light reactions are shown graphically in Fig. 3. The number of millimols of sodium sulfite oxidized in the light alone are plotted against time in minutes. It will be noticed that .001 N hydroquinone and .001 N phenol acted as positive catalysts to the light re-

action. The .002 N hydroquinone did not act as a positive catalyst until the reaction was nearly one-third over. All the other substances tried acted as negative catalysts; copper sulfate stopped the light reaction entirely. Hydroquinone in either .001 N or .002 N solution almost entirely stopped the dark reaction, (See Fig. 2) while quinine sulfate and phenol were somewhat less effective. $CuSO_4$ had practically no effect on the dark reaction.

Titoff[1] found copper sulfate to be a powerful positive catalyst, but his solutions were.very dilute as compared with the .1 M sulfite solution used here. Milbauer and Pazourek[2] found that copper salts had little or no effect upon catalysts when the solutions were very pure and dilute.

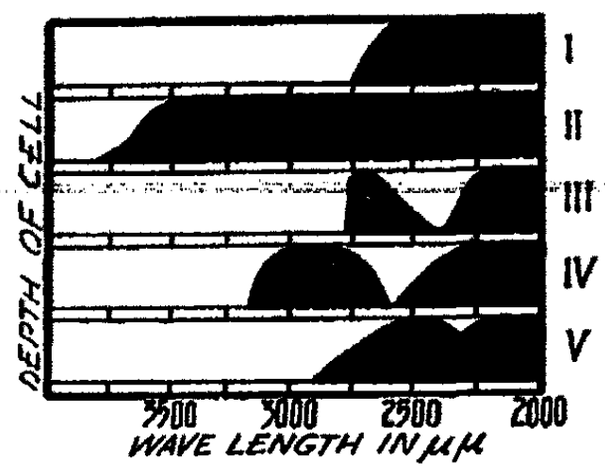



FIG. 4

I. Sodium sulfite
II. Quinine sulfate
III. Phenol
IV. Hydroquinone
V. Rubber

In Fig. 4 are shown the graphs made from the spectrograms. A thick glass plate cut out all the ultra-violet while the sodium sulfate, sugar and copper sulfate solutions showed only slight absorption in the extreme ultra-violet. Quinine sulfate absorbed some of the blue in the visible end of the spectrum as well as all the ultra-violet. Sodium sulfite solution and rubber showed strong absorption in the ultra-violet while phenol and hydroquinone showed a banded absorption with transmission at 2500 and 2600 Å respectively. The solutions containing hydroquinone and quinine sulfate were opalescent in the ultra-violet light and the one containing hydroquinone turned a permanent orange color before the reaction was over.

## Discussion

There does not appear to be any simple relation between the absorption of light by the catalyst and its effect upon the rate of the reaction. Copper sulfate absorbed only the extreme ultra-violet and acted as a negative catalyst to the light reaction and did not appreciably affect the rate of the dark reaction. Quinine sulfate absorbed all the ultra-violet light and acted as a negative catalyst both to the light and dark reactions.

[1] Z. physik. Chem., **45**, 641 (1903).

[2] Bull., 31, 676-8 (1922).

The fact that the light reaction increased with the rate of flow of air seems to indicate that the oxygen of the air was made much more active by the ultra-violet light and this active oxygen in the form of peroxide or ozone in turn oxidized the sulfite.

Hydroquinone acted as a powerful negative catalyst to the dark reaction. On the other hand, the rate of oxidation of the sulfite in the ultra-violet light was increased and the reaction was practically all photochemical.

Rubber acted as a weak negative catalyst to the light and dark reactions but became a strong negative catalyst to the dark reaction after exposure to ultra-violet light. The behavior of the hydroquinone may be explained by the formation of an intermediate complex with the sulfite, this intermediate compound being oxidized by ordinary oxygen. Under the influence of the ultra-violet light either the complex compound was broken down into the original constituents or the active oxygen produced by the light was active enough to oxidize the complex compound and change the sulfite to sulfate.

## Summary

1. The rate of oxidation of an aqueous sodium sulfite solution is highly dependent on the rate at which oxygen is bubbled through the solution. The shape and size of the bubble greatly influence the rate of oxidation.

2. Pure oxygen and ozone greatly increase the rate of reaction both in the dark and in the light. The rate of the light reaction is more than doubled when the flow of air is increased from 30 to 60 liters per hour.

3. Hydroquinone and phenol in .001 N solutions act as positive catalysts to the light reaction while sugar, quinine sulfate, rubber, and copper sulfate, act as negative catalysts to the light reaction.

4. Our experience with contamination due to some constituent of rubber re-emphasizes the necessity for the exercise of the utmost care in the exclusion of all possible contaminations in the study of photochemical effects.

5. There is no apparent relationship between the light absorption of the catalysts and their action upon the photochemical oxidation of sodium sulfite.

*Madison, Wis.*
*December, 1925.*

# NEW BOOKS

**A Comprehensive Treatise on Inorganic and Theoretical Chemistry.** *Vol. VI. By J. W. Mellor. 25 × 16 cm; pp. x+1024. London and New York: Longmans, Green and Co., 1925. Price: 63 shillings; $20.00.* We welcome the sixth of these remarkable volumes. This volume finishes the discussion of carbon, taking up the carbonates and carbon bisulphide. Well over eighty-five percent of the book is devoted to silicon. As was the case with the other volumes, this one is a treasure-house of interesting facts.

"Chamberlin estimated that 1,620,000,000 tons of carbon dioxide are withdrawn annually from the atmosphere in the formation of sedimentary rocks, p. 4. "It will be noticed that all animal and vegetable life is dependent upon the carbon dioxide⟶carbon reaction, which in turn is dependent upon the sun's energy. There is a kind of closed cycle, an alternation of oxidations and deoxidations:

Sun's energy stored——plants feed

deoxidation

C ⟵

$CO_2$ ⟶

oxidation

Energy dissipated——animals and plants breathe etc.,

maintained by a continuous supply of energy from the sun. If the supply should cease' the deoxidation of carbon dioxide would stop and the present conditions of life on the earth would come to an end because the available carbon would be transformed into unavailable carbon dioxide," p. 13.

The Poison Valley or the Valley of Death in Java is an old volcanic crater with fissures from which are evolved large quantities of carbon dioxide which fill the valley as water fills a lake. The flow is apparently intermittent because sometimes scarcely a trace of gas can be found, while at other times it fills the valley. The valley is about half a mile in circumference and is oval. The depth is from thirty to thirty-five feet. The bottom is quite flat, with no vegetation, and is covered with the skeletons of human beings, tigers, pigs, deer, peacocks, and all sorts of birds. "The Death Gulch of the Yellowstone Park is another such valley, where it is said that grizzly bears are sometimes found suffocated to death by the carbon dioxide which issues from the ground. The Laacher Sea is the water-filled crater of a prehistoric volcano, and near by is a depression filled with carbon dioxide. Birds and insects flying in this region are suffocated", p. 7.

"According to R. Brimmeyr, when carbon dioxide is separated from hydrogen by a moist bladder, more carbon dioxide diffuses to the specifically lighter gas then conversely; and with a dry porous partition, less carbon dioxide diffuses to the specifically lighter gas than conversely. Wiesner and Molisch also found that carbon dioxide diffuses through vegetable membranes more rapidly than hydrogen, oxygen, or nitrogen," p. 24. Carbon dioxide should diffuse more slowly through pores than hydrogen. When water is present and the diffusion is chiefly, or perhaps entirely, through the water, the solubility relations are the decisive ones.

The presence of air interferes with the liquefaction of carbon dioxide much more than can be accounted for by the pressure alone, p. 31. It seems a question in part of the air dissolving in the carbon dioxide and in part of the carbon dioxide dissolving in the air.

"Arrhenius tried to picture the effect of a change in the proportion of carbon dioxide in the atmosphere on the surface temperature of the earth. The temperature of the earth's surface was assumed to be in equilibrium with that of the atmosphere; if, by any increase in the amount of carbon dioxide, the atmosphere retained more heat than before, it would radiate more heat to the surface of the earth. The surface temperature would then rise until equilibrium between the two occurred. The rise was assumed to be governed by the

radiation law, and hence it was estimated that if the carbon dioxide is increased 2.5-3.0 times its present value, the temperature in the Arctic regions would rise 8°-9° and would produce a climate as mild as that of the Eocene Period; a decrease of 0.55 to 0.62 times its present value would cause a fall of 4°-5° and produce a glacial period. Frech and C. F. Tolman support Arrhenius' views. Kayser, Abbott, and Fowle hold that the carbon dioxide in the atmosphere cannot absorb more than sixteen percent of the terrestrial radiations; that variations in its amount are of small effect; and that the proportion of water vapor in the atmosphere is so large as to make the climatic significance [of carbon dioxide] negligible. The principal absorbent of terrestrial radiation is water vapor," p. 37.

In some cases stalagmites grow very rapidly. "The San Filippo spring (Tuscany) is said to deposit lime at the rate of twelve inches a month, and the spring has formed a bed of limestone rock 250 feet thick, 1.5 miles long and 0.33 miles wide. The building stone called travertine (Tiberstone) is probably a limestone deposited from a mineral spring," p. 81.

"Quartz which has been formed above 575° can be distinguished from quartz which has never reached that temperature. At ordinary temperature all quartz is α-quartz, but if at any time in its history a particular piece of quartz has passed the inversion point and has been heated above 575° it bears ever afterwards marks potentially present which on proper treatment can be made to appear just as an exposed photographic plate can be distinguished at once from an unexposed plate on immersion in a proper developer, although both plates may be identical in appearance before development. Wright and Larsen go further and say that quartz can be used as a geological thermometer, because if at any time quartz has been heated above 575°, this fact is recorded in its structure by the corrosion figures. Hence, also, quartz in any rock must have formed below 870°, and its peculiarities indicate whether it was crystallized above or below 575°," p. 247.

Pliny refers to a rare and costly cloth, the cremation cloth of kings. He thought that it was of vegetable origin, and gave an imaginary description of its growth in the deserts of India. Plutarch, in the first century of our era, said that asbestos was used in ancient times for making the wicks of the lamps used by the vestal virgins. In the thirteenth century, Marco Polo mentioned "an indestructible cloth made by the Tartars which was said to be made from the skin of the salamander, supposed to live in fire, but which was found to be woven from a fibrous mineral called amicanto. The knowledge of asbestos possessed by the ancients appears to have been forgotten. Apart from a few isolated cases, the industrial applications of asbestos did not attract serious attention until towards the middle of the nineteenth century," p. 425.

"Numerous observers have demonstrated the decomposition of felspar, mica, and related minerals by the action of water, and particularly water charged with carbon dioxide. Headden, for instance, said that water holding carbon dioxide in solution is nearly nine times as active as distilled water when in contact with felspar. Water can work its way into the body of granite rocks through pores and cleavage cracks; for, according to van Hise, granite rocks have a porosity of 0.2-0.5 percent. According to Bischof, one of the springs in the vicinity of Lake Leach (Germany) discharged nearly 176,000 lbs. of water carrying 0.13 percent of sodium carbonate in 24 hrs.; assuming that the sodium in felspar is converted into soluble sodium carbonate, this would represent the decomposition of nearly 18,000 lbs. of soda-felspar per annum. A few centuries would thus suffice to decompose enormous masses of granite rock. It does seem curious to find that a dilute solution of carbon dioxide has sufficient chemical strength to decompose a combination like felspar which is fairly resistant to the most powerful mineral acids; but H. Rose pointed out, in 1842, that the enormous quantities of carbonic acid which are brought into contact with the rock make up for its deficiency in chemical strength. According to L. von Struve and H. Müller, carbon dioxide under compression is more active than it is at ordinary pressures. A. Stahl considers that the clay deposits at Passau, Mederschlesien, and Odenwald have been formed from gneiss rocks by the action of the carbon dioxide. The china clay at Auvergne (France) is supposed to have been formed in this way; W. S. Bayley found that the china clay in the Piedmont Plateau, North Carolina, gradually merges downwards into felspar. The effect of carbonated waters can be easily overestimated, in contrast with the

action of organic acids which are probably more powerful than carbonic acid. Ginsberg, however, claims that the formation of china clay by the action of organic acids in natural waters has not been demonstrated. H. Stremme considers that the efficiency of all the different weathering agents is really due to the chemical activity of aqueous solutions of carbonic acid—cold or hot; and K. Endell has shown that the acidity of moor-waters is largely due to the carbonic acid they contain," p. 469.

"The remarkable effects of gum and other mucilages in enhancing the plasticity of clay has been utilized by potters for an indefinitely long time. In 1903 E. G. Acheson patented the use of aqueous solutions of the tannins and gallotannins, *e.g.* decoctions of oak-bark, etc.; and in 1918 G. Keppler, and A. Sprangenberg patented the use of decoctions of humic acid, peat, etc. *These plasticizing agents probably act indirectly by adsorption.* The clay particles adsorb the organic colloid, and, judging by results, this probably augments the surface attraction between the particles and the surrounding liquid. The plasticity of china clays, *practically free from organic matter*, shows that adsorbed organic colloids are not always the source of their plasticity. Clays which have been sodden with ground waters rich in organic matter are usually highly plastic; and those clays which can be shown geologically to have been deposited in swamps and bogs, or which have been in contact with such waters, are usually very plastic unless other metamorphic changes have occurred. Many such clays, however, are not plastic when freshly dug, but they become plastic during weathering. When first mined some of the clays are hard, but if they be moistened and exposed to sunshine and frost they disintegrate more or less quickly and crumble to fine-grained plastic clays. Clays which are allowed to stand for a long time in contact with moisture become more plastic, or, as the workmen express it, more "buttery." Clays which have been boiled with water also become more plastic. Clays prepared by fast processes—filter-press—are not so "buttery" as when prepared by a slower process—slip-kiln. China clays prepared by the elaborate, apparently primitive Cornish process—by slow sedimentation and slip-kiln—are more plastic than when the process of dewatering the clay is accelerated by filter-press. There is thus an intimate connection between the plasticity of a clay and its past history with respect to water. All this looks as if the clay in contact with water is being hydrated to form a colloidal gel," p. 490.

"The ancient writers attributed the discovery of the art of making glass to the Phoenicians, but excavations in Egyptian tombs have shown that the Egyptians must have been adept glass-makers long before the Phoenicians practiced the art. This indicates that the Phoenicians were probably distributors of Egyptian glass before their own factories were established at Sidon. In the work cited above, Pliny said that glass was made in Italy, and in the Gallic and Spanish provinces, by fusing sand with three times its weight of nitre; and he added that in India rock-crystal was used in place of sand. Bases other than the alkalies are needed to make the glass resist rapid attack by moisture. These might have been added deliberately, or brought in as impurities with the sand or alkalies," p. 520.

"Representations of these processes of glass-making are depicted on the walls of the tombs of Ben-Hassam near Thebus, 3000-1700 B.C. These tombs also contain vessels, etc., showing that the artisans were not only acquainted with the making and working of glass, but also with the coloring and cutting of glass in imitation of the precious stones. F. M. de Rozière also found samples of colored glass in early Egyptian tombs. W. M. F. Petrie collected at Tell-el-Amarna specimens illustrating all stages of the process of glass-making about 1400 B.C. F. Rathgen gave analyses of antique Babylonian glass. Theophrastus, about 300 B.C., mentioned the coloration of glass by copper; and in his *Clouds* Aristophanes referred to a glass lens used as a burning glass. From Cicero, it would appear that glass from Egypt was greatly prized by the Romans; so much so that when Augustus subdued Egypt, 29 B.C., a portion of the Egyptian tribute was ordered to be paid in glass. At the time of Tiberius, Egyptian workmen were imported to Rome, and Roman glass rivalling that from Egypt was soon obtained. Works were also established in Italy, France, and Spain at an early date. In the second century, H. Philo, in his *De legatione ad Caicum Caligulum*, alluded to the use of translucent stones as windows in the halls and chambers of the emperor's palace, and in the fourth century, L. C. Lactantius, in his *De opificio Dei*,

mentioned the use of glass itself for windows. It is therefore probable that about the third century glass was employed in the construction of windows; but, according to L. Dutens, the excavations of Pompeii, near Naples, show that at that time *les salles de bain étaient garnies de fenêtres en verre aussi belles que les nôtres*. After the fall of the Roman Empire the manufacture of glass was taken up in Byzantium, where it flourished for about five centuries. The fall of the Eastern Empire was attended by the migration of the glass-makers to other parts of Europe. Many were attracted to the Venetian Republic, and the Venetian glass became famous throughout the civilized world.

"In the early Middle Ages, glass-making was taken up in Germany; and in his *De re metallica* (Basiliae, 1546), G. Agricola gave a drawing of a glass furnace; and shortly afterwards H. Mathesius, in his *Sarepta* (Nürnberg, 1562), described the practice employed in Venice, Germany, and Bohemia. A. Neri published a number of recipes in 1612, and some years afterwards this work was elaborated by J. Kunckel.

"The factories in different localities acquired fame for some peculiarity in manufacture; the Bohemian manufacturers, for example, excelled in the production of colorless glass rivalling that from Venice. The manufacture of glass in Bohemia suffered a relapse owing to the heavy import duties levied against it, and the inducements held out to Bohemian workmen by foreign countries. Both the Venetian and Bohemian glass industries were revived in more recent years. The manufacture of the better types of glass in France commenced in the eighteenth century in factories erected at Paris and at St. Gobain. The latter is now famous for the manufacture of plate-glass. According to H. J. Powell, it is possible that during the Roman occupation a few beads, small cups, and bottles were made in England; but the resemblance of the scattered vessels and fragments of vessels to those found elsewhere makes it probable that there were only a few centres of glass manufacture in the Roman empire, and that the vessels were distributed from these to various parts. Glass was manufactured in England in the thirteenth century, for the industry was in existence at Chiddingfold, Surrey, in 1226. The south-eastern counties—Surrey and Sussex in particular—were favorite spots for the native glass-makers from the thirteenth to the sixteenth centuries. Glass was manufactured in Russia in the seventeenth century; and, in the United States, near the beginning of the nineteenth century.

"Theophilus, in the latter half of the eleventh century, related that, in Italy, flint glass was used for imitating gem-stones, and added that the Jews were engaged in the manufacture of these imitations. Towards the end of the eighteenth century, J. Strasser, of Vienna, was famous for his skill in this work. He made a flint glass very rich in lead, and of high refractive power and sp.gr., which was called *strass*, and which was tinted with the necessary coloring oxides— e.g. 0.8 percent of chromic oxide to imitate the emerald; a mixture with 0.8 percent of manganese oxide, 0.5 cobalt oxide, and 0.2 gold purple, to imitate the amethyst," p. 520.

"The early observers included mica in the same class as gypsum, which can also be split into thin flakes. It was afterwards noticed that, unlike talc and gypsum, the cleavage plates of mica are highly elastic, and not pliable. Pliny, in his *Historia naturalis* has a description of a mineral, *lapis specularis*, which applies very well to mica. The scales of this mineral were strewn over the *circus maximus* at the celebration of games with the object of producing a sparkling whiteness. This shows that a mica schist furnished the material employed; and Pliny's hammochrysos was probably a sand containing golden-colored scales of a biotitic mica. The Hindus appear to have used mica for decoration and other purposes, and they considered it to be endowed with extraordinary properties. Mica has also been found in the graves of prehistoric American races, east of the Mississippi, in localities where the mineral does not occur.

"The term *mica* is not likely to have been derived from the Latin *mica*, a crumb, or grain, but rather from the Latin *micare*, signifying, like the German *Glimmer*, to shine. In mediaeval times, scaly mica was called cat-silver, or cat-gold—Katzengold, or Katzensilber; *or des chats*, or *argent des chats*.Thus G. Agricola spoke of *Ammochrysos*, *Mica*, *Glimmer* or *Katzensilber*. A. B. de Boodt and J. G. Wallerius described several varieties. A. G. Werner, and A. Estner definitely adopted the term *Glimmer*, and described many

varieties. No great progress could be made in the classification of the micas until they had been distinguished from one another by chemical analysis, and optical measurements," p.604.

"Muscovite is a pyrogenetic mineral which occurs as a primary constituent in deep-seated igneous rocks rich in alumina and potash, and poor in iron and magnesia. It is common in granites, syenites, and pegmatites. From its water-content muscovite was probably formed in these rocks under pressure. It does not occur as a primary constituent in recent lavas and their glassy magmas. Muscovite is common as an alteration product of many minerals—andalusite, cyanite, topaz, felspar, nephelite, spodumene, scapolite, etc. As a secondary mineral it is often called sericite. Paragonite is one of the rarer varieties; it occurs in crystalline schists, but does not occur as a pyrogenetic mineral. Lepidolite occurs in granite and pegmatite where it may form violet or lilac-colored crystals associated with muscovite. It sometimes occurs as a secondary product after muscovite, when it occurs as margins on the plates of muscovite. Cryophillite similarly occurs on plates of leipdolite," p. 609.

"The most important use of mica is in the electrical industry as an insulator. It is one of the best insulators because of its resistance to puncture, pro-resisting qualities, impermeability to moisture, toughness, elasticity, and flexibility; and its cleavage into thin sheets. It is largely used for insulating the segments of commutators, armature wires and bars, *etc.* Scrap mica is made into sheets, plates, and boards by means of a suitable bonding agent—say, shellac—and under the commercial name *micanite*, is used for making washers, etc., for insulating lamp-sockets, fuse-blocks, cut-out boxes, *etc.* Sheet mica is used for lanterns and windows where glass does not withstand the shocks and vibrations. It is also used in place of glass where abrupt changes of temprature would be liable to crack glass—*e.g.* fire-screens, stove windows, lamp-chimneys, and some miners' lamps. Special sparking plugs for aeroplanes, etc., are built up from sheet mica. It is employed as a heat insulator in the lagging of steam-pipes, boilers, etc. It is used as a sounding-diaphragm in telephones, gramophones, etc. It is used as an absorbent for nitroglycerol and as a heavy lubricant. Mica is used in making wall-paper pigments; and various ornamental purposes—a mixture of gum arabic and ground white mica makes the so-called *silver ink;* and it is employed for inlaying buttons, in making lustrous hair-powder, and in making the bronze-like colors which bear the name *brocades, crystal colors, mica-bronzes*, etc., and in making frosted effects in decoration," p. 620.

"The water in zeolites possesses the property of mobility to a high degree whilst the silicate space-lattice must be considered as relatively rigid. The water molecules entering into the mesh cavities of this lattice will tend, according to their thermal pressure, to become uniformly distributed; on the other hand, the silicate molecules (or portions thereof) in the crystal lattice will tend to hold by attraction the water molecules, or a portion thereof, in position in entire conformity with the symmetry of the latice. Both tendencies can be simultaneously satisfied only if the number of water molecules is a complete multiple of the number of silicate molecules, for only under these conditions can the water molcules arrange themselves in identical formation round each of the other molecules of the silicate lattice. It is only exceptionally favorable mixtures such as these that give the straight line in the dehydration curve. All other mixtures correspond to points on the irregular curves. The zeolites are therefore considered to be solid solutions, but it is an open question whether the water in this solution reacts with the solvent, *i.e.* forms an intimate compound with the silicate, or whether it enters the lattice as a molecule dissociated into its atoms, or into ions.

*Wilder D. Bancroft*

**Wire-Drawing and the Cold-Working of Steel.** *By A. T. Adam. 26 × 19 cm; pp. 212. London: H. F. and G. Witherby. Price: 40 shillings.* We learn from Mr. Adam's preface to this book that since the publication in 1891 of Mr. Bucknall Smith's book on Wire, no text-book dealing exclusively with Wire and allied products of cold-working processes has appeared. The present author, who is in charge of Messrs. Brunton's research laboratory, has in the present book, written not an exhaustive treatise on the subject, but an account which aims at explaining the real nature of Wire and other cold-work products. It describes their

physical properties and it shows how these depend on the treatment the material has received. The book is intended for Metallurgists and Engineers and those who are interested in the product itself, rather than in the process of manufacture. Accordingly machinery and plant are only dealt with briefly, while such matters as quality and the preliminary treatment of the material, the extent of reduction by cold-work and the relation of these matters to the properties of the finished product, have been discussed more fully.

The book opens with an introductory chapter followed by two chapters on wire-drawing, including the cold-working operation. Then follow chapters on cold-rolling and other cold-working processes, heat treatment, and two chapters on the effect of cold-work on the physical properties of metals. The important subject of the effect of heat treatment after cold-work is then dealt with, and this is followed by a discussion of the theories of plastic flow in cold-worked metals. The last two chapters are concerned with the pathological aspect of cold-working operations and the application of cold-work to non-ferrous metals and alloy steels.

We think that Mr. Adam's book will be found very acceptable. It is well printed and illustrated: the photographs and drawings are excellent, and the whole treatment of the subject is scientific. The author has made a careful study of modern metallographic research bearing on wire-drawing operations, and his treatment shows that he has understood the vital bearing of certain researches in particular, which are probably destined to have an important influence on the progress of wire manufacture. To mention only one of these, now that the majority of the common metals can be obtained in the form of single crystals, which are characterized, for the most part, by remarkable ductility and malleability, it is clear that the wire-drawing of single crystals may ere long be destined to become a commercial operation. Actually, this is already so in the case of the metal tungsten. We cannot help regretting the high price at which the book is published, for we fear that it will severely limit its circulation and accessibility. *H. C. H. Carpenter*

**Der molekulare Brechungskoeffizient in der Reihe der Polymethylenverbindungen.** *By Fritz Eisenlohr. 25 × 14 cm; p. 48. Berlin: Borntraeger, 1925. Price: 4.20 marks.* Although the determination of the molecular refraction $[R^L]_D$, of liquid organic compounds has been of the greatest service to the organic chemist as an adjunct in the determination of structure, the application of the method for the latter purpose is limited. A number of constitutive factors do not find definite expression in the value for $[R_L]_D$ and it is only the presence of conjugated or semicyclic double linkings and three- and four-membered rings which produce exaltations from which inferences regarding structure can be made. The underlying cause of this is the fact that the refractive index and the density vary together so that the differences between related compounds are obscured.

The expression $N_D^{20} \times M$, in which the density is not taken into account, does not possess this disadvantage (Eisenlohr and Wöhlisch: Ber. **53**, 1746 (1920); it is claimed that the agreement between the observed values of this "molecular coefficient of refraction" and the calculated values is of the same order as for the value $[R_L]_D$ and a series of additive constants has been calculated..

Constitutive influences are, however, very pronounced giving "exaltations" (E) which are sometimes positive and sometimes negative. Thus, the branching of a carbon chain has a positive effect of 0.45 unit; the introduction of an ethyl group in the place of a hydrogen produces a different effect from that of a methyl group, etc.

Ring formation causes an appreciable negative exaltation, different for every type of ring and decreasing regularly from cyclopropane to cyclooctane. The effect of substitution in the benzene ring is different according to the position of the entering group, an ortho substituent giving the highest, para- the lowest exaltation. In alicyclic ring compounds a further factor has to be taken into consideration, namely cis-trans isomerism about the plane of the ring, doubtless owing to its effect on the "packing" of the molecules. The greater part of the work under review is devoted to the discussion of observations on hydrocarbons, alcohols, and ketones of the cyclohexane series.

The new method is doubtless a step forward towards the correlation of the physical properties of organic compounds with their structure. The choice of temperature (20°) and wavelength (D) appear to be arbitrary although it may be mentioned that dispersion is taken into account in the experimental portion of the work. In any case, the special value of the method would appear to lie in enabling conclusions to be drawn as to the structure of isomeric or otherwise closely related compounds, when discrepancies due to the calculated constants are eliminated. It is hoped that the systematic study of organic compounds from the point of view of their molecular refractive index will be materially extended in the near future and that Professor Eisenlohr's paper is but a forerunner of a more comprehensive work.

*G. A. R. Kon*

**Die gasanalytische Methodik des dynamischen Stoffwechsels.** *By Wilhelm Klein and Maria Steuber. 25 × 18 cm. Leipzig: G. Thieme. Price: 5.40 marks.* This small monograph of 100 pages deals with the various forms of apparatus used in determining the gaseous exchanges consequent upon physiological experiments, or upon pathological conditions met with in clinical practice.

The various methods used in physiological experiments for the measurement of oxygen uptake and carbon dioxide output are described with much practical detail, and the text is well illustrated with drawings of apparatus. Specimen calculations are appended as an aid to those unfamiliar with the technique. Amongst the methods described may be mentioned those of Pattendorf-Tigerstadt and Zuntz-Geppert.

The section devoted to apparatus for clinical use is much shorter, describing only the Benedikt and Krogh methods.

The gas analysis apparatus which is essential to experiments on gaseous exchange is described at length with working details.

Many useful hints are given on such practical points as the cleaning of mercury and the sampling and storage of gases, and a number of tables for the simplification of calculation are appended.

The order in which the matter is presented is good, but the division into sections is far from satisfactory. Such sections as "The Solubility of Gases in Liquids" and "The Sampling and Storage of Gases" are given equal importance with "Methods of Gaseous Exchange," which occupies over 70% of the total book, with the result that quite important subjects are almost lost under small sub-headings. A further improvement which may be suggested is that the references should be collected together and printed as an appendix, instead of being scattered throughout the book as foot-notes.

In conclusion it may be said that the book is written in easy straight-forward German, so that it may be used as a book for laboratory reference by those who do not read German fluently.

*W. K. Slater*

**Molekulargrössen von Elektrolyten in nichtwässerigen Lösungsmitteln.** *By Paul Walden. 23 × 15 cm; pp. xi+350. Dresden and Leipzig: Theodor Steinkopff, 1923. Price: paper $2.25, cloth $2.58.* The subject is presented under five headings: general remarks on molecules and polymerization; recognition and determination of molecular weights or of degree of polymerization of homogeneous liquids; molecular weights or degree of polymerization of dissolved substances; the molecular weights of dissolved electrolytes by the osmotic methods; general results of molecular weight determinations of salts, acids, and bases in non-aqueous solutions.

On p. 18 Walden quotes from Arrhenius. "If a star consisted of hydrogen alone and, like our sun, lost two gram calories per gram of its mass every year, it could keep that up for eighty-seven billion years in case the heat radiated were compensated by the condensation of hydrogen into heavy atoms."

Walden considers, p. 41, that the change of color of cupric bromide solutions from blue to dark-brown with increasing concentration is due to the increasing formation of polymerized cupric bromide $(CuBr_2)_x$. It is difficult to see how this is consistent with the as-

sumption of hundred percent dissociation; but of course Walden does not believe in hundred percent dissociation.

Ramsay's surface tension experiments make the degree of polymerization of water at 100° about 1.5 while Walden calculates it as nearly 2.0, p. 56. On either assumption there is a considerable degree of association and this must have its effect on boiling-point determinations. One would rather like to see a series run at about 200° which would only mean fifteen atmospheres or so. On p. 71, Walden quotes Küster to the effect that solid naphthalene and solid naphthol are both bimolecular.

Walden considers molecular weight determinations of 25000 for starch and 5000 for ferric oxide as not unreasonable, p. 84. He quotes results of 4500 for tetra-ethyl ammonium nitrate in chloroform, p. 198, and says that this substance is in true solution; but there must be some error about this.

"The constitutive factor of the electrolyte, which often does not show at all in aqueous solution, becomes of great importance for the strong binary salts in non-aqueous solutions. The non-aqueous solutions furnish the proof that the acids are electrolytes of a different type from the salts because the acids, like hydrochloric acid, trichloracetic acid, and tribromacetic acid, which are as highly dissociated in water as the binary salts, are practically not dissociated at all in solvents in which the salts are ninety percent dissociated," p. 311.

The associating power of a solvent varies inversely as the dielectric constant, the dissolved salts being polymerized more strongly, the lower the dielectric constant is. Conversely, the dissociating power of the solvent is greater, the higher its dielectric constant," p. 312.

"Through variation of the solvent the same salt of the type of a binary iodide, MI, can be obtained in all stages of polymerization or dissociation at the same concentration and temperature. At the same temperature and concentration we can therefore obtain a given salt in the form of highly polymerized molecules with an apparent molecular weight of infinity, or in the form of a molecule dissociated almost completely into free ions. We get this extraordinary plasticity of the apparently so firmly knitted salt molecule not by making use of special energy factors, but simply by dissolving it once in a so-called indifferent solvent, and the next time in a strongly ionizing solvent. From both solvents we recover the unchanged salt on crystallization," p. 312.

The author prides himself on the treatment being non-critical; but one cannot share this enthusiasm.

*Wilder D. Bancroft*

**Crystals and the Fine-Structure of Matter.** *By Friedrich Rinne. Translated by Walter S. Stiles. 23 × 15 cm; pp. ix+195. New York: E. P. Dutton and Company. Price: $4.20.*

"Crystals are proving themselves more and more the ideal substances of physics and chemistry. Even before the last great discoveries in this branch of knowledge the late Woldemar Voigt, Professor of Theoretical Physics at Göttingen, who had a unique knowledge of this subject, drew attention to the exceptional regularity of the crystalline parts of matter in a fine simile, which is quoted below:

"Imagine a couple of hundred picked violin players in a large room, all playing the same piece of music on faultless instruments, but beginning simultaneously at widely different places, and starting afresh each time they reach the end. The finest ear would be unable to recognise the piece actually played in this uniform medley of sound. Now such music is presented to us by the molecules of gaseous, liquid, and ordinary solid bodies. A crystal, on the other hand, corresponds to the orchestra described above when it is guided as a whole by one able conductor, so that all eyes hang on his slightest gesture, and all hands play the same bar. In this way the melody and rhythm of the piece presented became completely effective, the number of the performers not hindering but intensifying the result."

"This picture makes it clear how crystals can present a large series of phenomena which are absent in other bodies, and that, in them, certain characteristics are developed in wonderful variety and elegance, which elsewhere occur only as monotonous mean values," p. 2.

"I introduce the expression fine-structure-study, or leptology, because the customary term stereochemistry does not cover completely the field of the inquiry intended. In stereochemistry we study the form and arrangement of the particles comprising various substances in order to explain thereby their chemical properties. Alongside this science, another has arisen, which may justly be termed stereophysics, and this also is concerned with the constitution and association of the particles of matter, dealing especially with their movements and physical properties (e. g. crystal optics). Finally, a third allied subject is included, namely, crystal structure, or the study of the fine-structure of crystalline bodies from the point of view of their geometrical relations.

"Thus from the trunk of Greek Atomic Theory, which is more than two thousand years old, three branches of knowledge have sprung forth and blossomed—stereochemistry, stereophysics, and crystal structure. Their intimate relations to one another justify a name to include them all. If now the particles of matter, the electrons, atoms, ions, and molecules which constitute gases, liquids, and crystals are termed collectively fine-structure-particles or leptons (from λεπτος, fine, delicate), the name suggested above, fine-structure-study or leptology indicates precisely the end in view," p. 5.

"Substances built up of flakes, which lie with all their fibre axes or flake normals parallel, but otherwise indifferently, give on the passage of X-rays perpendicular to this direction and X-ray effect similar to that of a crystal plate which is rotated about an axis passing through it. The series of reflexions, one after the other, produced by the latter, as a result of the rotation, are shown by the pack of fibres or flakes simultaneously. All fibres or flakes, the structure planes of which satisfy the equation $n\lambda = 2\pi \sin a$ give rise to reflected rays. As was shown by H. Seeman and E. Schiebold, in particular for rotating plates, and M. Polanyi for fibrous substances and stretched metals, we get in this way characteristic diagrams," p. 17. On this statement of facts, X-ray photographs apparently do not show whether a fibrous or flaky substance is or is not crystalline.

"The idea of deriving the multiplicity of crystallographic forms from five types all mutually connected, which may be called primitive forms, has already been brought forward by G. v. Tschermak, and followed in his teaching," p. 28. The five primitive forms are called: pedion, pinacoid, sphenoid, doma, prisma.

"The chief difference in the construction of crystalline bodies and the individuals of amorphous substances lies in the restriction of the rhythm. In the fine-structure of crystals, owing to the fact that each structural unit is joined to its neighbours, this rhythm exhibits a three-dimensional periodicity. Such space-lattice structure is clearly only possible when the repetition is according to the numbers 2, 3, 4, and 6, or with no repetition at all. Pentad, septad, and compound axes of higher period are here theoretically excluded, nor are they found in practice," p. 49.

"The change of physical properties with direction is very obvious in crystals showing cleavage. Thus for rock-salt there are three directions, perpendicular to the cube surfaces, in which the cohesion of the crystal is a minimum. The resistance to splitting in these directions is only one-third of that in the direction of the cube diagonal. The cleavage planes are, therefore, regularly oriented surfaces of maximum brittleness. In like manner, many crystals show particular planes of maximum plasticity. These are surfaces in which internal displacements may easily occur; with ice they arise as planes parallel to the surface of the ice floe. Hardness is also a directional property in crystalline materials. The resistance to disrupture, which shows itself as hardness, is often different in different directions of the crystal; thus it is a familiar fact to diamond workers that the cube surfaces of the gem are more difficult to prepare by polishing than the octahedron surfaces. Garnet, too, is harder on the cube surfaces than on the octahedron and rhombic dodecahedron, according to the researches of P. J. Holmquist on polishing. Even on the same surface of a crystal the hardness, as measured by scratching, varies with the orientation of the scratch made by the test needle. Cyanite is a classical example of this," p. 55.

"The great disperseness of gases is enormously diminished on crystallisation; in liquids, too, in general, the same thing occurs. In this connection some figures for sodium and the diamond, as two extreme types, will be of interest to the reader.

| Number of atoms sodium per c.c. | | Ratio |
|---|---|---|
| 1. | Gas at boiling-point (820°C) | $5.5\times10^{18}$ } 3550 |
| 2. | Liquid at boiling-point | $19,500\times10^{18}$ } |
| 3. | Liquid at solidifying-point, 97.6°C. | $24,500\times10^{18}$ } 1.03 |
| 4. | Crystal at solidifying-point | $25,000\times10^{18}$ } |

"In solid sodium, with its body-centred space-lattice (only two atoms in the elementary cell) and its large $a$-value for the cube edge ($4.3\times10^{-8}$ cm.), we are dealing with a soft metal. The condensation from gas to fluid is considerable; that for fluid to crystal, small.

With the hard, compact diamond (eight atoms in the elementary cell, $a=3.53\times10^{-8}$ cm.), a much more extensive condensation occurs on crystallisation; 1 c.c. of this gem contains 180,000 trillion carbon atoms, compared with 1.3 trillion in carbon vapour at 5500°C. Naturally, with such close packing of the particles of matter, the cohesion between them becomes enormous," p. 66.

"Considering the results already obtained in crystal leptology with a view to a physical chemical interpretation, the desired organisation into radicals is, in fact, often definitely shown in the architecture. The Braggs, as originators of fine-structural schemes, have pointed out the dumbbell-like connection of the two sulphur atoms in iron pyrites, and, in somewhat greater detail, P. Niggli has expressed the opinion that the representation of the complete crystal as a purely atomistic space-lattice complex certainly may always be carried out formally, but that many inter-connections between certain atoms forming structural groups (as P. Niggli called them) stand out clearly on a merely architectural consideration of the schemes. These structural groups I have designated geometrical radicals or leptyles in adaptation to chemical ideas. Finally, groups of a molecular nature are occasionally unmistakable in the crystal arrangement. Such leptyles occur in iron pyrites with its doublet $S_2$, in calcspar with the ion $CO_3$, and in rutile and anatase with the molecular $TiO_2$ complex. A fine example of leptyle grouping has been investigated by Dickinson (1922). Moreover, for organic substances with ring formation, such a fine-structural grouping must be assumed according to P. v. Groth, who formerly brought into prominence the atomistic crystal structure. As regards cyclic chains of atoms so fundamental chemically, which can with certainty be attributed to the molecules of benzene, naphthalene, and other organic substances, it is more than probable that these chains persists in crystallisation. Crystallised organic compounds will often be molecular aggregates loosely knit into space-lattices. This conception W. H. Bragg has taken as fundamental in his present researches on organic compounds," p. 90.

"The undermining of crystals may, however, take place to an extent much greater than is represented by the removal of a relatively small part of the constituents which water usually represents. The calcium aluminium hydrosilicate $CaOAl_2O_3 6SiO_2$ ca.5.5 aq. of heulandite, for example, may be reduced fine-structurally to $SiO_2$. The entire filling of basic constituents is then removed, the result being just as though the skeleton of some siliceous plant had been prepared by burning the organic wrapping. The relict of the zeolite so obtained still shows (especially after glowing, probably under the influence of collective crystallisation) definite optical agreement with the original substance, the hard *rigid pseudomorph of which it represents. If, starting from desmine zeolite,* all the basic constituents are simultaneously withdrawn with hydrochloric acid, a $SiO_2$ optically analogous to the original desmine is obtained. Thus the same chemical substance $SiO_2$ appears here to have a varying structure depending on its previous history; in the one case it is a heulandite, in the other a desmine residue," p. 151.

"The space-lattice constitution of the crystal must serve as the fundamental conception in this work. In its particular fine-structural symmetry and special tectonic nature are characterised the physico-chemical connections of the particles. As a result of this, for every particular case we find at once certain indications as to the mechanics of the chemical processes in the bodies concerned, and a basis for generalisation is obtained. Since, for example, $CaCO_3$ of calc-spar, which is constructed from $Ca^{"}$ and $CO_3$ ions in a ternary

rhythm, undergoes, on heating, the well-known reaction of splitting into CaO and $CO_2$, it must be assumed for the fine mechanics of this process that, on account of the increased heat motions, first the geometrico-chemical radical $CO_3$, as a ring of three O's about a centre carbon, becomes loosened in the fine-structure. With increasing temperature these radicals, together with the calcium atoms, which are free moving groups in the material field, undergo a separation into $CO_2$ and O, which links up with Ca to form CaO.

"According to this, the loosening of the particles in the fine-structure is always to be regarded from the standpoint of symmetry action. Those particles of the structure, coupled together by rhythm or reflexion, participate simultaneously in the process, and since such coupling thus occurs throughout the entire crystal many million times, the process appears to us in analytical chemistry as a disontinuous change, possibly in a series of steps, if the new arrangement contains the departing component again in definite symmetry disposition, as is the case, for example, in the ignition of gypsum to the subhydrate. A practically steady variation can have its origin in complicated re-groupings of the point system, closely following on one another," p. 158.

*Wilder D. Bancroft*

**A Text-book of Organic Chemistry.** *By E. de Barry Barnett. 21 × 14 cm; pp. xii+380. Philadelphia: P. Blakiston's Son and Co., 1920. Price: $5.00.* In this general survey of the most important classes of organic compounds, the author has attempted to emphasize group reactions rather than the reactions of individual compounds, so that the number of individual substances mentioned is smaller than is generally the case. However, the group reactions are illustrated by means of specific cases in the usual way.

Although descriptions of analytical methods must necessarily be meager in a book of this type, mention might have been made of the use of the Parr bomb in determining halogens and sulfur in organic compounds, since it is extensively used.

Whether or not the arrangement of the material is the best possible one is probably a matter of personal opinion. All of the general theories (Isomerism, Stereoisomerism, etc.) are presented in the Introduction, "as they are more easily referred to when necessary". The compounds are classified in the usual way and all of the members of one class are considered together, rather than dealing with the simpler members of the various classes first and then treating the more complex substances later.

The material covered is quite up-to-date, although some things have been omitted that might well have been included. For instance:—The preparation of acetic aldehyde from acetylene and the conversion of the aldehyde into acetic acid and alcohol are discussed. No mention is made of the fact that the acetic acid thus obtained is converted into acetone by passing its vapors over hydrated lime at 485°. Bakelite is not mentioned.

Unusual features of the book for an elementary treatise are (1) a brief discussion of the available literature, (2) a list of the more important books dealing with the subject matter is placed at the end of each chapter and (3) the objections to the Kekulé formula for benzene are considered.

With regard to the index, the convenient feature of printing the main references in heavy type is not followed.

*Ralph T. K. Cornwell*

**A Systematic Handbook of Volumetric Analysis.** *By Francis Sutton. Eleventh edition. Revised by W. Lincoln Sutton and Alfred E. Johnson. 22 × 16 cm; pp. xii+629. Philadelphia: P. Blakiston's Son and Company, 1924. Price: $9.00.* The authors have endeavored in this edition to cover the volumetric methods for the analysis of ores, ferrous and non-ferrous materials, water and sewage, organic substances, urine and gas and "to describe all the operations and chemical reactions as simply as possible." Therefore, it is not surprising in a text covering so much material that some errors of omission are made, such as electrometric and conductivity titrations, benzoic acid as an alkalimetric standard, some of the better methods for aniline and phenol and most of the American advances in gas analysis apparatus.

It is surprising, however, to find in the 11th edition of a book the use of "floats" instead of the complete circling of burettes by graduation marks at major points as advocated by the U. S. Bureau of Standards and the statement that after a burette is rinsed with a solution, it "is nearly filled with the solution and a considerable amount of the liquid allowed to flow back into the bottle from which it is being filled." A few careless errors have been made such as "$2Na_2C_2O_4$ yield $O_2$" and the placing of a soda-lime guard tube for alkaline solutions in a vertical position.

However, this work contains a great variety of volumetric methods for all of the determinations covered and numerous references to the literature. For this reason it will undoubtedly be of value to analytical chemists as a very handy reference book. The reviewer feels, however, that the value of the book would be greatly enhanced if the authors had indicated which method they considered the best for each individual determination.

*M. L. Nichols*

**Quantitative Analysis.** *By Stephen Popoff. 20 × 14 cm; pp. xiii+342. Philadelphia: P. Blakiston's Son and Co., 1924. Price: $2.25.* The author states that his objects in writing his book are threefold: First, to incorporate in a single book, theory, laboratory instructions, problems and their explanation; second, to emphasize the law of mass action and the theory of equilibrium as applied to quantitative analysis and third, to incorporate some of the more recent advances in this field. In satisfying the first purpose, there is nothing to warrant an extra need of praise. A normal solution is defined as one which contains 1 g. of hydrogen equivalent per liter of solution.

In accomplishing his second purpose, much material is included which is generally found in texts for qualitative analysis and there are certain principles of physical chemistry not usually to be found in quantitative analysis texts, e.g., van der Waals' equation and for which the author feels it necessary to present an "excuse". In the section dealing with special topics, we find electro-analysis, food analysis, iron and steel analysis, and electrometric titrations. For laboratory practice in the first three topics, the author issues supplementary mimeographed instructions. The chapter on electrometric titration is the redeeming feature of this section.

*M. L. Nichols*

**The Properties of Matter.** *By Basil C. McEwen. 20 × 14 cm; pp. vii+316. New York and London: Longmans, Green and Co., 1923. Price: $3.20.* "The order followed is the reverse of that adopted in most Text-books dealing with the Properties of Matter.

"Commencing with the First Law of Thermodynamics, an extension is made to the more general Principle of the Conservation of Energy, and hence to the metaphysical conception of the Identity of Energy throughout its various transformations.

"Since our knowledge of mechanical systems is, in general, more complete than that relating to other modes of energy, a logical sequence leads to the study of the Kinetic Theory of Matter, the consequences of which can be most fully developed when applied to matter in the gaseous state.

"The Properties of Gases are, therefore, next investigated from the standpoint of the Kinetic Theory, and the continuity of the gaseous and liquid states supplies the natural transition to a detailed study of liquids. The Properties of Solids are dealt with last.

"It is thought that this method of treatment is simpler, and follows a more natural sequence than is attained by commencing with a study of the Properties of Matter in the solid state—and proceeding, in the reverse order, to a consideration of Liquids and Gases," p. 5.

The chapters are entitled: the first law of thermodynamics, the kinetic theory of matter and its application to the gaseous state; isothermal and adiabatic transformations and the specific heats of gases; the elasticity of gases, and the continuity of the liquid and gaseous states; the thermal expansion, diffusion, and solubility of gases; equations of state; liquids, capillarity; solids; gravity. There are also three appendices; the Joule-Thomson effect; the theorem of LeChatelier; units and dimensions.

*Wilder D. Bancroft*

# INDIVIDUAL THERMODYNAMIC BEHAVIORS OF IONS IN CONCENTRATED SOLUTIONS INCLUDING A DISCUSSION OF THE THERMODYNAMIC METHOD OF COMPUTING LIQUID JUNCTION POTENTIALS*

BY HERBERT S. HARNED

As a result of earlier experimental investigations[1], some tentative conclusions were reached regarding the individual activity coefficients of the ions of some simple electrolytes, and the hydrogen ion in certain chloride solutions. From the electromotive force data then available, an attempt was made to compute the individual ion activity coefficients of the hydrogen, lithium, sodium, and potassium ions in solutions of their chlorides, and the hydrogen and hydroxyl ions in solutions of chlorides. More recently, further data[2] have been obtained which complete this experimental study, and which will be assembled in this paper.

Since the difficulty in estimating liquid junction potentials is the only cause of our not being able to estimate exactly the individual activity coefficients of the ions, an analysis of the problem of liquid junction potentials will be made.

Hückel[3] has computed the individual ion activity coefficients of solutions of hydrochloric acid and sodium chloride by means of the general theory of Debye and Hückel and has found a qualitative but not quantitative agreement with our earlier conclusions. This, indeed, is to be expected since our conclusions have been considered to be but a rough approximation and not an exact solution of the problem, and since, on account of the theoretical complexity of the problem, it is not to be expected that the theory of Debye and Hückel is exact in the very concentrated solutions. In the following discussion, we shall consider these matters more fully.

### (1) *Electromotive Forces of the Cells:*

$$H_2 \mid HCl(m_o) \mid KCl(sat) \mid HCl(m_o), MCl(m) \mid H_2$$

$$H_2 \mid MOH(m_o), MCl(m) \mid KCl(sat) \mid MOH(m_o) \mid H_2$$

Throughout these studies, we have employed cells containing a saturated potassium chloride solution for the purpose of reducing the liquid junction potentials as far as possible experimentally. In all cases stationary junctions were employed. These were made by having a capillary tube from one electrode compartment dip into a cup containing the other electrode solution. A

* Contribution from the John Harrison Laboratory of Chemistry of the University of Pennsylvania.

[1] J. Am. Chem. Soc., 37, 2460 (1915); 38, 1986 (1916); 42, 180 (1920).

[2] J. Am. Chem. Soc., 47, 684, 689 (1925); Harned and Swindells: 48, 126 (1926).

[3] Physik. Z., 26, 93 (1925).

mixing of the two solutions across the boundary was therefore allowed to take place. The more recent results were obtained from cells of the types

$$H_2 \mid HCl(m_o),MCl(m) \mid KCl(sat) \mid Hg_2Cl_2 \mid Hg$$
$$H_2 \mid MOH(m_o),MCl(m) \mid KCl(sat) \mid Hg_2Cl_2 \mid Hg.$$

All these data are compiled in Table I. The standard calomel electrode has been eliminated, and the electromotive forces corresponding to the transfer of the hydrogen or hydroxyl ions plus the liquid junction potentials have been given. At the end of the table, the values of the reference cells have been tabulated. These data come from three sources. Those denoted (1) were taken from our earlier study[1]; those denoted (2) have been recently determined; and those denoted (3) have been recently obtained in this laboratory by Dr. Swindells. Molal concentrations have been employed. All measurements were carried out at 25°. The agreement between the more recent results and those previously determined was found to be good.

TABLE I

(1) Electromotive Forces of Cells:

$$H_2 \mid HCl(m_o) \mid KCl(sat) \mid HCl(m_o),MCl(m) \mid H_2$$

$m_o = 0.1$

| KCl | | NaCl | | LiCl | |
|---|---|---|---|---|---|
| m | $E_H$ (1) | m | $E_H$ (1) | m | $E_H$ (3) |
| 0.1380 | 0.0003 | 0.1867 | 0.0011 | 0.0705 | 0.0012 |
| 0.2775 | 0.0005 | 0.569 | 0.0041 | 0.1101 | 0.0017 |
| 0.560 | 0.0012 | 0.614 | 0.0041 | 0.2004 | 0.0021 |
| 0.848 | 0.0021 | 1.536 | 0.0128 | 0.3693 | 0.0041 |
| | | | (2) | | |
| 1.141 | 0.0036 | 0.0959 | 0.0012 | 0.704 | 0.0083 |
| 1.441 | 0.0052 | 0.1779 | 0.0014 | 1.007 | 0.0120 |
| 3.473 | 0.0169 | 0.3456 | 0.0024 | 2.198 | 0.0283 |
| | (2) | | | | |
| 1.341 | 0.0045 | 0.857 | 0.0063 | 3.695 | 0.0492 |
| 2.006 | 0.0082 | 1.707 | 0.0153 | ——— | ——— |
| 2.696 | 0.0123 | 2.130 | 0.0198 | ——— | ——— |
| 3.346 | 0.0161 | 2.599 | 0.0246 | ——— | ——— |
| ——— | ——— | 2.978 | 0.0285 | ——— | ——— |
| ——— | ——— | 3.424 | 0.0328 | ——— | ——— |

[1] Harned: J. Am. Chem. Soc., 37, 2460 (1915).

$m_o = 0.01$

| KCl m | $E_H$ (2) | NaCl m | $E_H$ (2) | LiCl m | $E_H$ (3) |
|---|---|---|---|---|---|
| 0.02 | −0.0003 | 0.02 | −0.0002 | 0.0077 | −0.0003 |
| 0.05 | −0.0008 | 0.05 | −0.0007 | 0.0103 | −0.0003 |
| 0.1 | −0.0015 | 0.1 | −0.0005 | 0.0194 | 0.0001 |
| 0.2 | −0.0021 | 0.2 | 0.0000 | 0.0422 | 0.0005 |
| 0.5 | −0.0015 | 0.5 | 0.0014 | 0.0727 | 0.0011 |
| 1. | 0.0016 | 1. | 0.0058 | 0.1989 | 0.0020 |
| 2. | 0.0071 | 2. | 0.0152 | 0.402 | 0.0035 |
| 3. | 0.0126 | 3. | 0.0254 | 0.699 | 0.0072 |
| ——— | ——— | ——— | ——— | 1.004 | 0.0104 |
| ——— | ——— | ——— | ——— | 2.189 | 0.0260 |
| ——— | ——— | ——— | ——— | 3.989 | 0.0526 |

(2) Electromotive Forces of Cells:

$H_2 \mid MOH(m_o), MCl(m) \mid KCl(sat) \mid MOH(m_o) \mid H_2$

$m_o = 0.1$

| KOH,KCl m | $E_{OH}$ (1) | NaOH,NaCl m | $E_{OH}$ (1) | LiOH,LiCl m | $E_{OH}$ (3) |
|---|---|---|---|---|---|
| 0.262 | −0.0013 | 0.472 | −0.0044 | 0.1512 | −0.0051 |
| 0.527 | −0.0015 | 0.943 | −0.0071 | 0.2908 | −0.0082 |
| 1.357 | −0.0009 | 1.445 | −0.0094 | 0.432 | −0.0108 |
| 2.167 | 0.0004 | 1.946 | −0.0107 | 1.071 | −0.0201 |
| 3.280 | 0.0044 | 2.458 | −0.0120 | 1.709 | −0.0284 |
| | (2) | | (2) | | |
| 0.1285 | −0.0004 | 0.1704 | −0.0029 | 2.675 | −0.0384 |
| 0.2645 | −0.0009 | 0.336 | −0.0041 | 3.521 | −0.0461 |
| 0.647 | −0.0016 | 0.841 | −0.0075 | ——— | ——— |
| ——— | ——— | 1.696 | −0.0108 | ——— | ——— |
| ——— | ——— | 2.500 | −0.0135 | ——— | ——— |
| ——— | ——— | 4.14 | −0.0149 | ——— | ——— |

$m_o = 0.01$

| KOH,KCl m | $E_{OH}$ (2) | NaOH,NaCl m | $E_{OH}$ (2) | LiOH,LiCl m | $E_{OH}$ (3) |
|---|---|---|---|---|---|
| 0.0496 | −0.0036 | 0.0621 | −0.0054 | 0.0078 | −0.0005 |
| 0.1026 | −0.0048 | 0.1462 | −0.0076 | 0.0221 | −0.0020 |
| 0.1928 | −0.0067 | 0.302 | −0.0094 | 0.0423 | −0.0036 |
| 0.4889 | −0.0081 | 0.362 | −0.0096 | 0.0864 | −0.0070 |
| 1.051 | −0.0081 | 0.572 | −0.0117 | 0.844 | −0.0217 |
| 1.830 | −0.0071 | 0.853 | −0.0133 | 1.854 | −0.0360 |
| 2.446 | −0.0050 | 1.288 | −0.0157 | 2.746 | −0.0469 |
| ——— | ——— | 1.724 | −0.0172 | 3.810 | −0.0573 |
| ——— | ——— | 2.835 | −0.0202 | ——— | ——— |
| ——— | ——— | 3.575 | −0.0217 | ——— | ——— |

(3) Reference Cells:

| | |
|---|---|
| $H_2$ \| HCl(0.1) \| KCl(sat) \| $Hg_2Cl_2$ \| Hg; | $E = 0.3102$ |
| $H_2$ \| HCl(0.01) \| " ; | $E = 0.3679$ |
| $H_2$ \| KOH(0.1) \| " ; | $E = 1.0040$ |
| $H_2$ \| KOH(0.01) \| " ; | $E = 0.9491$ |
| $H_2$ \| NaOH(0.1) \| " ; | $E = 1.0031$ |
| $H_2$ \| NaOH(0.01) \| " ; | $E = 0.9485$ |
| $H_2$ \| LiOH(0.1) \| " ; | $E = 1.0028$ |
| $H_2$ \| LiOH(0.01) \| " ; | $E = 0.9483$ |

### (2) *Discussion of Experimental Results*

According to the dissociation theory of Arrhenius and van't Hoff, it was assumed that the thermodynamic coefficients of the two ions of a uniunivalent electrolyte in a given solution were identical. Both ions were assumed to have the same van't Hoff coefficient as long as this quantity was taken as a measurement of the degree of dissociation. More recently, many investigators have come to the conclusion that the thermodynamic coefficients such as the activity, osmotic, or van't Hoff coefficients[1] are not the same for the two ions of a given electrolyte but that each ion is characterized by an individual value for this thermodynamic property.

As a first step towards evaluating the individual ion activity coefficients of highly polar electrolytes, we have made the very simple assumption that at a given concentration the relative partial free energies of the ions of the alkaline chlorides are additive. This assumption was first adopted by MacInnes for moderately dilute solutions. MacInnes[2] also assumed that in a solution of potassium chloride the activity coefficients of the potassium and chloride ions are equal. On account of the complicated nature of this problem, and the consideration of the numerous factors which may influence activity coefficients, these too simple assumptions are not to be expected to be more than a first rough approximation when applied to the very concentrated solutions. Our first step, however, in the following discussion will be to apply these assumptions to the completed data in hand.

If $\overline{F}_1$, $a_1$, and $\overline{F}_2$, $a_2$ are the relative partial free energies and activities of an electrolyte or an ion in two solutions of concentrations $m_1$ and $m_2$, respectively, then

$$\overline{F}_2 - \overline{F}_1 = RT \ln a_2/a_1 \qquad (1)$$

The electromotive force of a concentration cell, $E_1 - E_2$, or $\Delta E$ at constant temperature and pressure is given by

$$NF\Delta E = NF(E_1 - E_2) = \overline{F}_2 - \overline{F}_1 = (-\Delta F) \qquad (2)$$

From these two equations, it is seen that a change in partial free energy of an ion or electrolyte in passing from one concentration to another is pro-

[1] For definitions of these quantities, see Taylor: "Treatise on Physical Chemistry", pp. 728, 753, 754 (1924).

[2] J. Am. Chem. Soc., 41, 1086 (1919).

portional to the electromotive force of a concentration cell containing the electrolyte at these two concentrations, which in turn is proportional to the logarithm of the ratio of the activities at the two concentrations. With these relations in mind, we shall state the above postulates as follows:

(1) The relative partial free energies, or electromotive forces of the ions of potassium, sodium, and lithium chlorides in aqueous solution at a given concentration and referred to a given concentration are additive,

(2) $E_K$ equals $E_{Cl}$ (referred to a given concentration) in an aqueous potassium chloride solution of a given strength, and follow the consequences of their adoption.

In this discussion, the nomenclature and conventions regarding the signs of electromotive forces employed by Lewis and Randall[1] will be adopted. Let us first consider the cells:

Type (1): $H_2 \mid HCl(m_o) \mid Hg_2Cl_2 \mid Hg$; ($E'$ has a positive value)

Type (2): $H_2 \mid HCl(m_o),MCl(m) \mid Hg_2Cl_2 \mid Hg$; ($E''$ has a less positive value than $E'$). If the second be subtracted from the first, we obtain

Type (3): $Hg \mid Hg_2Cl_2 \mid HCl(m_o),MCl(m) \mid H_2 \mid HCl(m_o) \mid Hg_2Cl_2 \mid Hg$; ($E_{HCl}$ has a positive value). The equation which relates $E_{HCl}$ to the activities is at 25°

$$E_{HCl} = 0.05915 \log \frac{a_{H(s)}\, a_{Cl(s)}}{a_{H(m_o)} a_{Cl(m_o)}}$$

$$E_H + E_{Cl} = 0.05915 \log \frac{a_{H(s)}}{a_{H(m_o)}} + 0.05915 \log \frac{a_{Cl(s)}}{a_{Cl(m_o)}} \qquad (3)$$

where $a_H$ etc. are the activities of the ions denoted by subscript, (s) refers to the solution containing the salt, and $E_H$ and $E_{Cl}$ are the electromotive forces corresponding to the relative partial free energies of the hydrogen and chloride ions, respectively. $E_H$ would be the electromotive forces of the cells

Type (4): $H_2 \mid HCl(m_o) \mid HCl(m_o),MCl(m) \mid H_2$

where the liquid junction potential has been eliminated by some means (indicated by italic letter $E$). The electromotive forces of cells of this type, we shall denote $E_{H(MCl)}$. The nearest approach which has been made to an experimental realization of such cells has been obtained by interposing a saturated potassium chloride solution between the two electrode solutions. Thus, we obtain the cells

Type (5): $H_2 \mid HCl(m_o) \mid KCl(sat) \mid HCl(m_o),MCl(m) \mid H_2$

and, the smaller the difference between the two liquid junction potentials, the nearer its electromotive force will be to the $E_H$. Their electromotive forces we denote $E_{H(s)}$ where the (s) refers to the saturated potassium chloride.

Our procedure will be as follows. We shall first calculate $E_{Cl}$ according to postulate (2). Values of $E_{KCl}$ have been given in another place[2] which when divided by 2 give the values of $E_K$ or $E_{Cl}$ in Table II. By subtracting these

[1] "Thermodynamics", (1923).

[2] J. Am. Chem. Soc. 47, 930 (1925).

from the revised values of $E_{HCl}$ obtained at round concentrations from the plots of electromotive computed from the results in Table III of a recent paper[1] we obtain $E_{H(MCl)}$ which we compare with the values of $E_{H(s)}$ read off curves of the results in Table I of this paper. This has been done for the cells containing acid at concentrations 0.01 and 0.1 M and potassium, sodium, and lithium chlorides at concentrations (m). The results are given in Part I, Table II.

In Part II, the data of the hydroxide cell electromotive forces have been compiled in a similar manner. In this case, for sake of convenience, we consider the cells

Type (6): $H_2 \mid MOH(m_o),MCl(m) \mid M_xHg \mid MOH(m_o) \mid H_2$; ($E_{MOH}$ has a positive value) where M may be either lithium, sodium, or potassium. The electromotive forces of these cells are given by

$$E_{MOH} = 0.05915 \log \frac{a_{M(s)}\, a_{OH(s)}\, a_{H_2O(m_o)}}{a_{M(m_o)}\, a_{OH(m_o)}\, a_{H_2O(s)}}$$

$$E_M + E_{OH} = 0.05915 \log \frac{a_{M(s)}}{a_{M(m_o)}} + 0.05915 \log \frac{a_{OH(s)}\, a_{H_2O(m_o)}}{a_{OH(m_o)}\, a_{H_2O(s)}} \qquad (4)$$

$E_M$ for the sodium and lithium ions have been calculated by subtracting $E_{Cl}$ from $E_{NaCl}$ and $E_{LiCl}$ and the values are given in second and third columns in Part II, Table II. $E_{NaCl}$ were obtained from the data compiled by Harned[2] and $E_{LiCl}$ from the data of Harned and Swindells[3]. If $E_M$ be subtracted from $E_{MOH}$, we obtain $E_{OH}$ which corresponds to the cells

Type (7): $H_2 \mid MOH(m_o),MCl(m) \mid MOH(m_o) \mid H_2$

and the cell reaction

$$OH^-(s) + H_2O(m_o) = OH^-(m_o) + H_2O(s).$$

Thus, if $E_{OH}$ is negative, $a_{OH(m_o)}$ will be greater than $a_{OH(s)}$ and the reaction will tend to take place from right to left. The values of $E_{OH}$ calculated by the above method in the cases of the three chlorides are given in the table and there compared with the values of $E_{OH(s)}$, or the electromotive forces of the cells

Type (8): $H_2 \mid MOH(m_o),MCl(m) \mid KCl(sat) \mid MOH(m_o) \mid H_2$

These latter results were read off plots of the results in Table I.

In Fig. 1, the values of $E_H$ and $E_{OH}$ of the solutions containing 0.1 M acid and hydroxide calculated by means of our postulates are plotted against m. $E_{H(s)}$ and $E_{OH(s)}$ are similarly plotted and represented by the dashed lines. The maximum difference between the two sets of curves occurs at 3M lithium chloride in the acid solution and amounts to 5 millivolts. In general, the curves separate rapidly upon the first addition of salt and then become approximately parallel with a slowly widening difference. $E_{OH}$ coincides with

[1] J. Am. Chem. Soc., 48, 326 (1926).
[2] J. Am. Chem. Soc., 47, 930 (1925), Table III, $E_2$ in Part I and II, B.
[3] J. Am. Chem. Soc., 48, 126 (1926).

TABLE II

Comparison of $E_H$ and $E_{OH}$ to $E_{H(s)}$ and $E_{OH(s)}$

Part I. The Acid System

$m_o = 0.1$

| | | KCl | | NaCl | | LiCl | |
|---|---|---|---|---|---|---|---|
| m + 0.1 | $E_K = E_{Cl}$ | $E_H$ | $E_{H(s)}$ | $E_H$ | $E_{H(s)}$ | $E_H$ | $E_{H(s)}$ |
| 0.1 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.2 | 0.0154 | −0.0003 | 0.0002 | 0.0004 | 0.0012 | 0.0006 | 0.0017 |
| 0.4 | 0.0316 | −0.0002 | 0.0004 | 0.0008 | 0.0018 | 0.0015 | 0.0030 |
| 0.6 | 0.0410 | 0.0002 | 0.0010 | 0.0016 | 0.0032 | 0.0031 | 0.0050 |
| 0.8 | 0.0473 | 0.0007 | 0.0017 | 0.0034 | 0.0050 | 0.0054 | 0.0077 |
| 1.1 | 0.0546 | 0.0022 | 0.0030 | 0.0060 | 0.0078 | 0.0086 | 0.0116 |
| 2.1 | 0.0705 | 0.0074 | 0.0082 | 0.0159 | 0.0182 | 0.0207 | 0.0256 |
| 3.1 | 0.0804 | 0.0132 | 0.0140 | 0.0250 | 0.0285 | 0.0344 | 0.0396 |

$m_o = 0.01$

| | | KCl | | NaCl | | LiCl | |
|---|---|---|---|---|---|---|---|
| m + 0.1 | $E_K = E_{Cl}$ | $E_H$ | $E_{H(s)}$ | $E_H$ | $E_{H(s)}$ | $E_H$ | $E_{H(s)}$ |
| 0.01 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.02 | 0.0169 | −0.0014 | −0.0003 | −0.0013 | −0.0003 | −0.0013 | −0.0003 |
| 0.05 | 0.0389 | −0.0028 | −0.0006 | −0.0025 | −0.0007 | −0.0023 | 0.0005 |
| 0.1 | 0.0552 | −0.0036 | −0.0014 | −0.0032 | −0.0006 | −0.0030 | 0.0012 |
| 0.2 | 0.0711 | −0.0040 | −0.0021 | −0.0035 | −0.0002 | −0.0029 | 0.0020 |
| 0.5 | 0.0921 | −0.0037 | −0.0015 | −0.0022 | 0.0014 | −0.0010 | 0.0045 |
| 1. | 0.1078 | −0.0013 | 0.0016 | 0.0022 | 0.0058 | 0.0048 | 0.0104 |
| 2. | 0.1243 | 0.0044 | 0.0073 | 0.0115 | 0.0154 | 0.0171 | 0.0231 |
| 3. | 0.1349 | 0.0091 | 0.0126 | 0.0211 | 0.0254 | 0.0303 | 0.0368 |

## Part II. Hydroxide System

$m_o = 0.1$

| m + 0.1 | $E_{Na}$ | $E_{Li}$ | KCl $E_{OH}$ | KCl $E_{OH(s)}$ | NaCl $E_{OH}$ | NaCl $E_{OH(s)}$ | LiCl $E_{OH}$ | LiCl $E_{OH(s)}$ |
|---|---|---|---|---|---|---|---|---|
| 0.1 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.2 | 0.0164 | 0.0182 | −0.0012 | −0.0007 | −0.0022 | −0.0022 | −0.0040 | −0.0040 |
| 0.4 | 0.0328 | 0.0364 | −0.0023 | −0.0015 | −0.0035 | −0.0038 | −0.0080 | −0.0085 |
| 0.6 | 0.0429 | 0.0480 | −0.0027 | −0.0018 | −0.0045 | −0.0050 | −0.0105 | −0.0116 |
| 0.8 | 0.0500 | 0.0572 | −0.0027 | −0.0016 | −0.0054 | −0.0063 | −0.0135 | −0.0144 |
| 1.1 | 0.0587 | 0.0675 | −0.0027 | −0.0016 | −0.0065 | −0.0077 | −0.0167 | −0.0188 |
| 2.1 | 0.0783 | 0.0948 | −0.0012 | 0.0000 | −0.0098 | −0.0112 | −0.0284 | −0.0316 |
| 3.1 | 0.0957 | 0.1176 | 0.0017 | 0.0030 | −0.0148 | −0.0145 | −0.0398 | −0.0420 |

$m_o = 0.01$

| m + 0.1 | $E_{Na}$ | $E_{Li}$ | KCl $E_{OH}$ | KCl $E_{OH(s)}$ | NaCl $E_{OH}$ | NaCl $E_{OH(s)}$ | LiCl $E_{OH}$ | LiCl $E_{OH(s)}$ |
|---|---|---|---|---|---|---|---|---|
| 0.01 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.02 | 0.0169 | 0.0169 | −0.0020 | −0.0018 | −0.0020 | −0.0020 | −0.0020 | −0.0020 |
| 0.05 | 0.0392 | 0.0392 | −0.0042 | −0.0036 | −0.0045 | −0.0045 | −0.0045 | −0.0045 |
| 0.1 | 0.0560 | 0.0561 | −0.0054 | −0.0050 | −0.0065 | −0.0065 | −0.0079 | −0.0071 |
| 0.2 | 0.0725 | 0.0738 | −0.0065 | −0.0065 | −0.0083 | −0.0083 | −0.0117 | −0.0114 |
| 0.5 | 0.0943 | 0.0985 | −0.0097 | −0.0097 | −0.0105 | −0.0108 | −0.0175 | −0.0185 |
| 1. | 0.1119 | 0.1199 | −0.0080 | −0.0080 | −0.0126 | −0.0141 | −0.0244 | −0.0244 |
| 2. | 0.1326 | 0.1487 | −0.0065 | −0.0065 | −0.0162 | −0.0180 | −0.0376 | −0.0376 |
| 3. | 0.1465 | 0.1717 | −0.0037 | −0.0037 | −0.0189 | −0.0206 | −0.0500 | −0.0500 |

$E_{OH(s)}$ in sodium chloride solutions up to 0.3 M above which concentration it is less negative. It is important to note that $E_{OH}$ is more negative than $E_{OH(s)}$ in potassium chloride solutions but less so in sodium and lithium chloride solutions. This interesting behavior will be explained later.

The results in 0.01 M acid are similar to these except that the differences between $E_H$ and $E_{H(s)}$ are about 1.5 millivolts greater in the concentrated

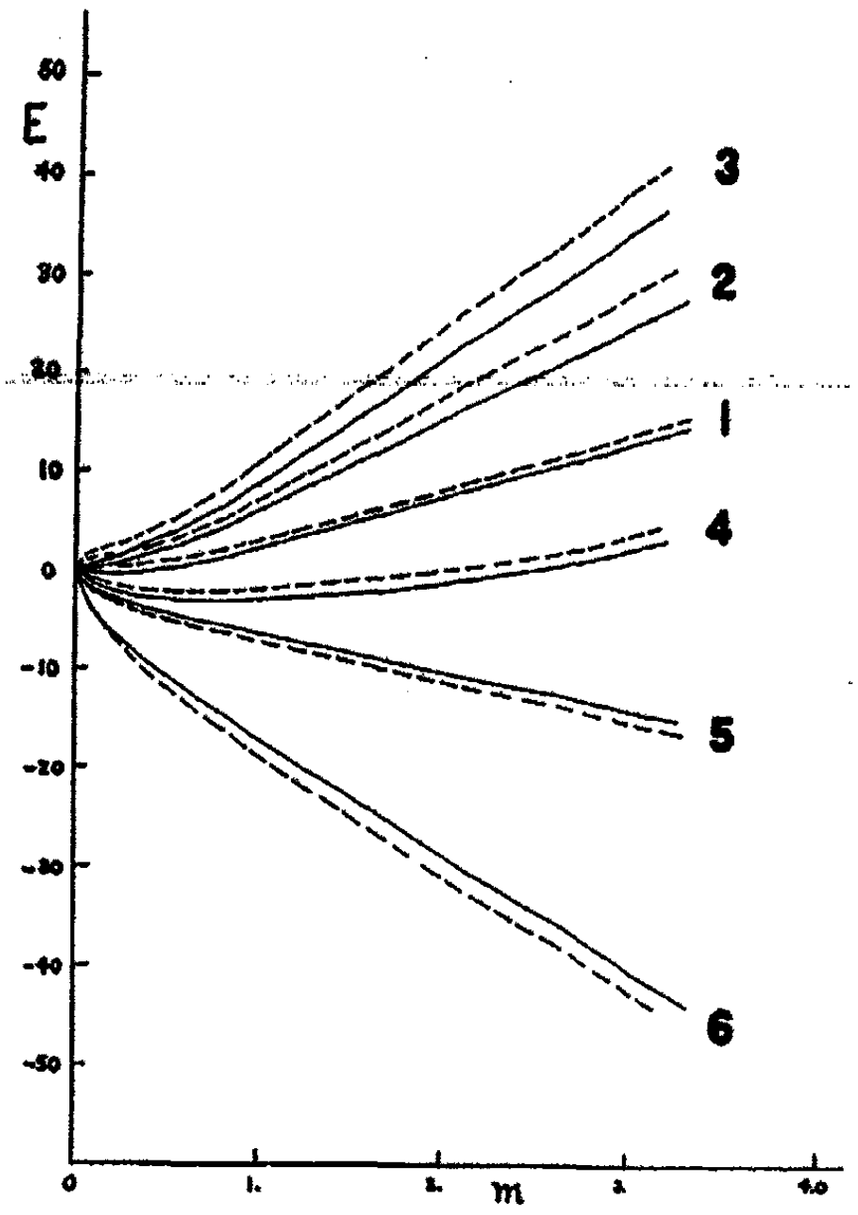



FIG. 1

Electromotive Forces of the Hydrogen and Hydroxyl Ions in Uniunivalent Chloride Solutions.

1. $E_H$(HCl(0.1), KCl(m))
2. $E_H$(HCl(0.1), NaCl(m))
3. $E_H$(HCl(0.1), LiCl(m))
4. $E_{OH}$(KOH(0.1), KCl(m))
5. $E_{OH}$(NaOH(0.1), NaCl(m))
6. $E_{OH}$(LiOH(0.1), LiCl(m))

solutions. $E_{OH}$ and $E_{OH(s)}$ of the 0.01 M potassium hydroxide—chloride series are identical. The 0.01 M sodium hydroxide—chloride series are similar to the 0.1 M series. On the other hand, $E_{OH}$ and $E_{OH(s)}$ in the case of the 0.01 M lithium hydroxide chloride series are identical. This apparent inconsistency may be due to an error in the results of Harned and Swindells with amalgam cells containing these mixtures, and therefore at present we shall attach no significance to this coincidence.

On account of the difficulties inherent in judging the magnitudes of the liquid junction potentials, and the nature of liquid junction potential calculations by means of thermodynamics, it would be wrong to regard this uniformity of behavior as an exact proof but rather as a qualitative indication. It is improbable, on the other hand, that such a distribution of curves is purely fortuitous. In our previous articles on this subject, these postulates have been regarded as an approximation in the more concentrated solutions and as becoming more exact as the salt concentration is decreased.

### (3) *Analysis of the Liquid Junction Potentials.*

#### (a) Some Qualitative Considerations

Let us first consider the electromotive forces of the cells

$$H_2 \mid HCl(0.1) \mid KCl(sat) \mid HCl(0.1),MCl(m) \mid H_2,$$

represented in Fig. 1 by the dotted lines. In the cases of potassium, sodium, and lithium chlorides, the anion has a greater mobility than the cations, although the difference is very small in case of potassium chloride. The addition of the salt will charge the saturated potassium chloride solution negatively to the acid-salt solutions, and small liquid junction potentials would be produced which would cause a positive electromotive force from left to right within the cell. Thus, in all cases, these electromotive forces would be greater than the calculated electromotive forces of the cells

$$H_2 \mid HCl(0.1) \mid HCl(0.1),MCl(m) \mid H_2.$$

From inspection in Fig. 1, we find that the values of the cells containing the saturated chloride are always somewhat more positive than the calculated values, and that the differences between $E_{H(s)}$ and $E_H$ are greater in the order potassium, sodium, lithium chlorides as would be expected since the differences in mobilities of the anion and cation of these salts vary in the same order.

The electromotive forces of the cells

$$H_2 \mid MOH(0.1),MCl(m) \mid KCl(sat) \mid MOH(0.1) \mid H_2$$

are given by the dotted lines 4, 5 and 6 in Fig. 1. In these cases, by similar reasoning, the addition of the salt should increase the negative electromotive force, and the dotted lines should lie below the calculated values. This is found to be true in the concentrated solutions for the sodium hydroxide—sodium chloride, lithium hydroxide—lithium chloride cells, but not for those containing potassium hydroxide—chloride mixtures. This would appear to be an inconsistency in the results but will be seen to disappear when we come to consider the situation more carefully. The negative increase in liquid junction potential is greater for lithium than for sodium than for potassium chloride which would be expected from the mobilities.

Another important point concerning the plots in Fig. 1 should be considered. The dotted and smooth curves diverge from one another up to about 0.5 M and then run nearly parallel to one another in all six cases. Since the liquid junction potential in any case will be a function of the logarithm of the ratios of two concentrations, it is obvious that it will change the least throughout the concentration ranges where the concentration ratio varies the least.

This fact is qualitatively in agreement with the calculations of liquid junction potentials by either Planck's equation[1] or Henderson's equation[2].

Exactly similar considerations hold for the 0.01 M acid-salt series in which case, however, the differences between $E_{H(s)}$ and $E_H$ are somewhat greater. This behavior is also to be expected. $E_{OH(s)}$ is identical with $E_{OH}$ for the 0.01 M potassium hydroxide—chloride series. This indicates a greater negative liquid potential change than in the case of the 0.1 M series. $E_{OH(s)}$ differs from $E_{OH}$ by a slightly greater negative amount in the 0.01 M than in the 0.1 M sodium hydroxide—chloride series. These results, therefore, agree with the ordinary qualitative considerations of the liquid junction behaviors.

### (b) Analysis of the Thermodynamic Method of computing Liquid Junction Potentials.

Let us bring together two solutions containing ions of different kinds of which the ion 1 is of the $1^{th}$ kind. Let us assume that between solution 1 and solution 2 there is a uniform mixing according to the assumption employed by Henderson. Across the boundary, the decrease in free energy accompanying the reversible transfer of 1 Faraday at constant temperature and pressure will be

$$(-dF) = NF dE_e = -\Sigma RTt_i d \ln a_i \qquad (5)$$

where $t_i$ and $a_i$ are the transference number and activity of the ion of the $i^{th}$ kind. The summation is to be taken for all the ions. The liquid junction potential, $E_l$, may then be evaluated by integrating each integral throughout the region of mixing or between the limits 1 and 2 where 1 refers to solution 1 and 2 to solution 2. Thus

$$E_l = -\Sigma \frac{RT}{NF} \int_1^2 t_i d \ln a_i \qquad (6)$$

or for univalent ions which is the only case we shall consider,

$$E_l = -\Sigma 0.05915 \int_1^2 t_i \, d \log a_i \qquad (7)$$

Now, since $\log a_i$ becomes minus infinity as $m_i$ becomes zero, it is more convenient for our purposes to make use of the definition, $a_i = \gamma_i m_i$, and split equation (7) into two parts, one of which contains only the activity coefficients $\gamma_i$, and one which contains the molal concentrations, $m_i$. Thus, we obtain

$$E_l = -\left[\Sigma 0.05915 \int_1^2 t_i \, d \log \gamma_i + \Sigma 0.05915 \int_1^2 t_i \, d \log m_i\right] \qquad (8)$$

The first integral may be more easily obtained than the integral of (7) since $\gamma_i$ for a single electrolyte is defined so as to equal 1 when $m_i$ equals zero. The second integral of equation (8) is recognized to be that which Henderson

[1] Wied. Ann., 39, 161 (1890); 40, 561 (1890).
[2] Z. physik. Chem., 59, 118 (1907); 63, 325 (1908).

evaluated except that we shall employ molal concentrations. Thus, the second part of $E_l$ which we shall denote $E_m$ will be given by Henderson's equation, or

$$E_m = -0.05915 \frac{(U_1 - V_1) - (U_2 - V_2)}{(U_1' + V_1') - (U_2' + V_2')} \log \frac{U_1' + V_1'}{U_2' + V_2'}$$

where

$$\begin{aligned} U_1' = U_1 &= u_1m_1 + u_2m_2 + u_3m_3 + \cdots \\ V_1' = V_1 &= \bar{u}_1\bar{m}_1 + \bar{u}_2\bar{m}_2 + \bar{u}_3\bar{m}_3 + \cdots \\ U_2' = U_2 &= u_1'm_1' + u_2'm_2' + u_3'm_3' + \cdots \\ V_2' = V_2 &= \bar{u}_1'\bar{m}_1' + \bar{u}_2'\bar{m}_2' + \bar{u}_3'\bar{m}_3' + \cdots \end{aligned}$$

and where $U_1$, etc. refer to solution 1, $U_2$ etc. to solution 2, $u_1$ and $\bar{u}_1$ etc. are the mobilities of the cations and anions in solution 1, and $\bar{u}_1'$ and $\bar{u}_1'$ etc. are the mobilities of the same in solution 2. The second term on the right of (8) may be regarded as solved if our assumption concerning the mixing of the solutions is correct, and we may write

$$E_l = -\left[\Sigma\, 0.05915 \int_1^2 t_i \, d \log \gamma_i + E_m\right] \qquad (9)$$

The summation of the integrals in this equation is the value which we must add to $E_m$ in order to obtain $E_l$.

Equation (9) contains a part which depends on the concentrations of the ions, but it also contains a part which is a function of the "$\gamma_i$s" or the thermodynamic coefficients of each of the ions taken individually. Thus in order to obtain $E_l$, we must know the "$\gamma_i$s" but in order to evaluate the "$\gamma_i$s" by this thermodynamic method, we must know $E_l$. Thus, thermodynamics leads us into a circular situation from which it is at once clear that the above qualitative discussion cannot be regarded as a proof of our postulates. All we can say is that such a uniform distribution of the results for $E_H$, $E_{OH}$, and $E_{H(s)}$, $E_{OH(s)}$ would not be obtained if our postulates were not a first approximation. Further, any postulates which lead to the evaluation of the individual ion activities are equivalent to an evaluation of the liquid junction potentials. That is to say, if we should employ values of the activity coefficients of the individual ions calculated by our postulates in equation (9), we should obtain values of $E_l$ which should be just equal to the estimated liquid junctions if our experimental results are consistent and if we are measuring reversible electromotive forces. To illustrate, if from the values of the activity coefficients of the hydrogen, potassium and chloride ions throughout the mixtures HCl(0.1), MCl(m) to KCl(sat) were evaluated by means of our postulates and $E_l$ then calculated by equation (9), then $E_l$ would be found to equal $E_{H(s)} - E_H$. From this, we see that it is illegitimate to use equation (9) in order to verify our postulates.

Then, to what end may we employ this general thermodynamic equation? The answer is merely to test whether the estimated liquid junction potentials agree with the Henderson assumption regarding the mixing of the solutions, to test the consistency of the experimental results, and to show that such apparent anomalies as the distribution of curves of $E_{OH}$ and $E_{OH(s)}$ for the

potassium and sodium chloride solutions (Fig. 1) are really not anomalies or caused by experimental error. Further, it is instructive to carry the thermodynamic analysis of liquid junction potentials further than Henderson, and thus show the approximate nature of Henderson's equation. To this end, we shall employ equation (9) in a further analysis of the simplest liquid junctions which we have to consider.

(c) Analysis of the Liquid Junction Potentials at the Boundaries:

$$HCl(0.1),KCl(m) \mid KCl(sat)$$

where $m$ is varied from 0 to 3.

Since we are dealing with ratios of ionic mobilities, we have employed the ionic conductances at 18° in place of the mobilities. The ratios of these quantities do not vary greatly between 18° and 25°. Thus, we have taken $\Lambda_H$, $\Lambda_K$, and $\Lambda_{Cl}$ to be 314.5, 64.5, and 65.5, respectively, and employed these in calculating the transference numbers[1]. We have also taken the mobilities to be invariant with respect to the total concentration. All concentrations are expressed in mols per 1000 gs. water.

$E_m$ was calculated by Henderson's formula at 0, 0.3, 0.5, 1, 2, and 3M potassium chloride concentrations and the values obtained are given in the second column of Table V.

We have now to determine the value of the integrals, $E_{\gamma i} = 0.05915 \int_1^2 t_i d \log \gamma_i$ for the hydrogen, potassium, and chloride ions and sum them up according to equation (9). Since the integration is to extend between solution 1 and solution 2, it is necessary to know $\log \gamma_i$ as a function of $t_i$ throughout the intermediate solutions for each of these ions. Since we have no analytical expression for this variation, we have resorted to a graphical integration. That is, we have plotted $t_i$ against $\log \gamma_i$ for the three ions and for values of m equal to 0.0, 0.3, 0.5, 1, 2, and 3, and determined the integrals by evaluating the corresponding areas.

Firstly, it is necessary to evaluate $\log \gamma_i$ at definite total concentrations between solution 1 and solution 2. Thus, if solution 1 is HCl(0.1),KCl(0.3), then in mixing all total concentrations between 0.4 and 4.8, or pure saturated potassium chloride will occur. Now, we make the following assumptions:

(1) $\gamma_H$ throughout these mixtures of decreasing hydrochloric acid content is the same as in a mixture of 0.1 acid and potassium chloride at the same total concentration. This is known to be very nearly true as a result of the law of the linear variation of $\log \gamma$ at a given total concentration[2]. According to this law, there is little difference between $\log \gamma_H$ in a 0.1 acid − (m) salt mixture and a 0.0 acid − (m + 0.1) salt mixture.

(2) $\gamma_K$ equals $\gamma_{Cl}$ at the same total concentration. Thus, $\gamma_K$ in HCl(0.1), KCl(m) equals $\gamma_{Cl}$ in this mixture. When m equals zero, $\gamma_K$ will equal $\gamma_{Cl}$ in 0.1 HCl. This is our postulate (2).

---

[1] Since the final values for $E_1$ are small, no great error is caused by these assumptions. All calculations were made with a 20-inch slide rule.

[2] Harned: J. Am. Chem. Soc., 48, 326 (1926).

The values of $\gamma_i$ and log $\gamma_i$ obtained by the use of these assumptions are given in Table III.

## TABLE III

### Activity Coefficients of the Hydrogen, Potassium, and Chloride Ions

| m | $E_H^{(1)}$ | $\gamma_H$ | log $\gamma_H$ | $\gamma_K = \gamma_{Cl}$ | log $\gamma_K$ = log $\gamma_{Cl}$ |
|---|---|---|---|---|---|
| 0.0 | 0.0000 | 0.842 | 9.925 | 0.779 | 9.891 |
| 0.3 | −0.0002 | 0.835 | 9.922 | 0.675 | 9.829 |
| 0.5 | 0.0002 | 0.849 | 9.929 | 0.645 | 9.810 |
| 1. | 0.0022 | 0.920 | 9.968 | 0.608 | 9.784 |
| 2. | 0.0077 | 1.136 | 0.0555 | 0.566 | 9.756 |
| 3. | 0.0128 | 1.385 | 0.141 | 0.577 | 9.761 |
| 4.8 | 0.0220 | 1.985 | 0.298 | 0.620 | 9.792 |

It is now necessary to calculate the "$t_i$s" throughout the mixtures. In the present case

$$t_H = \frac{\Lambda_H m_{H(1)} x}{\Sigma \Lambda_i m_{i(1)} x + \Sigma \Lambda_i m_{i(2)} (1-x)} = \frac{\Lambda_H m_{H(1)} x}{S}$$

$$t_{Cl} = \frac{\Lambda_{Cl} m_{Cl(1)} x + \Lambda_{Cl} m_{Cl(2)} (1-x)}{S}$$

$$t_K = \frac{\Lambda_K m_{K(2)} (1-x)}{S}$$

where $x$ is the degree of mixing or the percentage of solution 1 in the mixed layer divided by 100 at the concentration in question. Thus, if we consider the boundary HCl(0.1) | KCl(4.8), we have all the intermediate mixtures between these concentrations. We select convenient total concentrations such as 0.4, 0.6, etc. and calculate $x$ by assuming a uniform mixing law. Thus, we find that at 0.4 M, $x$ equals 0.937, at 0.6 M, $x$ equals 0.895 etc. These values are sufficient for calculating the "$t_i$s" of our first integral. Then, in a similar manner, we consider the boundary HCl(0.1),KCl(m) | KCl(4.8), compute the degrees of mixing and calculate the "$t_i$s" at 0.6 M, 1.1 M total concentrations etc, etc. All these results are given in Table IV. The first column contains the values of m at the intermediate concentrations. The columns with Roman numerals contain the values of the "$t_i$s" at the total concentrations m. I, II, III, IV, V, and VI refer to the boundaries: HCl(0.1),KCl(m) | KCl(4.8) where the solutions 1 contain salt at concentrations 0.0, 0.3, 0.5, 1, 2, and 3, respectively. Thus, if we consider the boundary HCl(0.1),KCl(0.5) | KCl (4.8), in an intermediate solution at a total concentration of 2, $t_H$, $t_K$, $t_{Cl}$ will be 0.073, 0.455, 0.473, respectively. I, II, etc. are the values which we shall employ in our integrals and which we shall designate integrals I, II, etc.

[1] This calculation was made before Table II in this paper was compiled. The values of $E_H$ are somewhat different from those in Table II.

TABLE IV

Transference Numbers of the Hydrogen, Potassium, and Chloride Ions

$t_H$

| m | I | II | III | IV | V | VI |
|---|---|---|---|---|---|---|
| 0.0 | 0.828 | —— | —— | —— | —— | —— |
| 0.3 | 0.394 | 0.408 | —— | —— | —— | —— |
| 0.5 | 0.283 | 0.294 | 0.305 | —— | —— | —— |
| 1. | 0.154 | 0.161 | 0.170 | 0.187 | —— | —— |
| 2. | 0.051 | 0.068 | 0.073 | 0.080 | 0.105 | —— |
| 3. | 0.029 | 0.030 | 0.032 | 0.036 | 0.049 | 0.073 |
| 4.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

$t_K$

| m | I | II | III | IV | V | VI |
|---|---|---|---|---|---|---|
| 0.0 | 0.0 | —— | —— | —— | —— | —— |
| 0.3 | 0.260 | 0.251 | —— | —— | —— | —— |
| 0.5 | 0.327 | 0.320 | 0.313 | —— | —— | —— |
| 1. | 0.404 | 0.400 | 0.394 | 0.384 | —— | —— |
| 2. | 0.458 | 0.457 | 0.455 | 0.448 | 0.433 | —— |
| 3. | 0.479 | 0.478 | 0.477 | 0.475 | 0.467 | 0.452 |
| 4.8 | 0.496 | 0.496 | 0.496 | 0.496 | 0.496 | 0.496 |

$t_{Cl}$

| m | I | II | III | IV | V | VI |
|---|---|---|---|---|---|---|
| 0.0 | 0.172 | —— | —— | —— | —— | —— |
| 0.3 | 0.346 | 0.340 | —— | —— | —— | —— |
| 0.5 | 0.391 | 0.386 | 0.381 | —— | —— | —— |
| 1. | 0.442 | 0.438 | 0.436 | 0.429 | —— | —— |
| 2. | 0.478 | 0.475 | 0.473 | 0.472 | 0.462 | —— |
| 3. | 0.499 | 0.491 | 0.491 | 0.489 | 0.484 | 0.476 |
| 4.8 | 0.504 | 0.504 | 0.504 | 0.504 | 0.504 | 0.504 |

In Figs. 2 and 3, the values of $\log \gamma_i$ in Table III have been plotted against the values of $t_i$ in Table IV. Integral I refers to the boundary HCl(0.1) | KCl(4.8), integral II to the junction HCl(0.1),KCl(0.3) | KCl(4.8), etc., up to integral VI which corresponds to HCl(0.1),KCl(3) | KCl(4.8). There are in all 18 integrals, six for each ion. The scale was chosen so that 100 sq. cm. equalled 0.000296 volt. Each integral is designated according to the ion considered. Thus H-I is the first integral of the hydrogen ion. 1 and 2 refer to solutions 1 and 2. The sign of the integral is also given. From these plots the values of the integrals were obtained by counting squares, and these in volts are given in Table V. These are added to $E_m$, and their negative according to equation (9) is $E_l$.

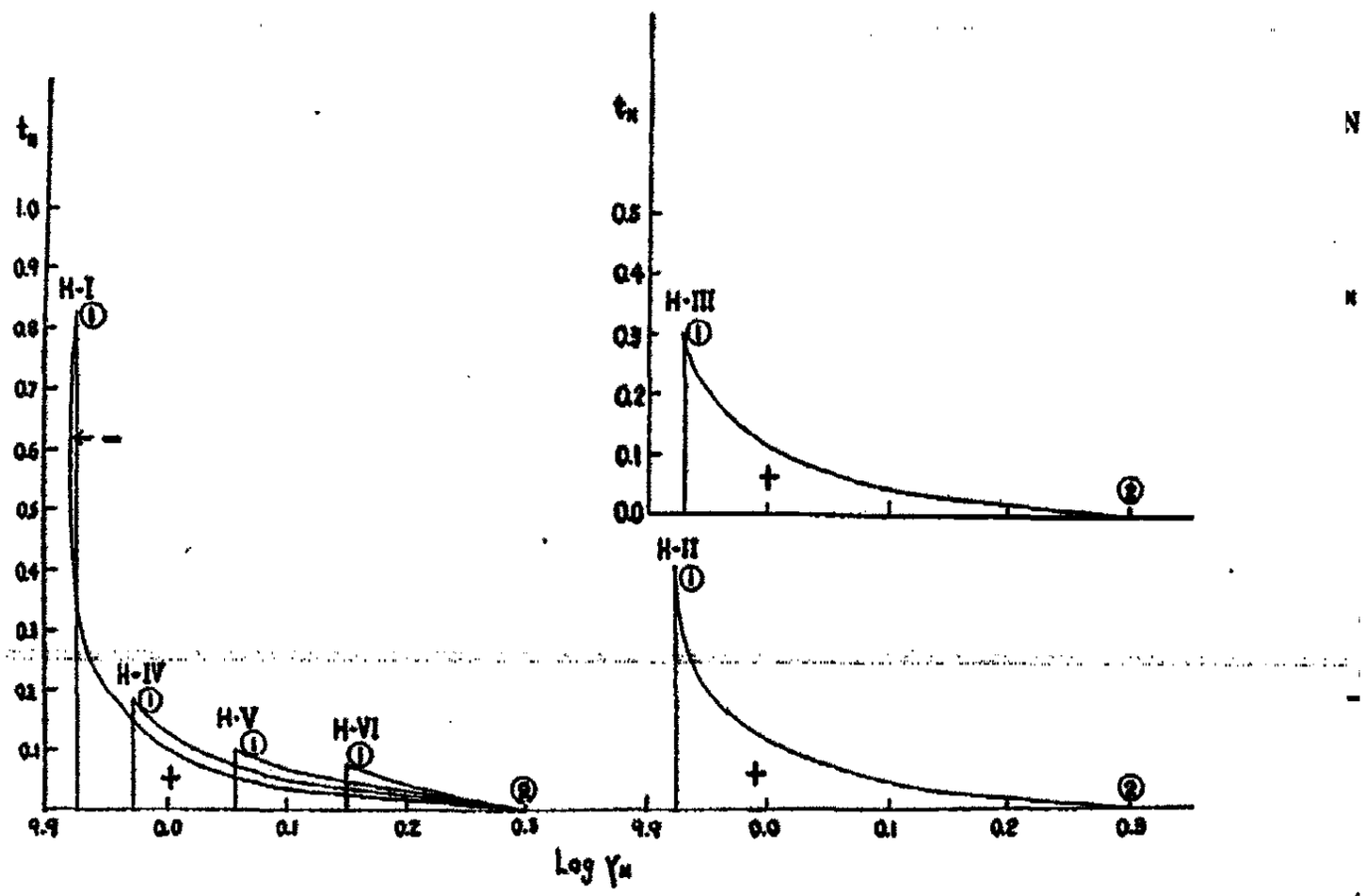



FIG. 2
Hydrogen Ion Integrals

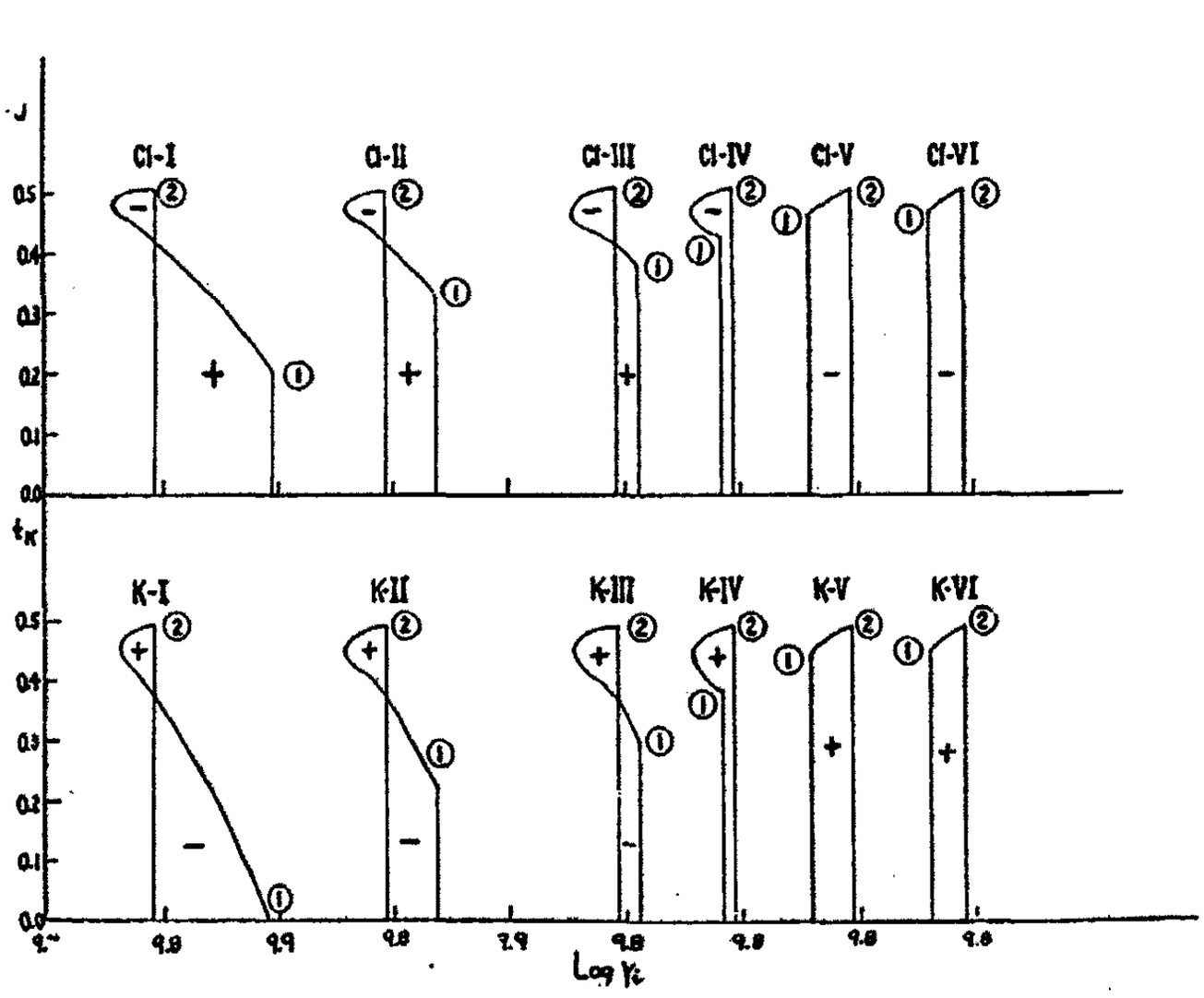



FIG. 3
Potassium and Chloride Ion Integrals

TABLE V

Liquid Junction Potentials by Equation (9)

| m | $E_m$ | $E_{\gamma(H)}$ | $E_{\gamma(K)}$ | $E_{\gamma(Cl)}$ | $E_l$ | $\Delta E_l$ | $E_{H(s)}$-$E$ |
|---|---|---|---|---|---|---|---|
| 0.0 | −0.00363 | 0.00130 | −0.00103 | 0.00178 | 0.00158 | 0.00000 | 0.0000 |
| 0.3 | −0.00289 | 0.00152 | −0.00053 | 0.00085 | 0.00105 | 0.00052 | 0.0006 |
| 0.5 | −0.00258 | 0.00148 | −0.00021 | 0.00042 | 0.00089 | 0.00069 | 0.0008 |
| 1. | −0.00192 | 0.00107 | −0.00038 | −0.00035 | 0.00082 | 0.00076 | 0.0008 |
| 2. | −0.00161 | 0.00060 | 0.00104 | −0.00088 | 0.00085 | 0.00073 | 0.0008 |
| 3. | −0.00123 | 0.00027 | 0.00087 | −0.00083 | 0.00082 | 0.00076 | 0.0008 |

In the next to last column, the values of $\Delta E_l$ or the calculated sum of the liquid junction potentials

HCl(0.1) | KCl(sat) | HCl(0.1),KCl(m)

are given. These are positive and agree very well as they should with the differences $E_{E(s)}$-$E_H$ computed from the results in Table II and given in the last column.

It is very important to emphasize at this juncture the fact previously mentioned that this does not constitute a proof of the second of our postulates. To illustrate this, another calculation was made in which we assumed that $E_H$ was 0.0003, 0.0005, 0.001, 0.002, and 0.003 volts less than in our first calculation at 0.3, 0.5, 1, 2, and 3 M salt concentrations. With these new values, log $\gamma_H$, log $\gamma_K$, and log $\gamma_{Cl}$ were calculated, and the above calculation of $E_l$ repeated. We obtained 0.0012, 0.0013, 0.0016, 0.0030, and 0.0035 for $\Delta E_l$ which agree as well as could be expected with the new values of $E_{H(s)}$-$E_H$, namely, 0.0009, 0.0013, 0.0018, 0.0028, and 0.0038 volts at values of m equal to 0.3, 0.5, 1, 2, 3, respectively.

(d) Analysis of the Liquid Junction Potentials at the Boundaries:

KOH(0.1),KCl(m) | KCl(sat)

In a similar manner, we have computed the liquid junction potentials at the boundaries between potassium hydroxide—chloride solutions and saturated potassium chloride. As in the first calculation we have assumed that log $\gamma_K$ equals log $\gamma_{Cl}$ at a given concentration. $\Lambda_{OH}$ has been taken to be 174. In Fig. 4, the values of log $\gamma_{OH}$ are shown plotted against $t_{OH}$. The plots for the potassium and chloride ions are similar to those in Fig. 3 so they have not been given. The integrals I-OH and II-OH differ considerably from the corresponding ones for the hydrogen ion in Fig. 2, and also from each other. Thus, as shown by Table VI, the first of these integrals equals 0.00106 and the second equals −0.00006 volts. This has an effect which causes the sign of $\Delta E_l$ to be opposite to that which would be obtained by Henderson's equation, or which would be expected from the ordinary qualitative considerations. The values of $E_m$, $E_{\gamma(i)}$, $E_l$, $\Delta E_l$ and $E_{OH(s)} - E_{OH}$ are given in Table VI.

TABLE VI

Calculations according to Equation (9)

| m | $E_m$ | $E_{\gamma(OH)}$ | $E_{\gamma(K)}$ | $E_{\gamma(Cl)}$ | $E_l$ | $\Delta E_l$ | $E_{OH(s)} - E_{OH}$ |
|---|---|---|---|---|---|---|---|
| 0.0 | 0.00088 | +0.00106 | −0.00218 | 0.00130 | −0.00106 | 0.00000 | 0.0000 |
| 0.3 | 0.00066 | −0.00006 | −0.00085 | 0.00070 | −0.00045 | 0.00061 | 0.0007 |
| 0.5 | 0.00063 | −0.00021 | −0.00040 | 0.00029 | −0.00031 | 0.00073 | 0.0009 |
| 1. | 0.00056 | −0.00024 | 0.00042 | −0.00035 | −0.00032 | 0.00079 | 0.0011 |
| 2. | 0.00049 | −0.00016 | 0.00104 | −0.00119 | −0.00033 | 0.00083 | 0.0012 |
| 3. | 0.00046 | −0.00006 | 0.00090 | −0.00110 | −0.00039 | 0.00087 | 0.0013 |

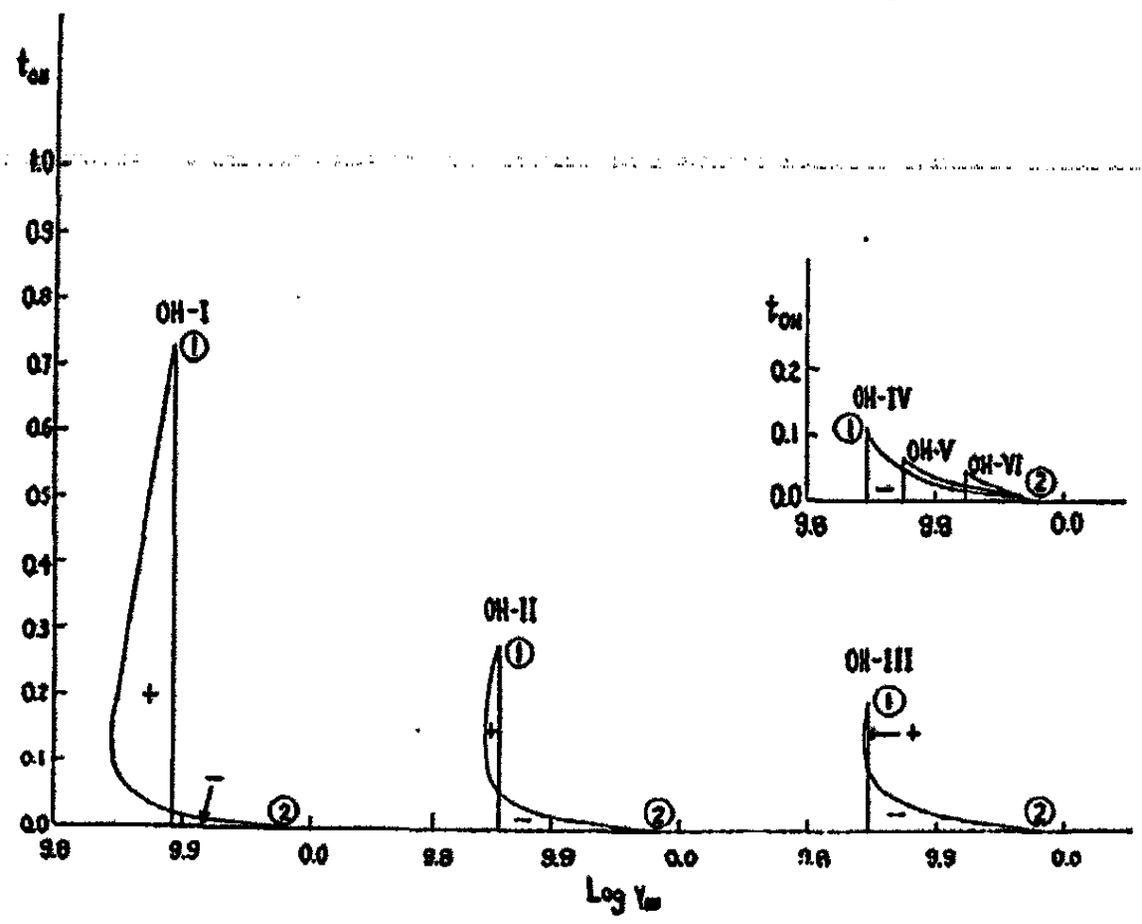



FIG. 4
Hydroxyl Ion Integrals

In order to fit the previous conventions, $\Delta E_l$ is obtained by subtracting $E_{l(o)}$ from $E_{l(m)}$, is positive, and corresponds to the sum of the liquid junction potentials of the system

$$KOH(0.1),KCl(m) \mid KCl(sat) \mid KOH(0.1).$$

The agreement between $\Delta E_l$ and $E_{OH(s)} - E_{OH}$ is again very good considering the complicated calculation. It is particularly interesting to note that the sign of $E_{OH(s)} - E_{OH}$ which at first glance appeared to be anomalous agrees with the calculated by the general equation.

A like consistency was found for similar calculations of the potentials HCl(0.01), KCl(m) | KCl(sat), and KOH(0.01), KCl(m) | KCl(sat). Cases of the junctions such as HCl(0.1), NaCl(m) | KCl(sat) are much more complicated involving as they do four ions, and a knowledge of the variation of $\gamma_{Na}$ and $\gamma_K$ in mixed potassium and sodium chloride solutions. A simple but

approximate mixture law was assumed, and a similar calculation was made for the junctions, HCl(0.1), NaCl(m) | KCl(sat), HCl(0.1), LiCl(m) | KCl (sat), etc. Suffice it to say that fairly good agreements between $E_{H(s)} - E_H$ and $\triangle E_l$ were obtained.

(e) A Summary of the Above Analysis of the Thermodynamic Calculation of Liquid Junction Potentials.

(1) It is shown that Henderson's equation does not give the liquid junction potential but only part of it. The other part can only be determined thermodynamically by the evaluation of the expression

$$\Sigma\, 0.05915 \int_1^2 t_i d \log \gamma_i.$$

To do this, a knowledge of the individual activity coefficients, the "$\gamma_i$s", of all the ions involved must be known as a function of the transference numbers, the "$t_i$s", throughout all mixtures between solutions 1 and 2.

(2) Henderson's assumption of uniform mixing of the two solutions leads to correct results as far as can be determined by the above data. In other words, the method of measuring the liquid junctions here employed seems to agree with Henderson's mixing assumption.

(3) The calculations prove that our experimental results are consistent. This is important since it is good evidence that we are measuring reversible electromotive forces in all cases.

(4) The "apparent anomaly" of the sign of the liquid potentials of the junctions, KOH(0.1), KCl(m) | KCl(sat) | KOH(0.1), is shown to be in accord with calculations by the general equation.

(5) It is shown that the thermodynamic liquid junction calculation cannot be used to prove or disprove the validity of postulates I and II. Our earlier conclusions on the question of the independent ion activities depend only on the conviction that unless these postulates are an approximation, the distribution of the curves in Fig. 1 would not be observed. This is a point which we have had in mind from the beginning of these investigations.

(4) *Comparison with the Results of the General Theory of Debye and Hückel:*

In a recent publication, Hückel[1] has considered the problem of the individual ion activity coefficients in the light of his extension of the theory of Debye and Hückel[2], and as a result has found a qualitative but not a quantitative agreement with the postulate of the additivity of the relative partial free energies of the ions of the alkaline chlorides and hydrochloric acid. In view of the difficulty in obtaining the individual activity coefficients by direct measurement which certainly has been made obvious by the preceding discussion of the liquid junction potentials, this qualitative agreement is encouraging. It will therefore be of considerable interest to compare the results obtainable

[1] Physik. Z., 26, 93 (1925).
[2] Physik. Z., 24, 185 (1923).

from Debye and Hückel's theory with those derived by means of our postulates. To do this, we shall calculate the chloride ion activity coefficients of the chlorides by Hückel's general equations.

Following Hückel's procedure, we let

$$\log f_{Cl} = \log f^{\circ}_{Cl} + \log f^{x}_{Cl} \qquad (10)$$

where $f_{Cl}$ is equal to $a^{1}_{Cl}/N$ where $a^{1}_{Cl}$ is the activity of the chloride ion and N is mol fraction. From $f_{Cl}$, $\gamma_{Cl}$ or $a^{1}_{Cl}/m$ may be obtained by the equation

$$\log \gamma_{Cl} = \log f_{Cl} - \tfrac{1}{2} \log (1 + 0.036m). \qquad (11)^{1}$$

From equations (64), (68), and (85a) in Hückel's paper, we obtain

$$\log f^{\circ}_{Cl} = -0.354 \sqrt{\Gamma}\, 2 \left[ \frac{1}{2 x^{\circ}_{Cl}} - \frac{1}{x^{\circ 2}_{Cl}} + \frac{1}{x^{\circ 3}_{Cl}} lu\,(1 + x^{\circ}_{Cl}) \right]$$
$$+ \frac{3}{2}\left[ \frac{1}{x^{\circ 2}_{Cl}} + \frac{1}{x^{\circ 3}_{Cl}} \frac{1}{1+x^{\circ}_{Cl}} - \frac{2}{x^{\circ 3}_{Cl}} lu\,(1 + x^{\circ}_{Cl}) \right]$$
$$+ \frac{3}{2}\left[ \frac{1}{x^{\circ 2}_{M}} + \frac{1}{x^{\circ 3}_{M}} \frac{1}{1+x^{\circ}_{M}} - \frac{2}{x^{\circ 3}_{M}} lu\,(1 + x^{\circ}_{M}) \right] \qquad (12)^{*}$$

where $\Gamma$ equals $2c$, and

$$x^{\circ} = 0.232 \times 10^{8} a_i \sqrt{2c}$$

where $a_i$ is the apparent ionic diameter of the ion and c is the normal concentration.

According to equation (85b) in Hückel's paper, we obtain

$$\log f^{x}_{Cl} = 0.0194 \times 10^{-8}\, \Gamma \left[ \frac{1}{a_{Cl}} \frac{1}{1 + A_{Cl}\sqrt{2c}} \frac{\delta_M + \delta_{Cl}}{2} + \frac{\delta_{Cl}}{2} \left[ \frac{1}{a_{Cl}} \right.\right.$$
$$\left.\left. \frac{1}{1 + A\sqrt{2c}} + \frac{1}{a_M} \frac{1}{1 + A_M\sqrt{2c}} \right]\right] - 0.00225\, \Gamma^{3/2} \frac{\delta_M + \delta_{Cl}}{2} \left[ \frac{1}{2} \right.$$
$$\left. \frac{1}{[1 + A_{Cl}\sqrt{2c}]^2} + \frac{1}{2} \frac{1}{[1 + A_M\sqrt{2c}]^2} \right] + 0.000246 \times 10^{-8}\, c^2\, (\delta_M + \delta_{Cl})$$
$$\left\{ \frac{1}{a_{Cl}} \left[ \tfrac{3}{4} \frac{1}{1 + A_{Cl}\sqrt{2c}} + \frac{1}{4} \frac{1}{[1 + A_{Cl}\sqrt{2c}]^2} \right] (\delta_M + \delta_{Cl}) + \frac{2\delta_{Cl}}{a_{Cl}} \left[ \tfrac{3}{4} \right.\right.$$
$$\frac{1}{1 + A_{Cl}\sqrt{2c}} + \tfrac{1}{4} \frac{1}{[1 + A_{Cl}\sqrt{2c}]^2} \left.\right] + \frac{2\delta_{Cl}}{a_M} \left[ \tfrac{3}{4} \frac{1}{1 + A_M\sqrt{2c}} + \frac{1}{4} \right.$$
$$\left.\left. \frac{1}{[1 + A_M\sqrt{2c}]^2} \right] \right\} \qquad (13)$$

[1] Scatchard: J. Am. Chem. Soc., 47, 2098 (1925); Harned: 48, 326 (1926).

* The second member on the right of Equation (68) in Hückel's paper should be positive.

In this equation, $A_i$ equals $0.232 \times 10^8\, a_i$, and $\delta_i$ is a constant characteristic of the effect of the ion on the dielectric constant of the medium.

In this calculation, we have employed the values of the constants obtained in another paper[1]. We have assumed that both the apparent ionic diameters of the potassium and chloride ions and their $\delta$ values are identical according to the second of our postulates, and have calculated the values of $a_i$ and $\delta_i$ for the other ions upon this assumption. The values of these constants are given in Table VII. By using these constants in equation (11), (12), and (13), the values of $\gamma_{Cl}$ given in this table were calculated.

TABLE VII

Activity Coefficients of the Chloride Ion in Uniunivalent Chlorides according to Hückel's General Equations

(1) Constants

| Ion | $a_i \times 10^8$ | $\delta i$ |
|---|---|---|
| $H^+$ | 3.38 | 20.6 |
| $Li^+$ | 3.84 | 19.8 |
| $Na^+$ | 3.82 | 8.6 |
| $K^+$ | 3.38 | 3.2 |
| $Cl^-$ | 3.38 | 3.2 |

(2) $\gamma_{Cl}$

| c | $\gamma_{Cl}$ (KCl) | $\gamma_{Cl}$ (NaCl) | $\gamma_{Cl}$ (LiCl) | $\gamma_{Cl}$ (HCl) |
|---|---|---|---|---|
| 0.5 | 0.654 | 0.665 | 0.695 | 0.700 |
| 1.0 | 0.607 | 0.629 | 0.686 | 0.698 |
| 2.0 | 0.578 | 0.613 | 0.747 | 0.775 |

As a result, we find that the activity coefficient of the chloride ion is greater in the solution of the electrolyte which has the greater activity coefficient. The differences between the results from Debye and Hückel's theory and our postulate (1) correspond to 0.4, 1.5, 1.8, millivolts at 0.5 N; 0.9, 3.1, and 3.7 millivolts at 1 N; and 1.5, 6.5, and 7.5 millivolts at 2 N in the cases of sodium and lithium chlorides and hydrochloric acid solutions, respectively. To make this comparison more clear, the values of $E_H$ and $E_{OH}$ in the 0.1 M hydrochloric acid-salt mixtures and the 0.1 M hydroxide salt series have been calculated from these values of $\gamma_{Cl}$ and the results are shown plotted against the molal salt concentrations in Fig. 5. The dashed lines are the values obtained by our postulates and previously shown in Fig. 1. The full lines are those obtained by Hückel's equations.

A small difference in distribution of the curves of $E_H$ and $E_{OH}$ in the potassium and sodium chloride solutions as predicted by the two theories is noticeable. $E_H$ in the lithium chloride solution as predicted by Hückel's equation lies considerably closer to $E_H$ in the sodium chloride solutions than does the

[1] J. Am. Chem. Soc., 48, 0000 (1926).

dashed line of our earlier theory. The general similarity of distribution of these plots requires no further comment. Like calculations leading to a somewhat closer agreement were obtained for the activity coefficient of the chloride ion in the alkaline earth chloride solutions but this question need not be considered here.

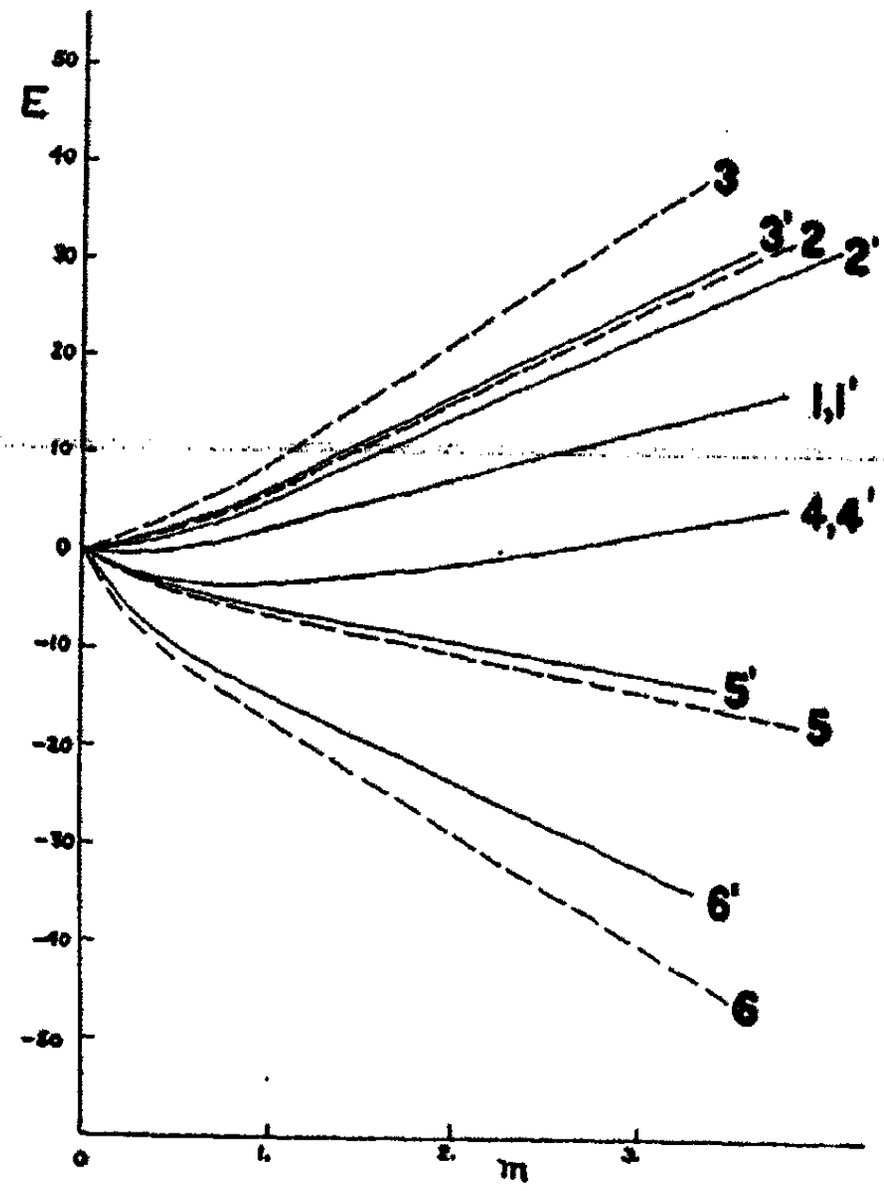



FIG. 5

Comparison of $E_H$ and $E_{OH}$ (Fig. 1) with the Values obtained by Hückel's General Equations.

1, 2, 3, 4, 5, and 6, are taken from Fig. 1.
1′, 2′, 3′, 4′, 5′, and 6′, are the curves obtained by Debye and Hückel's general theory.

| | |
|---|---|
| 1,1′ | $E_H$(HCl(0.1), KCl(m) ) |
| 2,2′ | $E_H$(HCl(0.1), NaCl(m) ) |
| 3,3′ | $E_H$(HCl(0.1), LiCl(m) ) |
| 4,4′ | $E_{OH}$(KOH(0.1), KCl(m) ) |
| 5,5′ | $E_{OH}$(NaOH(0.1), NaCl(m) ) |
| 6,6′ | $E_{OH}$(LiOH(0.1), LiCl(m) ) |

## (5) *Theoretical Considerations:*

In the last section, two series of results were compared, one of which depends on a probable conclusion based on experimental behaviors, and the other derived from a theory. It is not to be expected that the results from either of these methods are exact.

According to Debye and Hückel's theory, the difference between the activity coefficients of univalent ions of different kinds is due, firstly, to the dif-

ference in apparent ionic diameters, and, secondly, to the difference in effects of the ions of different kinds on the dielectric constant of the medium. The first of these causes turns out to be small since we find a small difference in ionic diameters of the ions here considered, and therefore this factor will be omitted in the following discussion. Hückel assumes that the dielectric constant, D, of the medium varies according to the linear law

$$D = D_o - \Sigma \delta_i c_i \qquad (14)$$

where $D_o$ is the dielectric constant of the pure solvent, $\delta_i$ is a constant characteristic of an ion of the $i^{th}$ kind, and $c_i$ is its concentration. The introduction of this equation into the theory leads to an equation for the activity coefficient of a strong electrolyte containing an approximately linear term which is found to conform with the behavior of uniunivalent and biunivalent chlorides, and hydrochloric acid in chloride solutions. D is supposed to be uniform between all the ions. That is to say the medium is considered macroscopically. $\delta_i$ is greater for the ion which appears to cause the greatest electrostriction in its immediate neighborhood. Thus, $\delta_{Li}$: $\delta_{Na}$: $\delta_K$ as 19.8: 8.6: 3.2 which is the order of their hydration values[1], a possible measure of electrostriction. This fact would suggest that the change in dielectric constant of the medium is not uniform but is greater in the immediate environment of the ions, or in the regions where the greatest electrostriction would occur, and that when we consider the individual activities, it may be necessary to take a microscopic point of view. According to this theory the variation of these microscopic dielectric constants would be expressed by

$$D_1 = D_o - \delta_1' c \; ; D_2 = D_o - \delta_2' c,$$

and these should be employed separately in calculating the individual ion activities of a uniunivalent electrolyte. Such a theory would lead to a result in conformity with our postulates. But this theory is seen to be an extreme point of view since it requires a change in dielectric constant of the solvent in the immediate neighborhood of the ions while the intermediate solvent is not influenced. Further, in mixtures at the same total concentrations, or total chloride ion concentration, this theory would require that as the cation concentrations were varied, the values of the dielectric constants in the immediate neighborhood of the cations should vary with changing cationic concentrations while that in the neighborhood of the chloride ion would not be influenced. Such a condition would not be expected to be strictly valid.

There is another important consideration which indicates that the true values lie between those calculated by the postulate of additivity and those predicted by Hückel's theory. Equation (14) cannot be valid in very concentrated solutions of electrolytes such as hydrogen, lithium, or calcium chlorides because the calculated $\delta$ — values are so high for these electrolytes that the dielectric constant, D, would pass through 0 and become negative in the neighborhood of 4M lithium chloride and 2M calcium chloride, a condition

[1] Washburn: J. Am. Chem. Soc., 31, 322 (1909); 35, 751 (1913); 37, 694 (1915).

which is obviously an impossibility. If the general idea of the theory of Debye and Hückel is correct, that is to say that the dielectric constant change is the important factor in the concentrated solutions, then $\delta_i$ of the ions such as lithium, hydrogen and calcium ions and also the chloride ions must decrease with increasing concentration. Such a decrease would bring the results of Hückel's into closer agreement with those predicted by the postulate of additivity.

Looked at in this way, it would seem that both "the hypothesis of the independent ion activities" and Hückel's theory are extreme points of view. The first would require only a change in dielectric constant with changing electrolyte concentration in the immediate environment of the ion, the intermediate solvent not being influenced, and the second assumes a uniform dielectric between the ions. Such considerations would lead us to expect that the values of the individual ion activity coefficients should be somewhere between those predicted by these two theories. We have considered this question from the narrow point of view that the dielectric constant is the only factor to be considered. A similar argument could have been made if we had considered another factor or group of factors which would account numerically for the behaviors of these concentrated solutions.

Neither of these theories should be applied to solutions of ions other than the alkaline, alkaline earth metal, hydrogen and halide ions, which are characterized both by their simplicity and the symmetrical space distribution of electron orbits. The more complex ions such as $NO_3^-$, $SO_4^{--}$ or the unsymmetrical ions such as $OH^-$ do not conform to the principle of additivity or to Debye and Hückel's theory unless some further factor be introduced.

## Summary

(1) Measurements of cells of the types

$$H_2 \mid HCl(m_o),MCl(m) \mid KCl(sat) \mid Hg_2Cl_2 \mid Hg$$
$$H_2 \mid MOH(m_o),MCl(m) \mid KCl(sat) \mid Hg_2Cl_2 \mid Hg$$

have been revised, completed, and tabulated.

(2) These data have been considered from the point of view of "the hypothesis of the independent ion activity coefficients".

(3) A comprehensive study of the general thermodynamic method of computing liquid junction potentials has been made.

(4) The results from the "hypothesis of the independent ion activities" are compared with those obtained from Hückel's extension of the Debye and Hückel theory.

*Philadelphia, Pa.*

95-174
34-84

# THE NATURE OF THE STRUCTURE OF CELLULOSE AND ITS SIGNIFICANCE IN CHEMICAL TRANSFORMATIONS*

BY R. O. HERZOG

In the first part of the present paper the previous X-ray spectrographic investigations[1], carried out with untreated and mercerised cellulose respectively, have been controlled, and new evidence obtained as to the behavior of cellulose in the magnetic and electric field.

Further, the results of X-ray analysis of certain derivatives of cellulose (cellulose nitrate and cellulose acetate) are described.

In the second part, a parallel is drawn between the dimensions of crystallites of cellulose and of its derivatives, and the particles found in colloidal solution, and evidence of a relation between the size of particles and the size of molecules is brought forward.

## PART I

### *X-Ray Spectrographic Investigation of Cellulose*
### (*Carried out with W. Jancke*)

It has been clearly shown, that cellulose, in its natural condition, consists of aggregates of crystallites as found in the bast fibres, seed hairs, and other plant[2] tissue as well as in the animal body (Tunicin)[3]. In the bast fibres, the crystallites are often arranged with one crystal-axis in the fibre-axis, or, (at any rate those of the same layer) at a definite angle to it; in cotton, they are—with respect to this axis—twisted spiral-like, etc; it may be said with some degree of certainty that the observations made by means of double refraction, and interpreted on the basis of Nägeli's micellar hypothesis,[4] or by the theory of Wiener[5] are completely confirmed by X-ray spectrography.

It is also possible to use the experimental data obtained in the present investigation for a revision of the determination of the crystalline system of cellulose. Since among the bast fibres, ramie, hemp, Titaric[6], broom, and mulberry-tree show the best defined interferences, and the ratio of the distances of these on the equator are identical within the limits of experimental error, these fibres, in addition to that of cotton, were chosen as suitable objects for investigation. In Table I $A_1$ $A_2$ . . . indicate the interference points on the equator of the sphere, I, II, III, IV, etc., those on the corresponding

---

* Contribution from the Kaiser Wilhelm-Institut für Faserstoffchemie, Berlin-Dahlem.

[1] Z. angew. Chem. **34**, 385 (1921).

[2] Ber. **53**, 2162 (1920); Naturw. **12**, 955 (1924).

[3] Z. physiol. Chem. **141**, 63 (1924).

[4] Sitzungsber. Akad. Wiss. München, **9**, 389 (1879).

[5] Pogg. Ann., **118**, 79 (1863).

[6] A tropical bast fibre placed at our disposal, the exact nature of which it was impossible to ascertain.

hyperbola (layer-lines). Figure 1 shows the crystallographic indices of the points according to Polanyi[4].

The second column records the intensity of the interference spots v.str. = very strong; st. = strong; m. = moderate; w. = weak; v.w. = very weak). D/2 denotes the observed angle of reflection. (Glanzwinkel).

TABLE I

Observed point-positions for natural cellulose using vertical incidence. (Average value)

| Point | Intensity | $\sin^2 \theta/2$ | Possible error of $\sin^2 \theta/2 \pm$ u. $10^{-4}$ |
|---|---|---|---|
| $A_1$ | str. | 0,01675 | 3 |
| $A_2$ | m. | 0,02105 | 3 |
| $A_3$ | w. | 0,03210 | 3 |
| $A_4$ | v.str. | 0,03923 | 3 |
| $A_5$ | m. | 0,1600 | 9 |
| $I_1$ | w. | 0,01296 | 10 |
| $I_2$ | m. | 0,08940 | 17 |
| $I_3$ | w. | 0,1142 | 30 |
| $II_1$ | str. | 0,03260 | 6 |
| $II_2$ | s. | 0,06480 | 7 |
| $II_3$ | s. | 0,07070 | 8 |
| $II_4$ | v.w. | 0,1335 | 40 |
| $II_5$ | v.w. | 0,1683 | 80 |
| $III_1$ | m. | 0,0604 | 20 |
| $III_2$ | m. | 0,0690 | 8 |
| $III_3$ | str. | 0,0894 | 10 |
| $III_4$ | w. | 0,1332 | 30 |
| $III_5$ | w. | 0,1455 | 60 |
| $IV_1$ | w. | 0,1102 | 18 |
| $IV_2$ | str. | 0,1295 | 7 |
| $IV_3$ | w. | 0,1710 | 20 |

Calculations made from these values together with certain other considerations[1], which are reported elsewhere, point to rhombic symmetry. We obtain from these values the quadratic equation

$$4 \sin^2 \theta/2 = 0{,}03210\, h^2 + 0{,}03923\, k^2 + 0{,}02275\, l^2$$

[1] Naturw., 12, 956 (1924).

[2] With monoclinic symmetry, a considerable splitting off of points is to be expected but does not occur. Also it is not possible to include the points $A_1$ up to $A_4$, within the limits of experimental error.

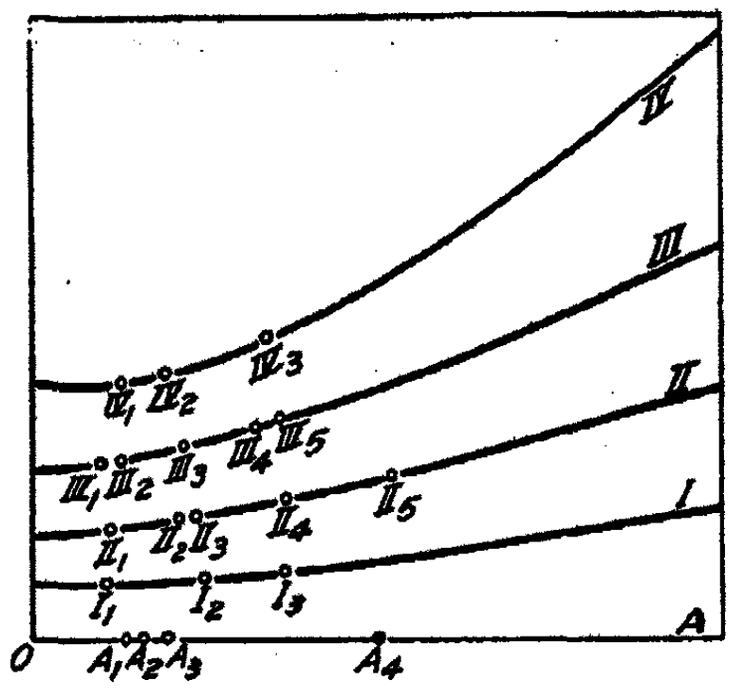



FIG. 1

*Diagram of the Cellulose Interference Points in One Quadrant.*
O = Point of penetration of the X-ray beam
A = Equator
I, II, III, IV = Layer-lines (hyperbola)
$A_1$, $A_2$, $A_3$, etc. = Positions of interferences.

## TABLE II

Rhombic form for 4 molecules

| Point | $\sin^2 \theta/2$ observed | $\sin^2 \theta/2$ calculated | Indices |
|---|---|---|---|
| $A_1$ | 0,01675 | 0,01783 | 110? |
| $A_2$ | 0,02105 | — | — |
| $A_3$ | 0,03210 | 0,03210 | 200 |
| $A_4$ | 0,03923 | 0,03923 | 020 |
| $A_5$ | 0,1600 | 0,1569 | 040? |
| | | 0,1605 | 330 |
| $I_1$ | 0,01296 | 0,01371 | 101 |
| $I_2$ | 0,08940 | 0,08772 | 311 |
| $I_3$ | 0,11420 | 0,11714 | 321 |
| $II_1$ | 0,03260 | 0,03255 | 012 |
| $II_2$ | 0,06480 | 0,06466 | 212 |
| $II_3$ | 0,0707 | 0,0700 | 122 |
| $II_4$ | 0,1335 | 0,1342 | 322 |
| $II_5$ | 0,1683 | 0,1610 | 412 |
| $III_1$ | 0,06040 | 0,05921 | 103 |
| $III_2$ | 0,06900 | 0,06902 | 113 |
| $III_3$ | 0,08940 | 0,09040 | 023 |
| $III_4$ | 0,1332 | 0,1332 | 313 |
| $III_5$ | 0,1455 | 0,1395 | 133 |
| $IV_1$ | 0,1102 | 0,1088 | 114 |
| $IV_2$ | 0,1295 | 0,1302 | 024 |
| $IV_3$ | 0,1710 | 0,1730 | 314 |

$A_1$, however, does not fall within the limits of experimental error, and the same is true of $A_2$; (110) lies between the 2 points, and closer to $A_1$. It is probable that these discrepancies are due to impurities in the cellulose. Moreover, it appears that the deviations between the calculated and observed values of $\sin^2 \theta/2$ are within the limits of experimental error (strong deviations only at weak intensities).

From the above quadratic equation the following values for the lengths of the edges of the crystallographic unit-cell may be calculated, and these agree fairly well with the numbers previously reported.

$$a = 8{,}60 \cdot 10^{-8} \text{ cm},$$
$$b = 7{,}78 \cdot 10^{-8} \text{ cm},$$
$$c = 10{,}22 \cdot 10^{-8} \text{ cm}.$$

Hence the volume V is $684 \cdot 10^{-24}$ cm$^3$, and from the equation

$$\frac{M.n}{N.s} = V,$$

(where M is the molecular weight, $(C_6H_{10}O_5) = 162$; N, Avogadro's number, $= 6{,}06 \cdot 10^{23}$; s the density of cellulose $= 1{,}52$; and $n$ the number of $(C_6H_{10}O_5)$ — groups united in the cell) it follows, that $n = 3{,}9$; in other words, there are 4 $(C_6H_{10}O_5)$ groups in the unit-cell, as already calculated by Polanyi from our previous measurements. (Error $\pm$ 2, 7%)[1].

It has been previously mentioned (l.c.), that with so-called "oblique" photographs, i.e. where the preparation is inclined relative to the X-ray beam, 2 interferences occur, at variance with the calculated value. But a number of other anomalies (splitting off, etc.) are also found. These may be accounted for by assuming the presence of more than one substance—as for example two modifications, which are chemically quite similar. A further explanation is possibly to be found in certain physical phenomena such as the tension produced in the crystallites during their growth. Various factors seem to indicate that both assumptions are probably correct.

### *X-Ray Analysis of Mercerised Cellulose*

When cellulose fibres are mercerised by treating with a strong solution of caustic soda, they give, after removal of the sodium hydroxide with water, a

---

[1] If a greater unit cell, for example one with 16 $(C_6H_{10}O_5)$ groups is assumed to exist, the calculated results are in no better agreement than those tabulated above. But in this case only 27% of the possible interferences are observed, as compared with 72% for 4 $(C_6H_{10}O_5$ radicals). From the evaluation of Debye-Scherrer-diagrams, O. L. Sponsler assumes cellulose to have a tetragonal form. However sufficient reliability as to the position of the interference spots cannot be secured on this basis. Sponsler in fact has only taken into consideration the strongest interferences; the weak ones do not fit in with the quadratic equation.

A quadratic equation for hexagonal symmetry can with good approximation be given, assigning 32 $(C_6H_{10}O_5)$ to the unit cell:

$$4 \sin^2 \theta/2 = 0{,}005135 (H^2 + k^2 - hk) + 0{,}02275 l^2.$$

in which case only 25% of the possible positions of points are found.

point-diagram somewhat different from that of the original cellulose, and this difference becomes more pronounced the more complete the mercerisation. This holds especially for fibres which are prevented from shrinking by carrying out the mercerising under tension. With fibres mercerised without tension, distortion of the particles soon occurs, and the interference points degenerate into indistinct arcs. It is possible to follow the progress of the mercerisation by X-ray spectrography.

On the equator, the points $A_3$ and $A_4$ exhibit a very different ratio of intensities. This ratio of about 1:5 for untreated cellulose, is changed to 1:2 during the initial stage of mercerisation (i.e. when about 8% sodium hydroxide solution is employed); the positions of these and other interferences of the fibre diagram remain the same. It can even be stated that with only slight mercerisation all points stand out more distinctly, an advantage which is lost and reversed by stronger mercerisation. With the latter, using a concentration of sodium hydroxide of 14% (or a little above) at room temperature, the ratio of the intensities of the points $A_3$ and $A_4$ is further altered, but in this case the positions of their interferences also change, the points moving closer to the point of penetration of the primary beam. With total mercerisation, (by means of 28% or even stronger sodium hydroxide solution), the ratio of the above named points, which are now to be named $B_3$ and $B_4$, is found to be 1 : 1, these being still closer to the point of penetration.

The equatorial points $A_1$ and $A_2$, which as we have already stated, do not fit in with the quadratic equation, are weakened in intensity by progressive mercerisation and finally disappear completely. They also seem to change their positions, in the sense that they move simultaneously somewhat apart.

Only in the final stage of total mercerisation does a new point, $B_0$, appear on the equator, and this is closer to the point of penetration than any of the other interferences observed, but it does not fit in with any quadratic equation appropriate to mercerised cellulose.

The points on the hyperbola are much weakened in intensity by strong mercerisation, and they move in a manner such that the origin of the hyperbola on which they lie, moves away from the point of penetration.

Table III throws some light on the alteration of the intensities and the displacement of the positions of the most important points. In this table, the various stages of mercerisation are indicated as follows: 0 = untreated; 1 = treated with weak sodium hydroxide solution (8 – 10%); 2 = treated at a concentration of about 14%; 3 = totally mercerised (use of a sodium hydroxide solution of 28% or above).

As all weaker points of the original cellulose diagram gradually disappear with progressive treatment, and only the most intense remain measurable, we have only these few available for the purpose of deriving the quadratic equation for mercerised cellulose.

## Table III

List of the most essential Point-Positions, and their intensities, with progressive mercerisation.

| Point | Stage of treatment | $\theta/2$ | Intensity | $\sin^2\theta/2$ observed | Error | $\sin^2\theta/2$ calculated (totally mercerised.) |
|---|---|---|---|---|---|---|
| — | 0 | — | — | — | — | — |
| — | 1 | — | — | — | — | — |
| — | 2 | — | — | — | — | — |
| $B_0$ | 3 | 6° 8,5′ | w. | 0,01143 | 0,0004 | ? |
| $A_1$ | 0 | 7° 26′ | str. | 0,01675 | 0,0003 | |
| ” | 1 | ” | m. | ” | ” | |
| ” | 2 | 7° 19′ | w. | 0,01623 | ” | |
| — | 3 | — | — | — | — | |
| $A_2$ | 0 | 8° 20′ | m. | 0,02103 | 0,0003 | |
| ” | 1 | ” | m. | ” | ” | |
| ” | 2 | 8° 28′ | w. | 0,02170 | ” | |
| — | 3 | — | — | — | — | |
| $A_3$ | 0 | 10° 19′ | w. | 0,03210 | 0,0003 | |
| ” | 1 | ” | m. | ” | ” | |
| ” | 2 | 10° 14′ | str. | 0,03160 | 0,0004 | |
| ” = $B_3$ | 3 | 10° 6,5′ | str. | 0,03080 | ” | 0,03080 |
| $A_4$ | 0 | 11° 25,5′ | v.str. | 0,03923 | 0,0003 | |
| ” | 1 | ” | str. | ” | ” | |
| ” | 2 | 11° 12′ | str. | 0,03760 | 0,0004 | |
| ” = $B_4$ | 3 | 11° 2′ | str. | 0,03660 | ” | 0,03660 |
| $II_1$ | 0 | 10° 24′ | str. | 0,03260 | 0,0006 | |
| ” | 1 | ” | str. | ” | ” | |
| ” | 2 | 10° 31′ | m. | 0,03330 | ” | |
| ” | 3 | 10° 33′ | w. | 0,03350 | ” | 0,03345 |
| $III_3$ | 0 | 17° 24′ | str. | 0,08940 | 0,0010 | |
| ” | 1 | ” | m. | ” | ” | |
| ” | 2 | 17° 32′ | w. | 0,09080 | ” | |
| ” | 3 | 17° 35′ | v.w. | 0,09120 | ” | 0,09127 |
| $IV_d$ | 0 | 17° 34′ | v.str. | 0,09100 | 0,0008 | |
| ” | 1 | ” | v.str. | ” | ” | |
| ” | 2 | 18° 1′ | m. | 0,09580 | 0,0020 | |
| ” | 3 | 18° 4′ | w. | 0,09620 | ” | 0,09720 |

Assuming a unit-cell with four molecules, and rhombic symmetry, the quadratic equation is given by:

$$4 \sin^2 \theta/2 = 0{,}03080\, h^2 + 0{,}03660\, k^2 + 0{,}02430\, l^2$$

From this quadratic equation a: b: c = 8,88: 8,05: 9,88 is obtained, and the volume V of the unit-cell is seen to be 706 sq. Å.U., a value in exact agreement with that computed from the molecular weight (704).

As already stated, the new point $B_0$ does not fit in with this form, and is therefore due to the presence of another substance. Possibly it is also related to the points $A_1$ and $A_2$ which have disappeared, and which likewise could not be classified. The alteration of the intensities of the points $B_3$ and $B_4$, as compared with those of $A_3$ and $A_4$, (unless attributed to distension), forces one to the conclusion that the lattice planes are now otherwise occupied.

For the sake of comparison, we have also examined a sample of β-cellulose, prepared from wood cellulose by dissolving in NaOH and reprecipitating, this procedure being repeated three times. The values obtained with mercerised cellulose and with this β-cellulose are shown in the following Table IV (w = weak; str. = strong).

TABLE IV

| Mercerised cellulose | β-cellulose |
|---|---|
| 6° 8′ w. | 6° 3′ w. |
| 10° 6′ str. | 10° 1′ str. |
| 11° 2′ str. | 10° 56′ w. |
| 14° 19′ w. | 14° 14′ w. |
| 17° 50′ w. | 17° 30′ w. |
| 20° 20′ w. | 20° 25′ w. |

By comparing the dimensions of the unit-cells of the untreated and mercerised cellulose, it appears that the distance along the direction of the fibre has diminished from 10,22 to 9,88 Å.U. This means a contraction of 3% along the direction of the fibre. An even higher value has actually been observed during mercerisation. The horizontal dimensions, however, increase from 8,60 to 8,88 and from 7,78 to 8,05 Å.U.

That the points of mercerised cellulose, as well as the interferences of untreated cellulose do in fact fit in with a rhombic form of the same kind, enhances the probability of the accuracy of this form.

If the dimensions of the crystallites of the untreated cellulose are calculated according to Scherrer's[1] equation from the breadth of suitable interference spots, measured between points at which the intensity has decreased to half of its maximum value, two values, viz., 117 and 66 Å.U. are obtained as maxima. Since marked differences in the intensity of the interference spots do not exist, we may conclude that the third value is substantially the same.

[1] Zsigmondy: "Kolloidchemie", Appendix (1920).

*Behavior of Natural and Artificial Cellulose Fibres in the Magnetic and Electric Field.*

Bast fibres proved to be diamagnetic, but bundles of fibres arranged parallel behave like irregular crystals.

In the present investigation parallel-arranged fibres were formed by attaching them to thin plates by means of a solution of gum arabic and then, after hardening, making them plane parallel by strong pressure.

From these plates, thin circular disks 8 mm in diameter were punched by means of a very accurately worked punch, the centres of the disks being simultaneously pierced by a needle, inserted centrally into the punch, so that the plates could be easily attached to the lower end of a straight glass filament about 10 cm in length and 0,5 mm in thickness. To the upper end of the glass-filament, which was suspended on a thin cocoon filament, 30 cm in length, small mirrors of silver-plated cover-glass (about $1 \times 4$ mm) were cemented, by means of which the deflections and vibrations in all positions of adjustment could be optically observed. The suspension itself was found to be quite satisfactory. The disks under investigation had a mean weight of about 20 mg. They may be regarded as monaxial crystal-plates. They are also to be considered as rather homogeneous, since the embedding medium, gum arabic, was found to have, in the solid state, a refractive index $n_D = 1.51$ as compared with a mean value $n_D = 1.55$ for bast and artificial fibres.

In the magnetic, as well as in the uniform electric field, the orientation of the fibres was parallel to the lines of force.

The difference of the magnetic susceptibilities $(x-x')$ was computed according to Graetz[2]; $t_o$ and $t$ are the times of vibration without and within the field, respectively. The field of force was $3{,}25.10^3$ Gauss.

The electric measurements were carried out in an homogeneous alternating field of 220 v and 50 cycles, with the pole-plates at a distance of 1,2 cm. $E_2$ and $E_1$ are the dielectric constants, parallel and perpendicular to the optical axis, respectively.

Table V gives a survey of our experimental results, the optical measurements being also listed. $n_{D_1}$ and $n_{D_2}$ denote the refractive indices with the fibre orientated parallel and perpendicular to the plane of polarisation, respectively.

Table V illustrates the parallelism between the various values characteristic of anisotropy and are in remarkable agreement with the results of our X-ray investigations[3].

The turning moment in the electrical field is so strong that this method may possibly prove of practical value for technical purposes, such as, for example, a method of control in artificial silk manufacture.

---

[1] See J. Pauksch: Akad. Wiss. Wien, Math.-Naturwiss. Kl., 115, I, 553 (1906).
[2] "Handbuch der Elektrizität und des Magnetismus", 4, 829.
[3] Kolloid-Z., 35, 201 (1924).

TABLE V

Magnetic measurements

| | $\left(\frac{1}{t^2}-\frac{1}{t_0^2}\right)$ | mean error ± | $(x-x').10^6$ | mean error % |
|---|---|---|---|---|
| ramie | 0,581 | 0,0110 | 0,066 | 1,9 |
| cuprammonium silk | 0,224 | 0,0115 | 0,025 | 5,1 |
| viscose I | 0,213 | 0,0093 | 0,024 | 4,4 |
| viscose II | 0,090 | 0,0069 | 0,010 | 7,7 |
| viscose film (32% stretched) | 0,062 | 0,0077 | 0,007 | 12,5 |
| viscose film (20% stretched) | 0,039 | 0,0083 | 0,004 | 21 |

Dielectric measurements

| | $\left(\frac{1}{t^2}-\frac{1}{t_0^2}\right)$ | mean error ± | $E_2-E_1$ | mean error % |
|---|---|---|---|---|
| ramie | 0,120 | 0,004 | 4,84 | 10 |
| cuprammonium silk | 0,063 | 0,003 | 2,54 | 10 |
| viscose I | 0,062 | 0,002 | 2,50 | 4,7 |
| viscose II | 0,047 | 0,002 | 1,90 | 2,9 |
| viscose film (32% stretched) | 0,027 | 0,003 | 1,17 | 4,9 |
| viscose film (20% stretched) | 0,019 | 0,002 | 0,77 | 3,0 |

Optical measurements[1]

| | $n_{D_2}$ | $n_{D_1}$ | Double refraction |
|---|---|---|---|
| ramie | 1,5879 | 1,5331 | 0,0548 |
| cuprammonium silk | 1,5595 | 1,5249 | 0,0346 |
| viscose I | 1,5560 | 1,5221 | 0,0339 |
| viscose II | 1,5442 | 1,5273 | 0,0169 |
| viscose film (32% stretched) | — | — | 0,0115 |
| viscose film (20% stretched) | — | — | 0,0064 |

[1] The specific double refraction of the stretched films was determined by means of the Babinet compensator, that of the artificial silk by Becke's method.

*Röntgenspectrographic Investigation of Cellulose Nitrate and Cellulose Acetate.*
*(Carried out with Th. Nickl.)*

According to Hermann Ambronn[1] stretched cellulose nitrate films are doubly refractive, while X-ray investigations indicate an amorphous structure. In agreement with Hans Ambronn[2] it was only found possible to detect a crystalline structure in the case of a nitrocellulose prepared under conditions in which the fibrous structure was maintained and which had not been subjected to any process of solution. The same result was also found with cellulose acetate.[3]

The X-ray investigation of nitrated and of acetylated hemp fibre points to the conclusion, that these two derivatives of cellulose most probably crystallize in the rhombic system.

The dimensions of the unit-cells are approximately as follows:

| | (a) cellulose nitrate | (b) cellulose acetate |
|---|---|---|
| a = | 10,1 Å.U. | 9,2 Å.U. |
| b = | 8,6 Å.U. | 7,1 Å.U. |
| c = | 10,8 Å.U. | 9,8 Å.U. |

Hence v = 935 cubic Å.U. and v = 636 cubic Å.U. for (a) and (b) respectively.

*It is evident, that the values differ but little from each other and from those found for untreated cellulose.* (see p. 460). *This is obviously the fundamental condition for the possibility of a topochemical reaction.*

Fibres obtained from a denitrated cellulose nitrate and from a saponified cellulose acetate, both nitrate and acetate originally prepared from untreated cellulose, yield the diagram of the untreated cellulose, while the corresponding fibres obtained from mercerised fibres, instead of untreated cotton, show the diagram of mercerised cellulose (cellulose hydrate). In spite of this remarkable result, decisive conclusions cannot as yet be drawn as to whether the change produced by mercerisation is to be interpreted from a 'chemical' or 'physical' point of view.

The lengths of the edge of the crystallites of cellulose nitrate appear to be 100 and 58; of cellulose acetate 111 and 61 Å.U., that is about the same value as found for cellulose.

## PART II

*Effect of Previous Treatment on the Size of Particles of Dissolved Cellulose Nitrate*
*(Carried out with D. Krüger).*

It has long been recognized and was pointed out in Part I, of the present communication, that the nitration of cellulose fibres can easily be carried out in such a way that the fibrous structure remains unchanged. From various experiments it seemed probable that these and other chemical transformations

[1] Kolloid-Z., 18, 99, 222 (1916); 20, 173 (1917): Z. Mikrosk., 32, 43 (1915); Nachr. Göttingen ges. math.-phys. Kl. (1919).
[2] Dissertation. Jena (1914).
[3] Ber., 57, 329, 750 (1924); E Möhring: Wiss. und Ind., 2, 70 (1923).

of cellulose actually take place within the structural unit of each crystallite, partly without alteration in the mutual arrangement of the crystallites. It has been shown in Part I that in spite of chemical interaction, neither the dimensions of the unit-cell nor those of the crystallites are markedly changed. It is of equal importance to show that in colloidal dispersions the *size of particles is identical with that of the original crystallites*. It follows from this that primarily, the process of dispersion consists only in a separation of the crystallites.

A large number of celluloses of different origin and pre-treatment have been carefully nitrated, washed, dried, etc., and then dissolved in acetone or other solvents, the influence of the "process of dissolving" being studied separately.

The determination of the size of the particles in colloidal solution was carried out by free diffusion into the solvent.

The diameters of the particles, which may be approximately regarded as spheres, were calculated on the one hand from the formula given by Einstein[1]; on the other hand from the semi-empirical relation $M\sqrt{D} = 7$. (M = molecular weight; D = coefficient of diffusion in aqueous solution at 20°C)[2], the observed D being corrected for 20°C and converted to the value for aqueous solutions by means of the ratio of the viscosities of the solvent actually used to that of pure water.

The calculation of the diameter of the particles is based on the assumption of spherical particles and accomplished by the customary procedure from Avogadro's number N.

In Table VI; D is the coefficient of diffusion determined at 13°C, $2\rho_1$ and $2\rho_2$ the diameters computed according to Einstein's law and from the square root relation, respectively.

The table shows that with products of different origin, the size of particles is approximately of the same order, a conclusion based on the dimensions of the crystallites in the fibre.

Further it follows that a short grinding of cellulose in the beating-engine brings about a considerable reduction in the size of particles in the solution of cellulose nitrate.

The treatment of cellulose with reagents such as strong acid or alkali, results in a decreased size of particles in the solution of cellulose nitrate. The size of particles, as found in the case of viscose silk after nitration, corresponds approximately to the reduction in size, which takes place during the "dre-ripening" in the manufacture of viscose silk, i.e. the mercerisation process.

The values of $2\rho_1$ found are about 2 to 3 times those of $2\rho_2$. If the $2\rho_2$-value of the dissolved cellulose nitrate from hemp is compared with those calculated from the breadth of the interference blackening of hemp fibre and nitrated

[1] Ann. Phys., (4) 19, 303 (1906).
[2] L. W. Oeholm: Medd. Vetenskaps. Nobel-Institut, 2, Nr. 23 (1912).

TABLE VI

Size of particles of cellulose nitrate prepared from various celluloses.

| Material | | Solvent | D | $2\rho_1$[1] | $2\rho_1$[1] |
|---|---|---|---|---|---|
| cotton | (as nitrate) | acetone | 0,035 | 300 Å.U. | 94 Å.U. |
| " | " | methylethyl-keytone | 0,023 | 340 " | |
| hemp | " | " | 0,039 | 200 " | 74 " |
| ramie | " | " | 0,042 | 186 " | 66 " |
| flax | " | " | 0,043 | 182 " | 66 " |
| sulphite-cellulose | " | " | 0,045 | 174 " | 64 " |
| viscose silk | " | " | 0,053 | 148 " | 56 " |
| hemp, ground 25 min. in the beating-engine | " | " | 0,075 | 104 " | 44 " |
| cotton, mercerised 3-4 hrs. | " | " | 0,043 | 182 " | 66 " |
| cotton, mercerised 70 hrs. | " | " | 0,085 | 88 " | 41 " |
| cotton, treated with 50% $H_2SO_4$ 2 hrs. at room temperature | " | " | 0,039 | 200 " | 68 " |
| cotton, treated with 50% $H_2SO_4$ 20 hrs. at room temperature | " | " | 0,059 | 132 " | 52 " |

hemp cellulose, the agreement is strikingly good, as is shown by the following table:

Dimensions of crystallites of hemp fibre: 117 and 66 Å.U.

Dimensions of crystallites of cellulose nitrate from hemp (solid state): 100 and 58 Å.U.

Diameter of colloidal particles of nitrated hemp fibre (dissolved) 74 Å.U.

This result shows, as stated above, that the chemcial transformation is accomplished within the complex of atoms united in the crystallite, without the latter undergoing disintegration to single ($C_6H_{10}O_5$) groups, and is thus in complete agreement with the results of X-ray analysis. *It is thus possible, from the dimensions of colloidal particles as found in solutions of cellulose nitrate to determine the size of the original crystallites of cellulose.*

[1] In order to make the diameters of particles of cellulose nitrate and the length of crystallites of cellulose directly comparable with each other, the values of $2\rho_1$ and $2\rho_2$ quoted above are to be divided by $\sqrt[3]{\frac{M_1V_1}{M_2V_2}} = 1,2$. ($M_1$, $M_2$ and $V_1$, $V_2$ denoting the molecular weight and the molecular volume of cellulose nitrate and of cellulose, respectively.

## Summary

1. The results of the Röntgenspectrographic investigation of cellulose are given, and the observed values compared with those calculated from the quadratic equation for rhombic symmetry, assuming the unit-cell to consist of four ($C_6H_{10}O_5$) groups.

It is shown that rhombic symmetry and the adopted size of unit-cell are in better agreement with the experimental data than any other assumption.

2. The quadratic equation for mercerised cellulose is given.

3. The dimensions of crystallites of natural cellulose fibres have been determined.

4. It is shown that the behavior of bast fibres in both the magnetic and the electric field runs completely parallel to the results of optical measurements and X-ray investigations.

5. The X-ray investigation of cellulose nitrate and cellulose acetate indicates that the dimensions of these derivatives differ but little from those of the original untreated cellulose.

It has been pointed out that this fact is a necessary condition for assuming a topochemical reaction.

6. Cellulose fibres obtained by the denitration of a cellulose nitrate and from the hydrolysis of a cellulose acetate (both of them being prepared from an untreated cellulose) give the diagram of the latter. On the other hand, cellulose regenerated from esters prepared from a mercerised cotton give the diagram of cellulose hydrate.

7. The dimensions of the crystallites of nitrated and acetylated hemp cellulose are given, the esterification being carried out as carefully as possible, and under conditions in which the fibrous structure is maintained.

8. *The size of particles in colloidal solutions of cellulose nitrate as determined by the diffusion method corresponds exactly to the dimension of crystallites, computed from the X-ray diagram.*

9. The size of particles of cellulose of various origin and pre-treatment is given.

# THE THERMAL DECOMPOSITION OF FORMIC ACID

BY WM. L. NELSON AND C RL J. ENGELDER

In some investigations on formic acid recently carried out in this laboratory, it became necessary to study the thermal decomposition of this acid without the intentional addition of catalysts, in reaction tubes of various materials, over a temperature range from 250° to 550°C. Formic acid in its decomposition is so sensitive to catalytic influence that it was to be expected that the walls of the reacting vessel would reveal a specific effect and largely influence the course of the reaction. More extensive studies of this kind have recently been reported by Hinshelwood and his co-workers, who studied the decomposition in bulbs of various glasses and with platinum, palladium, silver, and titanium dioxide as catalysts at temperatures up to 350°C. Reference to their work will be made later. Muller and Peytral[1] passed the vapors of formic acid through a small platinum tube at 1150°C and concluded that the primary decomposition was into $CO_2$ and $H_2$.

## Experimental

The apparatus used in the experiments here recorded was substantially the same as that used in catalytic work of this kind. The vapor of formic acid was passed through the various tubes inserted in the hollow core of an electrically heated furnace, the liquid products condensed, and the gases collected over a saturated salt solution on top of which was a layer of heavy paraffin oil.

The formic acid, prepared by three vacuum distillations of 85% acid over anhydrous copper sulfate, was practically anhydrous, and had a specific gravity of 1.22. The flow of acid through the reaction tubes, accurately controlled by the method of displacement by mercury[2], was maintained uniformly at the rate of three cc. per hour. The acid was vaporized in a preheater maintained at a temperature somewhat above the boiling point of the acid.

The furnace was built upon a grooved silica tube, 24″ long and 1″ diameter, wound with nichrome wire and insulated with alundum and kieselguhr. The furnace was maintained at the desired temperatures by means of a Leeds and Northrup Thermo-Regulator. The reaction tubes were 30″ long and about 1″ external diameter and fitted snugly into the core of the furnace. The thermo-couple, cased in a pyrex tube, penetrated half way into the reaction tube.

Beginning at 350°C., the gaseous decomposition products were analyzed over mercury with the Hempel apparatus immediately after runs. In general, $CO_2$ was determined by absorption in potassium hydroxide and $H_2$ and CO were determined by slow combustion over mercury. Occasionally, when it seemed desirable to check up on the presence of hydrocarbons, the CO was

[1] Muller and Peytral: Bull., 29. 34 (1921).
[2] Adkins and Nissen: J. Am. Chem. Soc., 46, 140 (1924).

determined by absorption in acid cuprous chloride, and the residual gas analyzed for hydrogen and hydrocarbons by slow combustion. Only fractional percentages of saturated hydrocarbons, presumably methane, were ever found, so that it was deemed sufficiently accurate to determine, in general, only $CO_2$, CO, and $H_2$. The apparatus was always flushed by making a run of about one hour's duration before collecting and analyzing the gas mixture, yet traces of air were present, so that all analyses and volumes recorded below have been calculated to an air-free basis and corrected to N.T.P.

## Results

Representative samples of gas were analyzed for the runs at the temperatures indicated in the tables. In all cases, 3 cc. of formic acid was vaporized and passed through the reaction tube per hour. The analyses of the gas mixtures, together with the volume of gas at N.T.P. and the volumes of $CO_2$, $H_2$, and CO resulting from the decomposition of one cubic centimeter of liquid formic acid are here recorded for tubes of pyrex glass, unglazed porcelain, unetched and etched silica, and copper.

### *Pyrex Glass Tube*

Decomposition became evident at 250°C, yielding 10 cc. of gas per cc. acid. At 300°C the gas evolution reached 40 cc. per cc. acid.

| °C | Composition of Gas Mixture | | | 1 cc. Formic Acid yielded: | | | |
|---|---|---|---|---|---|---|---|
| | % $CO_2$ | % $H_2$ | % CO | cc. Total | cc. $CO_2$ | cc. $H_2$ | cc. CO |
| 350 | 49.1 | 49.1 | 1.8 | 270 | 132.6 | 132.6 | 4.8 |
| 400 | 49.6 | 48.0 | 2.4 | 580 | 287.7 | 278.4 | 13.9 |
| 500 | 45.3 | 40.3 | 14.4 | 750 | 339.7 | 302.2 | 108.0 |
| 600 | 42.5 | 39.4 | 18.1 | 910 | 386.7 | 358.5 | 164.7 |

### *Unglazed Porcelain Tube*

At 250°C. the gas evolution was 30 cc. and at 300°C it was 50 cc. per cc. acid.

| °C | Composition of Gas Mixture | | | 1 cc. Formic Acid yielded: | | | |
|---|---|---|---|---|---|---|---|
| | % $CO_2$ | % $H_2$ | % CO | cc. Total | cc. $CO_2$ | cc. $H_2$ | cc. CO |
| 350 | 49.0 | 48.7 | 2.3 | 440 | 215.6 | 214.3 | 10.1 |
| 450 | 53.4 | 43.9 | 2.7 | 910 | 485.9 | 399.5 | 24.6 |
| 550 | 53.2 | 36.9 | 9.9 | 800 | 425.6 | 295.2 | 79.2 |

### *Unetched Silica Tube*

The gas yield at 250°C was 30 cc. and at 300°C, 120 cc. per cc. acid.

| °C | Composition of Gas Mixture | | | 1 cc. Formic Acid yielded: | | | |
|---|---|---|---|---|---|---|---|
| | % $CO_2$ | % $H_2$ | % CO | cc. Total | cc. $CO_2$ | cc. $H_2$ | cc. CO |
| 350 | 50.0 | 48.4 | 1.6 | 730 | 365.0 | 353.3 | 11.7 |
| 450 | 51.3 | 47.1 | 1.6 | 980 | 502.7 | 461.6 | 15.7 |
| 550 | 50.8 | 45.6 | 3.6 | 950 | 482.6 | 432.2 | 34.2 |

*Etched Silica Tube*

The above tube was rather deeply etched with hydrofluoric acid and then used as reaction tube. Decomposition was the same at 250°C as with the unetched tube, but at 300°C the gas evolution reached 400 cc. per cc. acid.

| °C | Composition of Gas Mixture | | | 1 cc. Formic Acid yielded: | | | |
|---|---|---|---|---|---|---|---|
| | % $CO_2$ | % $H_2$ | % CO | cc. Total | cc.$CO_2$ | cc.$H_2$ | cc.CO |
| 350 | 50.2 | 49.5 | 0.3 | 940 | 471.9 | 465.3 | 2.8 |
| 450 | 51.1 | 47.5 | 1.4 | 1010 | 516.1 | 479.7 | 14.1 |
| 550 | 50.0 | 42.2 | 7.8 | 900 | 450.0 | 379.8 | 70.2 |

*Copper Tube*

| °C | Composition of Gas Mixture | | | 1 cc. Formic Acid yielded: | | | |
|---|---|---|---|---|---|---|---|
| | % $CO_2$ | % $H_2$ | % CO | cc. Total | cc.$CO_2$ | cc.$H_2$ | cc.CO |
| 300 | — | — | — | 110 | — | — | — |
| 350 | 48.7 | 47.8 | 3.5 | 360 | 175.3 | 172.0 | 12.6 |
| 450 | 49.7 | 49.9 | 0.4 | 1120 | 556.6 | 558.9 | 4.5 |
| 550 | 49.7 | 49.9 | 0.4 | 1130 | 561.6 | 563.9 | 4.5 |

## Discussion of Results

Sabatier and Mailhe[1], Hinshelwood[2] and others, and Adkins[3] have shown that formic acid undergoes decomposition according to one or more of the three primary reactions:—

$$(1)\quad HCOOH = CO_2 + H_2$$
$$(2)\quad HCOOH = CO + H_2O$$
$$(3)\quad 2HCOOH = CO_2 + H_2O + HCHO$$

the extent on each depending on the specific nature of the catalyst and the character of the reaction vessel.

In addition, over the temperature range covered here the decomposition of formaldehyde, according to the reaction:—

$$(4)\quad HCHO = H_2 + CO$$

must be taken into account.

Consideration of these four reactions shows that the $CO_2$ found may be accounted for by reactions (1) and (3); that the $H_2$ may have its origin in reactions (1) and (4), and that the CO may arise from reactions (2) and (4). That reaction (3) takes place to some extent is shown by the excess of the volume of $CO_2$ over that of $H_2$ and by the further fact that formaldehyde was found in the condensate of all runs at the lower temperatures. The thermal decomposition of formaldehyde according to reaction (4) has been studied by Bone and Smith[4] and more recently by Hofmann and Schibsted[5]. The more

[1] Sabatier and Mailhe: Compt. rend., 152, 1212 (1911).

[2] Hinshelwood, Hartley and Topley: Proc. Roy. Soc., 100A, 575 (1922); Tingley and Hinshelwood: J. Chem. Soc., 121, 1668 (1922); Hinshelwood and Topley: 123, 1014; Hinshelwood and Hartley: 1333 (1923).

[3] Adkins: J. Am. Chem. Soc., 45, 809 (1923).

[4] Bone and Smith: J. Chem. Soc., 87, 910 (1905).

[5] Hofmann and Schibsted: Ber., 51, 1398 (1918).

or less complete dissociation into $H_2$ and CO of the formaldehyde formed will contribute its quota of these gases to those arising from the direct decomposition of formic acid itself.

Turning to the data, inspection shows that by far the greater amount of gas ($H_2$ and $CO_2$) is produced by reaction (1). The consistent excess of $CO_2$ over that of $H_2$ must be attributed to reaction (3). This is substantiated by the finding of formaldehyde in the condensate. The volume of carbon monoxide shows a steady increase with rise in temperature for all tubes except that of copper. Its presence can be accounted for by the direct decomposition of formic acid according to reaction (2), which according to Hinshelwood takes place to an equal extent with reaction (1) at 280°C, and is the reaction that takes place almost exclusively at low temperatures in the presence of titanium oxide as catalyst, an observation first made by Sabatier and later confirmed by Hinshelwood and by Adkins. On the other hand, it is equally possible to account for the CO through the secondary decomposition of formaldehyde according to reaction (4), a reaction which does take place to a certain extent. This latter supposition is as consistent with our data as the former, so one cannot say with certainty which of these two reactions is the one yielding the CO. Probably both are involved.

Obviously, with the data at hand, bearing in mind that each of these gases may arise from at least two separate reactions, no exact calculation can be made of the extent to which each reaction proceeds under the conditions of the experiment. Tentative calculations based on the gaseous products have, however, been made of the amount of decomposition undergone by the acid in its passage through the tubes at the rate of 3 cc. per hour, and of the extent to which each primary reaction is influenced.

In the first set of such tentative calculations, the decomposition has been based on reactions (1), (2), and (3), not taking into separate account the amounts of CO and $H_2$ which come from the partial decomposition of formaldehyde. The total $H_2$ found is thus a measure of reaction (1), the total CO a measure of reaction (2), and the excess of $CO_2$ over that of $H_2$ a measure of reaction (3). If one cc. of liquid formic acid decomposes completely according to (1), there should result 1186 cc. of gas, consisting of equal volumes of $CO_2$ and $H_2$; if according to reaction (2), 593 cc. of pure CO; if according to (3), 296 cc. of $CO_2$, assuming here no decomposition of the HCHO. In this way the extent to which one cc. of acid was decomposed in the direction of (1), (2), and (3) was computed, the total percentage decomposition being the sum of all three. Thus, for example, for the unetched silica tube at 350°C, 59.4% of the acid passed through decomposed according to (1); 2.0% according to (2); and 4.0% according to (3); giving a total decomposition of 65.4%. The extent to which the three modes of decomposition are divided among themselves gives a better approximate idea of the course of these reactions. In the above example, for every 100 molecules decomposed, 90.8 follow reaction (1), 3.0 follow reaction (2), and 6.2 follow reaction (3). Typical results computed by this method are given in the table below for the etched and unetched silica

tube. These figures can only be taken as approximations, but they are useful in showing the differences obtainable with smooth and rough surfaces of the same material.

In another tentative method of calculation, the decomposition has been based on reactions (1) and (3), assuming that all the CO and an equal volume of $H_2$ have been derived from the secondary partial decomposition of the formaldehyde formed in reaction (3). The apparent extent to which reaction (1) proceeds can then be taken as the total $H_2$ formed, less a volume equal to that of the CO found. The excess of $CO_2$, as a measure of (3), will thus be somewhat larger than by the first method of computation. The volume of CO gives a measure of the gaseous decomposition of formaldehyde; the $CO_2$ attributed to reaction (3) is always in excess of the CO indicating that the formaldehyde does not decompose completely into gaseous products, but forms the oily and tarry polymerization products found in the condensate. The data for the tubes have been calculated in this manner and compared with the first method. The results for the two silica tubes are given below.

*Unetched Silica Tube*

| °C | Total % Decomp. | Method 1 Extent followed by reaction (1) per 100 molecules decomposed | (2) | (3) | Method 2 Extent followed by reaction (1) per 100 molecules decomposed | (3) |
|---|---|---|---|---|---|---|
| 350 | 65.4 | 90.8 | 3.0 | 6.2 | 87.9 | 12.1 |
| 450 | 94.3 | 82.5 | 2.8 | 14.7 | 79.8 | 20.2 |
| 550 | 95.7 | 76.2 | 6.1 | 17.7 | 70.1 | 29.9 |

*Etched Silica Tube*

| °C | Total % Decomp. | Method 1 Extent followed by reaction (1) per 100 molecules decomposed | (2) | (3) | Method 2 Extent followed by reaction (1) per 100 molecules decomposed | (3) |
|---|---|---|---|---|---|---|
| 350 | 81.2 | 96.7 | 0.6 | 2.7 | 96.0 | 4.0 |
| 450 | 95.6 | 84.7 | 2.5 | 12.9 | 79.0 | 21.0 |
| 550 | 99.6 | 64.3 | 11.9 | 23.8 | 52.5 | 47.5 |

Comparable results were obtained with the other tubes. In the case of the porcelain tube at 550°, the abnormally large excess of $CO_2$ gives an apparent total decomposition of over one hundred percent; either the data for this run are at fault, or the inadequacy of this tentative method of calculation is here revealed. The slight deficiency of $CO_2$ for the copper tube at the higher temperatures is well within the limits of error of the gas analysis.

Obviously, such calculations are only approximations and sweeping conclusions cannot be drawn from them. The matter becomes still more complicated when one considers the possibility of secondary reactions taking place, such as the reduction of carbon dioxide by hydrogen and the formation of methyl alcohol. The reaction:—

$$(5)\quad CO_2 + H_2 \longrightarrow CO + H_2O$$

according to Muller and Peytral accounts for the presence of CO at 1150°C, these investigators concluding that the only primary reaction in the decom-

position of formic acid at this high temperature is the one giving $CO_2$ and $H_2$. To what extent this reduction takes place over the temperature range covered has not been investigated by us. In some cases, equilibrium concentrations for the water gas equilibrium are reached, as shown by calculations of the equilibrium constant $CO \times H_2O/CO_2 \times H_2 = k$, yet no definite conclusions can be drawn from the data available here. This point requires more investigation.

## Conclusions

Formic acid when slowly passed through tubes of silica, pyrex, porcelain, and copper, heated to temperatures of from 350° to 550°C, decomposes principally into $CO_2$ and $H_2$, according to the reaction:—

$$HCOOH = CO_2 + H_2$$

A certain, usually small, amount decomposes according to the reaction:—

$$2HCOOH = CO_2 + H_2O + HCHO$$

The two reactions:—

$$HCOOH = CO + H_2O$$
$$HCHO = CO + H_2$$

account for the CO found.

The decomposition is 90% or more complete at 450°C. The pyrex glass tube is least active; the copper tube most active. The silica tube after being etched shows a much greater activity than it did in its unetched condition, showing the effect of increased active surface. With the copper tube reaction (1) takes place almost exclusively and brings about a decomposition of over 99% at 450° and 550°C.

No exact calculation can be made of the extent to which each reaction proceeds on account of the complications arising in the gas volume relationships.

The instability and sensitiveness of formic acid to the catalytic influence of the walls of the reacting tube are shown by the results here recorded. These results have an important bearing on the work of Wescott reported in the next paper.

*University of Pittsburgh,*
*Pittsburgh, Pa.*
*December, 1925.*

# THE CATALYTIC DECOMPOSITION OF FORMIC ACID

BY B. B. WESCOTT AND CARL J. ENGELDER

The experiments of Nelson, reported in the preceding paper, have shown that when formic acid is slowly passed through tubes of various materials heated to temperatures of 350° to 550°C, the decomposition is mainly in the direction of $CO_2$ and $H_2$, according to the reaction:—

$$(1)\quad HCOOH = CO_2 + H_2$$

The excess of $CO_2$ over $H_2$, together with the production of formaldehyde shows that the following reaction takes place to a certain extent:—

$$(3)\quad 2HCOOH = CO_2 + H_2O + HCHO$$

The decomposition of formaldehyde into CO and $H_2$ at these temperatures accounts for at least some of the CO and $H_2$ found in the gaseous decomposition products.

The dehydration of formic acid according to the reaction:—

$$(2)\quad HCOOH = CO + H_2O$$

undoubtedly takes place to some extent.

That these reactions are greatly influenced by dehydrating and dehydrogenating catalysts is well known from the work of Sabatier[1] and the recently published papers of Hinshelwood[2] and Adkins[3]. These investigators worked at temperatures up to 350°C. The former used a layer of catalyst 50 cm. long, heated in a Jena glass tube. Hinshelwood employed bulbs coated with the metallic catalyst or partly filled with the powdered material. The effect produced by relatively small amounts of alumina, titania and nickel as catalysts on the decomposition of formic acid over a temperature range from 200° to 500°C has been studied by Wescott and recorded in the present paper. The extent to which the wall reactions have been modified by the insertion of the catalysts is shown by the data here presented.

## Experimental Procedure

The apparatus consisted of a burette for measuring the acid used, a vaporizer, an electrically heated and controlled furnace containing the reaction tube, a suitable condensing train, and a gas collection vessel. The acid was practically anhydrous, obtained from Kahlbaum's and from Merck's. The acid was admitted at a uniform rate of about 10 cc. per hour. The gaseous products were analyzed by the usual methods of gas analysis. The undecomposed formic acid and formaldehyde were removed in the condensing train.

The reaction tube was an unglazed clay Johnson combustion tube such as used in steel mill laboratories for carbon determinations. It was 40 cm. long and about one and a half cm. internal diameter. It decomposed formic acid, when passed through it at the rate of 10 cc. per hour, mainly into $H_2$ and $CO_2$.

[1] Sabatier and Mailhe: Compt. rend., 152, 1212 (1911).
[2] Hinshelwood and Topley: J. Chem. Soc., 123, 1014 (1923).
[3] Adkins: J. Am. Chem. Soc., 45, 809 (1923).

The decomposition became apparent at 294°C yielding 7cc. gas per cc. acid. At 400° the gas evolution reached 320 cc. gas per cc. acid, of which 166.7 cc. were $CO_2$, 163.3cc. $H_2$, and 14.7 cc. CO. At 484° the gas yield was 274.7 cc. $CO_2$, 271.6 cc. $H_2$, and 36.7 cc. CO, or a total of 582 cc. per cc. acid. These values are lower than those obtained by Nelson with other tubes at a slower rate of passage but they are similar in general characteristics.

To get the superimposed effect of the catalysts, these were spread in a thin layer in a combustion boat about 10 cm. long and placed in the middle of the tube.

*Titania Catalyst*

A sample of ignited titanium dioxide ground to pass a 200-mesh sieve when used in a shallow layer about 10 cc. long gave the results shown in Table I. Another sample made by precipitation from titanium tetrachloride yielded similar results.

TABLE I

1 cc. Formic Acid yielded:

| °C | cc. Total Gas | cc. $CO_2$ | cc. $H_2$ | cc. CO |
|---|---|---|---|---|
| 202 | 38.8 | 2.7 | 1.8 | 33.7 |
| 234 | 63.4 | 4.9 | 3.8 | 54.6 |
| 280 | 177.6 | 19.5 | 16.0 | 142. |
| 340 | 439.0 | 128. | 112.3 | 197. |
| 375 | 657.0 | 241. | 222.0 | 189. |
| 398 | 820.0 | 274. | 246. | 293. |
| 498 | 777.5 | 248. | 211. | 308. |

*Alumina Catalyst*

The alumina catalysts were prepared in general by dissolving aluminum sulfate in water, largely diluting, and precipitating the aluminum hydroxide with dilute ammonium hydroxide. The precipitate was washed several times by decantation, filtered, dried at 250° and ground to pass a 200-mesh sieve. Portions of the dried $Al_2O_3$ from the same preparation were used in the series of temperature runs. The results of a typical series of runs are given in Table II. These results as well as those with titania have been confirmed in a general way by another student, Mr. E. H. Ohl, working in the same laboratory.

TABLE II

1 cc. Formic Acid yielded:

| °C | cc. Total Gas | cc. $CO_2$ | cc. $H_2$ | cc. CO |
|---|---|---|---|---|
| 287 | 178. | 9.4 | 6.0 | 164.0 |
| 311 | 243. | 12.4 | 10.5 | 223. |
| 338 | 422.5 | 91.2 | 85.0 | 242. |
| 373 | 619.0 | 215.5 | 199. | 205. |
| 417 | 850.0 | 300. | 287. | 259. |
| 491 | 763.0 | 221. | 189. | 354. |
| 503 | 754.5 | 214. | 183. | 354. |

### *Nickel Catalyst*

The nickel catalysts were prepared by ignition of the nitrate to the oxide followed by reduction to the finely divided metallic form in a stream of hydrogen in a separate furnace and subsequently transferred as needed to the catalytic apparatus without contact to the air. The results are given in Table III.

TABLE III

| | 1 cc. Formic Acid yielded: | | | |
|---|---|---|---|---|
| °C | cc. Total Gas | cc. $CO_2$ | cc. $H_2$ | cc. CO |
| 210 | 327. | 157.6 | 152. | 18.6 |
| 257 | 490. | 235. | 220.5 | 34.6 |
| 353 | 873. | 453. | 395.5 | 36.7 |
| 455 | 814. | 365. | 311. | 138. |
| 524 | 801. | 283. | 257. | 262. |

## Discussion of Results

The results show that with titania and alumina the dehydrating reaction ($HCOOH = CO + H_2O$) greatly predominates up to temperatures somewhat above 300°C, reactions (1) and (3) being of minor importance. This is what would be expected of these dehydrating catalysts and the results confirm in general the work of earlier investigators. With nickel, the dehydrogenating reaction ($HCOOH = CO_2 + H_2$) takes place almost exclusively at the lower temperatures, as indicated by the large volume of $CO_2$ and $H_2$ evolved, reactions (2) and (3) taking place to a minor extent. That these minor reactions with all three catalysts are not solely the effects of the tube can be deduced from the blank runs made under otherwise identical conditions and from Nelson's data on other tubes where the wall decompositions were studied under more nearly equilibrium conditions.

At the higher temperatures the course of the main reaction is more difficult to follow and the volume relationships become complicated. With the titania catalyst at 340° reaction (2) comes to the front, accounting for about 51% of the gas yield; at 398° it accounts for about 63% of the total gas evolved. This reaction is the one taking place selectively at the walls of the tube but the wall reaction accounts for only about one-half the amounts of $CO_2$ and $H_2$ found here, hence the titania itself catalyzes this reaction to some extent as well.

The alumina catalyst, like $TiO_2$, catalyzes the dehydrating reaction almost exclusively at lower temperatures. At 373° the dehydrogenating reaction becomes of equal importance. At the highest temperatures observed, 491° and 503°C, the CO production is again in excess of that of $CO_2$ and $H_2$. Adkins[1] found that the extent to which these two reactions are selectively catalyzed depends upon the method of preparation of the alumina catalysts.

[1] Adkins: J. Am. Chem. Soc., **45**, 809 (1923).

The abnormally large amounts of CO found in the nickel runs at 455° and 524° are difficult to account for. It seems unlikely that the primary decomposition of the acid into CO and $H_2O$ should show this sudden increase at these temperatures with nickel as catalyst. The tube reaction at these temperatures follows this direction to only a minor extent. Formaldehyde, decomposing into CO and $H_2$, cannot yield these large amounts of CO consistently with the other data. The possibility of nickel catalyzing the reaction:

$$(5)\quad CO_2 + H_2 \longrightarrow CO + H_2O$$

presents itself. This reduction of $CO_2$ by $H_2$ was noted by Sabatier and Senderens[1] for an active copper catalyst, but with nickel, hydrogenation to methane is the usual result:

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

With the nickel used by Wescott, no methane was found. The corresponding decrease in the volumes of $H_2$ and $CO_2$ favor this explanation. The effect of active metal catalysts on the water gas equilibrium is under investigation and may throw light on the results here presented.

Reaction (3) takes place to a small extent in all the runs and can be attributed solely to the effect of the walls of the tube.

The extent to which the primary decompositions are influenced by the introduction of the catalysts is readily seen at the lower temperatures. The wall-reactions and secondary effects partly obscure the specific catalytic effect at higher temperatures. Calculations based on the effect of the catalysts would, therefore, be misleading.

## Conclusions

The catalytic effect of small amounts of alumina, titania, and nickel on the decomposition of formic acid between 200° and 500°C has been studied. The reactions taking place at the walls of the reaction tube have been greatly modified through the presence of added catalysts. Alumina and titania catalyze the dehydration reaction:—

$$HCOOH = CO_2 + H_2$$

The tube itself decomposes the acid chiefly according to this reaction, with the dehydrating reaction and the reaction:

$$2HCOOH = CO_2 + H_2O + HCHO$$

playing minor roles. Formaldehyde decomposes partially into $H_2$ and CO. The effect of the tube becomes marked above 350°.

*University of Pittsburgh,*
*Pittsburgh, Pa.*
*December, 1925.*

[1] Sabatier and Senderens: Ann. Chim. Phys. (8), 4, 426 (1905).

# INFLUENCE OF TEMPERATURE ON METABOLISM AND THE PROBLEM OF ACCLIMATIZATION

BY N. R. DHAR

It is well known that the temperature of a warm-blooded animal is maintained at the normal even though the temperatures of the outside environments vary from zero and lower to 30° or 35°. In cold-blooded animals, on the other hand, the temperature of the body is only slightly higher than that of the environment at the time. The metabolism of such animals varies with the temperatures in such a manner that the respiratory exchange almost always rises with the increase in temperature, but generally irregularly and to a very different degree in different animals. The frog in the mud during the winter at a temperature of 4° has quite a different metabolism from that which he enjoys during the summer sunshine as it sits on the river bank and snaps at passing flies.

Röhrig and Zuntz[1] first showed that a curarized warm-blooded animal at ordinary room temperatures lost the power of maintaining its body temperature and that the intensity of metabolism decreased accordingly. Curare prevents the transmission of motor impulses to voluntary muscles. Krogh[2] states that the curve of oxygen absorption as influenced by body temperature is the same in the anesthetized frog and fish as in the curarized dog. In warm-blooded animals the temperature is maintained at a constant level independent of the climatic condition and this level is a favorable one for the activity of nerve and muscle. It would indeed be inconvenient were the active life of a man dependent upon the temperature of the environment. The essential mechanism for the regulation of body temperature is nervous.

In warm-blooded animals a fall in the surrounding temperatures regularly causes not a decrease but an increase in the respiratory exchange, thanks to the mechanism of chemical heat regulation. The most elaborate study of the chemical heat regulation has been made by Rubner[3] who obtained the results given in Table I in the case of a guinea pig.

TABLE I

| Temperature of air °C. | $CO_2$ per Kg. and Hour Gr. |
|---|---|
| 0° | 2.91 |
| 11° | 2.15 |
| 21° | 1.77 |
| 26° | 1.54 |
| 30° | 1.32 |
| 35° | 1.27 |
| 40° | 1.45 |

[1] Pflüger's Archiv, 4, 57 (1871).
[2] Internat. Z. physik-chem. Biologie, 1, 492 (1914).
[3] "Die Gesetze des Energieverbrauchs bei der Ernährung" (1902).

At 35° the regulation breaks down and the respiratory exchange rises with increase in temperature of the body as seen in the last experiment of the above series.

In the foregoing paper[1] we have shown that under standard conditions where the effect of nervous influence is excluded increase in temperature causes greater metabolism in both warm and cold blooded animals.

After studying a considerable range of animals, Rubner has found that all animals transform nearly the same total amount of energy per kilogram of body weight in the whole period from the birth to the natural death. The mean value of the constant Rubner finds to be 191600 calories, the values for different species ranging from 141091 and 265500 calories. Small animals with an intensive metabolism live a relatively short time; large animals with more sluggish metabolism live a longer time. Rubner's view is that a definite sum of living action or energy transformation determines the physiological end of life. It is Rubner's law that the metabolism is proportional to the superficial area of an animal.

Erwin Voit[2] has calculated the following results, Table II, for showing the heat production in resisting animals of various sizes at medium temperatures of the environment:—

TABLE II

| | Weight in Kg. | Calories produced | |
|---|---|---|---|
| | | Per Kilo | per Sq. M. Surface |
| Horse | 441 | 11.3 | 948 |
| Pig | 128 | 19.1 | 1078 |
| Man | 68.3 | 32.1 | 1042 |
| Dog | 15.2 | 51.5 | 1039 |
| Rabbit | 2.3 | 75.1 | 776 |
| Goose | 3.5 | 66.7 | 969 |
| Fowl | 2.0 | 71.0 | 943 |
| Mouse | 0.018 | 212.0 | 1188 |
| Rabbit (without ears) | 2.3 | 75.1 | 917 |

This table supports the generalization of Rubner.

Voit shows that the metabolism of the pigeon may be doubled after removing its feathers. From the experiments of Rubner it appears that the presence of adipose tissue acts in the same way as does a warm fur to extend the range of the physical regulation and to delay the onset of chemical regulation of body temperature. That the range of physical regulation of temperature of a small dog was due to his long hair, is shown by the change in his metabolism after shaving him. Rubner shows this in Table III.

[1] Dhar: Proc. Akad. Wet. Amsterdam, 23, 44 (1920).
[2] Z. Biologie, 41, 120 (1907).

TABLE III

| Temperature | Calories per Kilo. Normal coat of hair | Shaved |
|---|---|---|
| 20° | 55·9 | 82.3 |
| 25° | 54.2 | 61.2 |
| 30° | 56.2 | 52.0 |

It is clearly seen that this dog lost its power of physical regulation between 20° and 30°. As soon as he lost his covering of hair his metabolism became like that of a guinea pig, increasing with a reduction of temperature from 30° downwards, an illustration of chemical regulation.

To determine the influence of the protective layer of fat Rubner investigated the influence of temperature on the metabolism of a fasting short haired dog at a time when he was emaciated and compared it with the fasting metabolism after the same dog had been fattened, Table IV.

TABLE IV

| Dog (thin) | | Same dog (fat) | |
|---|---|---|---|
| Temperature | Cal. per Kilo. | Temperature | Cal. per Kilo. |
| 5.1° | 121.3 | 7.3° | 120.5 |
| 14.4° | 100.9 | 15.5° | 83.0 |
| 23.3° | 70.7 | 22.0° | 67.0 |
| 30.6° | 62.0 | 31.0° | 64.5 |

It appears from this table that the metabolism of the dog was the same at a low temperature in both cases but that the minimum metabolism was almost reached at a temperature of 22° when the dog had a protective covering of fat which was not the case when he was thin.

The physical regulation may be increased by certain voluntary acts, such as are observed when a dog or man exposed to cold lies down and curls himself up in such a way as to offer as small an exposed surface as possible. The contrast to this is offered when on a hot day the dog lies on his back and extends his legs so as to promote loss of heat.

In Table V are Voit's results on the effect of temperature on the metabolism of a fasting man (six hour periods.)

TABLE V

| Temperature | $CO_2$ excreted in grams | Temperature | $CO_2$ excreted in grams |
|---|---|---|---|
| 4.4° | 201.7 | 23.7° | 164.8 |
| 6.5° | 206.0 | 24.2° | 166.5 |
| 9.0° | 192.0 | 26.7° | 160.0 |
| 14.3° | 155.1 | 30.0° | 170.6 |
| 16.2° | 158.3 | | |

Voit believed the increase in metabolism to be a reflex stimulus of cold on the skin which raised the power of muscle cells to metabolise.

Another factor in the heat regulation of man is clothes. Certain savage races living in cool climates do without clothes, as, for example, aborigines of Tierra del Fuego, who according to the reports of travellers, substituted a covering of oil. In such races the process of "hardening" or development of physical regulation must be carried to a maximum. In civilized countries man endeavors to remove all the influence of chemical regulation by keeping his skin covered. Only about 20% of his surface is normally exposed to the air. The most important constituent of clothes is the air, which is a much worse conductor of heat than is fibre. Two experiments cited by Rubner indicate the effect of clothes on metabolism. An individual was kept at a temperature of between 11° and 12° and wore different clothes at different times. His $CO_2$ and water excretion are given in Table VI.

TABLE VI

Influence of Clothes on Metabolism in Man at a Temperature of 11° to 12°

| | $CO_2$ in gram. per hour. | Remarks. |
|---|---|---|
| Summer clothes | 28.4 | Cold, occasional shivering |
| Summer clothes and winter overcoat. | 26.9 | Chilly part of the time. |
| Summer clothes and fur coats. | 23.6 | Comfortably warm. |

When a man was comfortable the chemical regulation of temperature was eliminated.

Fat persons have been directly observed to have a smaller respiratory action than lean ones. Benedict and Smith[1] have shown by comparing a number of athletes with normal subjects of similar heights and weights that the metabolism of athletes is on the average distinctly greater than that of non-athletes.

While it had often been observed that smaller animals had per unit weight a greater respiratory exchange than larger ones, a quantitative study of the influence of size upon metabolism was first made by Rubner on grown dogs weighing from 30.4 to 3.4 kilograms. Rubner found that the metabolism calculated per kilogram increases regularly with decreasing size. When however the surface of the animal is taken into account a practically constant metabolism per sq. surface was found for all.

From experiments on guinea pigs of different age and weights Kettner[2] finds that the metabolism per kilogram an hour decreases fairly regularly with increasing weight whilst the differences in the results per sq. meter are independent of size. On the other hand, in a recent discussion Benedict[3] denies

[1] J. Biol. Chem., 20, 243 (1915).
[2] Archiv Physiol., 1909, 447.
[3] J. Biol. Chem., 20, 263 (1915).

that there is any close relationship between size and metabolism and deprecates especially the use of the surface as a basis for comparison. His own figures and charts show, however, that such relationships exist that the metabolism per kg. of the body weight decreases fairly regularly with increasing weight.

The surface S of an animal is approximately proportional to the square of a linear dimension e.g. length of the body, while the weight is proportional to the third power of a linear dimension. We have therefore $S = CW^{\frac{1}{3}}$ the constant C has been worked out for different species. It does not vary very much even in forms of very different shapes. For man and also for a dog we have $C = 12.3$ for the rabbit 12.9, the horse 9.0, the rat 9.1 and the guinea pig 8.9.

It is quite possible that the surface as at present defined $CW^{\frac{1}{3}}$ does not give the very best agreement in comparisons of different individuals. The main point is that metabolism in warm-blooded animals is not proportional to the weight W but to $W^n$ where $n$ is certainly not far from $2/3$.

On the whole, looking at the problem from a broad point of view, it seems pretty certain that the surface law of Rubner is generally proved as far as the metabolism of warm-blooded animals are concerned.

In the following pages, I shall try to find out a physical significance of Rubner's generalization and other facts regarding the influence of temperature on metabolism in both warm and cold blooded animals. We can look at the problem of metabolism of different warm-blooded animals from the following considerations:—

(1) The body temperature of warm-blooded animals is normally much higher than the surrounding air. In the case of some birds, sparrow, hen, etc., the body temperature is about 42°. In the case of rabbit it is 39°.6 and in the case of dog it is 39°.2.

(2) Experimental results have shown that radiation is the most important factor in the loss of heat from animal body. . Let us assume that a metallic ball of radius $r$ and density of the material $\rho$, is placed in air at say $T_o$ and we are supplying heat to the ball so that the temperature of the ball may be kept constant at T where T is greater than $T_o$. Now in order to maintain this constant temperature a supply of heat has to be given to the ball, otherwise the body loses heat and cools down to the temperature of the surrounding air ($T_o$). From Stefan's law of radiation, we know that the loss of energy from the surface is equal to $4\pi\gamma^2\sigma(T^4 - T_o)$, where $4\pi\gamma^2$ is the surface of the body in question and $\sigma$ is Stefan's constant. Therefore the rate of supply of heat to the body per unit mass in order to keep the body temperature constant to T is equal to

$$\frac{4\pi\gamma^2\sigma\ (T^4 - T_o^4)}{4/3\pi\gamma^3\rho} = \frac{3\rho\sigma}{\gamma}(T^4 - T_o^4)$$

From the foregoing relation it will be seen that the rate of supply of heat per unit mass varies inversely as the radius of the body in question. In other words, a small ball of the same material requires a much larger quantity of heat per unit mass of the body. Let us apply these considerations to the

question of metabolism in animals. Ordinarily warm-blooded animals are surrounded by air of a much lower temperature than the temperature of the animal body. In other words, the animal is constantly giving out heat to the outside surroundings mainly by radiation and in order that this phenomenon can take place the metabolism of the system should increase in order to keep the body temperature constant. From the foregoing considerations it will be evident that the amount of heat per unit weight of the body lost by the animal due to this radiation is greater, the smaller the size of the animal. This conclusion is actually corroborated by experiments. Consequently from physical principles it follows that the loss of heat per unit weight of the body and the consequent metabolism in the animal body to keep up this loss of heat is greater the smaller the size of the animal.

From the relation already obtained it is seen that the rate of supply of heat per unit mass is proportional to the difference in temperature between the body and the surrounding air; in other words, the greater is the difference in temperature the greater is the rate of supply of energy per unit mass of the substance. Consequently when a warm-blooded animal is surrounded by air which is colder than the air with which it is normally surrounded, his rate of supply of energy and consequently his metabolism should also increase and that is the reason why the metabolism in the case of warm-blooded animals increases with the fall of surrounding temperature.

We have already shown that the loss of energy from the surface $= 4\pi\gamma^2\sigma(T^4 - T_o^4)$. Now if we express this loss per unit surface, the expression becomes $\sigma(T^4 - T_o^4)$; in other words, the question of radius or the size of the body does not come into consideration and the loss of energy per unit surface becomes proportional only to the difference between the body temperature and that of the surrounding air. This has been experimentally obtained by Rubner who has obtained the following results with guinea pig:

| Temperature | $CO_2$ |
|---|---|
| 0° | 2.91 |
| 11° | 2.15 |
| 21° | 1.77 |

If we calculate the metabolism according to the relation $\sigma(T^4 - T_o^4)$, we find that the ratio of the metabolisms at 0° and 11° is about 1.2, whilst the observed ratio of the metabolism is about 1.3; the calculated value between 21° and 26° is 1.38 and the observed value is 1.2, taking the average temperature of guinea pig to be 38.2. Hence we get a physical significance of Rubners law.

From the foregoing pages, it will be evident that Rubner's generalization would be applicable mainly to warm-blooded animals, because usually they maintain a higher body temperature irrespective of the temperatures of the surroundings and the laws of radiation would be applicable to such cases.

In the case of cold-blooded animals the body temperature is only slightly higher than the temperature of the surroundings and the foregoing considera-

tions are not applicable in these cases and Rubner's generalization is not valid for cold-blooded animals.

We have already suggested that life principle depends essentially on the activity of the catalyst or the enzymes existing in the body. In the foregoing pages, we have observed that usually smaller animals have more metabolism per unit weight of the body than larger animals; in other words weight for weight, the catalysts or the enzymes in smaller animals are more reactive than the catalysts in larger animals. It sounds very queer that the activity of the enzymes present in the system of a dog is much greater than the activity of those present in the case of a man or we have to assume that the amount of the catalyst per unit weight of the body is much greater in the case of smaller animals than in large animals. It will be seen in the subsequent discussion that the former proposition is more reasonable than the latter. In other words, we are led to the conclusion that the physical activity and the amount of oxidation per unit weight of the body are much greater in the case of a dog than in the case of a man. Even a most casual observation of the domesticated animals has shown that as a rule, small animals do not live so long as large ones. As a general rule, it may be said that a large animal takes more time than a small one to reach maturity and it has been inferred from this that the length of the period of growth is in proportion to longevity. Hence small animals with intensive metabolism live a relatively short time. Large animals with more sluggish metabolism live a longer time. We have already mentioned that Rubner's view is that a definite sum of living action or energy transformation determines the physiological end of life.

There are chemical analogies to these biological facts. Sabatier and his colleagues have shown that when metallic nickel, which is used as a catalyst in the hydrogenation processes, is prepared under suitable conditions at as low a temperature as possible, the activity of the catalyst is extremely great but it loses its activity very readily. From our experience with other catalysts, we know that an extremely active catalytic surface deteriorates also very rapidly. In other words, an extremely active catalytic surface is more liable to be poisoned or undergo other changes which would effect its activity as a catalyst than the surface of moderately active catalysts.

Consequently it seems probable that in the biological processes of metabolism extremely active catalysts are likely to lose their activity more readily than moderately active catalysts. In other words, the catalysts which accelerate the metabolism or oxidation in the case of dogs induces in an unit time more oxidation than the moderately active catalysts present in the human system, but the more active catalyst present in smaller animals is more liable to lose their activities by poisoning or other alterations than the moderately active catalysts present in the human body and that is why death is more rapid in the case of animals having more active catalysts than in animals having moderately active ones. In this connection the following experiments of Slonaker[1] on rats will be of interest. Slonaker kept four albino rats in cages

[1] J. Animal Behavior, 2, 20 (1912).

like the old-fashioned revolving squirrel cages, with a properly calibrated odometer attached to the axle, so that the total amount of running which they did in their whole lives could be recorded.

It was observed that the amount of exercise taken by these rats was astonishingly large. For a rat to run 5,447 miles in the course of its life is indeed a remarkable performance. Now these four rats attained an average age at death of 29.5 months. But three control rats confined in stationary cages so that they could only move about to a limited degree, but otherwise under conditions, including temperature, identical with those in the revolving cages, attained an average age at death of 40.3 months. All were stated to have died of "old age". From this experiment it clearly appears that the greater the total work done, or total energy output, the shorter the duration of life, and vice versa.

We shall now try to explain the possibility of acclimatization of warm-blooded animals from this point of view. As we have already mentioned, when there is a fall in the surrounding temperature the metabolism of warm-blooded animals is increased; in other words when a warm-blooded animal is brought from a warmer climate to a cooler climate its metabolism and the catalytic activity of the body enzymes are increased. In other words, there is a strain in the system. In the case of human beings this relation should also be valid. We have already mentioned that usually 20% of the body surface is exposed to air in the case of human beings, the remaining 80% is covered by clothes, so that we have to consider only the exposed portion. Now even for this comparatively small exposed portion the metabolism of the body should increase on lowering the temperature of the surroundings. Consequently the catalyst in the body would be activated; but, as Rubner has shown, the standard metabolism cannot undergo rapid changes as the oxidative energy of the cells is adapted to the usual conditions regarding the loss of heat and is altered very gradually with those conditions; hence the system of a human being or an animal brought from a warmer climate to a cooler climate will be in a state of strain.

In the case of cold-blooded animals it is evident that the metabolism is much slower than in the case of warm-blooded animals. Hence the catalytic activity of the enzymes present in cold-blooded animals is not as great as those in the warm-blooded animals of the same size. Consequently the duration of life of a cold-blooded animal is usually greater than that of a warm-blooded animal of the same size and this is corroborated by evidence from biology, because experience show that cold-blooded animals live much longer than warm-blooded animals of the same size.

When warm-blooded animals are transported from a warmer climate to a cooler climate, metabolism is increased. The effect of this is that the catalytic activity of the enzymes has to increase in order to produce greater combustion in a unit of time.

I have already emphasised that when the catalyst is made to work at a greater speed than the normal one the life period of the catalyst is decreased.

Consequently one effect of the transportation of a warm-blooded animal from a warmer climate to a cooler climate will be to activate the enzymes in the body and it will lead to its shortening of the life period.

The temperature of a warm-blooded animal remains constant whatever may be the temperature of the surroundings. Consequently the catalyst has to work at the same temperature irrespective of the temperature of the outside surroundings. Thus, in the case of warm-blooded animals, the question of ageing of the catalyst at a greater rate due to the increase in temperature does not arise, because the catalyst works at a constant temperature which is the body temperature of the animal in question provided the external temperature is less than the body temperature. So the main effect of transporting a warm-blooded animal from a warmer country to a colder country is to increase the activity of the body enzymes and to increase the metabolism and to shorten the life period of the animal in question. Now if the enzymes which were used to generate smaller quantity of heat in a warmer climate are required to produce greater quantity of heat in a cooler climate, they will, by and by, be tired out. In course of time the individual or the animal in question would feel the strain and it seems possible that as years go he will feel the strain more and more. It seems probable thus that an human being transported from a warmer climate to a cooler climate will feel the cold more and more as years go by.

On the other hand, if a warm-blooded animal is transported from a cooler climate to a warmer climate, let us see what will be the result on his system by this transportation. As soon as he is surrounded by a warmer atmosphere the amount of metabolism which he was used to produce in a cooler surrounding has to become less because now he is surrounded by a warmer atmosphere. Consequently the catalyst inside the body has to work less in a warmer climate than in a colder climate. Hence the life period of the individual in question is likely to be increased when he is transported from a cooler to a warmer climate provided that the exterior temperature is not greater than his body temperature.

I am of the opinion, therefore, that it is more advantageous for a man living in a colder climate to come to a warmer climate than the reverse. When a warm-blooded animal has to live in a country where the outside temperature is usually greater than the body temperature, then the animal will age and grow old and die more readily than an animal living in a cold country; because at the higher temperature, the body catalysts will age more quickly. Thus this case of an warm-blooded animal will be allied to that of a cold-blooded animal.

In this discussion, I have all along neglected the consideration of humidity and its influence on human beings and animals.

There is another factor that of the color of the skin surface; animals with deeper color are likely to radiate heat more readily than animals with fair complexion.

I have emphasised that the metabolism of cold-blooded animals is much less than in the case of warm-blooded animals under the same conditions; in other words, the enzymes present in cold-blooded animals are not as active as those present in warm-blooded animals. We have also observed that the body temperature of a cold-blooded animal is usually slightly higher than the temperature of the surrounding air and that the metabolism in the case of a cold-blooded animal goes on increasing as the surrounding temperature is increased.

Let us see what takes place when a cold-blooded animal living in a warmer country is taken to a cooler country. The metabolism in the system will decrease and the animal has to live a life of lesser intensity and possibly with a lesser sense and feeling of well being. The enzymes have to generate lesser quantities of heat in the cool atmosphere and consequently their period of life will be increased and the animal is expected to live a longer life in a cooler surrounding. Moreover, the body catalysts will not age as rapidly in the cooler surroundings as would have been the case in a warmer country. Consequently these two factors will both lead to a greater longevity of the cold-blooded animal in question when transported from a warmer to a cooler country.

On the other hand, when a cold-blooded animal habituated to a cooler locality, is transported to a warmer country, his metabolism in an unit of time will be increased and the catalysts in the body have to perform more work. Consequently the period of activity of the catalyst will be decreased and the life of the animal is likely to be shortened, though the animal has a more intense and active life in a warm surrounding. Moreover, in a warmer country the body catalyst is likely to age more rapidly than in a cool country. Consequently the effect of both these factors is that old age and death would follow more rapidly in a cold blooded animal transported from a cooler atmosphere to a warmer place.

## Summary and Conclusion

1. (a) Rubner from his experiments concluded that metabolism in different warm-blooded animals was constant when expressed per square metre of the body surface. (b) Experimental results show that smaller animals have greater metabolism in a unit time per kilogram than larger animals. (c) The metabolism of warm-blooded animals increases when there is a fall in the temperature of the surroundings. These biological facts have been explained from Stefan's law of radiation.

2. The physical activity and amount of oxidation per unit weight of the body are greater in the smaller animals than in the larger ones. In the process of metabolism, extremely active catalysts are likely to lose their catalytic activity more readily than moderately active catalysts and that is why death is more rapid with smaller animals than with larger ones.

3. The effect of transporting a warm-blooded animal from a warmer country to a colder country is to increase the activity of the body enzymes and to increase the metabolism and to shorten the life of the animal in question.

If a warm-blooded animal is transported from a cooler climate to a warmer climate, the catalytic activity of the enzymes and the metabolism are decreased. Hence the longevity of the animal in question is likely to be increased.

When the warm-blooded animal has to live in a country where the outside temperature is usually greater than the body temperature, then the animal is likely to age and grow old and die more readily than an animal living in a cold country.

4. When a cold-blooded animal is transported from a warmer to a cooler country, the metabolism is decreased and the body enzymes will not age as rapidly as they would do in a warmer country. Consequently both these factors lead to a greater longevity of the cold-blooded animal by this transportation.

When a cold-blooded animal is taken from a cooler to a warmer country, the metabolism will be increased and the enzymes will age more rapidly. Hence, the effect of both these factors will be that old age and death will follow more readily, though the animal will live a more intense in a warmer country.

*Chemical Laboratory,*
*Allahabad University,*
*Allahabad, India.*

491

# THE REDUCTION OF NITROUS OXIDE*

BY M. L. NICHOLS AND I. A. DERBIGNY

This study was made as part of the investigation to determine the mechanism of the reduction of nitric acid, since nitrous oxide is a secondary product[1] of this reduction. The nitrous oxide was reduced by bubbling it through aqueous solutions of the different reducing agents, which were placed in E, Fig. 1.

The reduction with hydrogen by slow combustion at a red hot platinum surface has been used as a method for the quantitative determination of nitrous oxide. Winkler[2] obtained nitrogen and water by this method but Kemp[3], using the same method, found that ammonia was also formed. Lunge[4] obtained quantitative reduction to nitrogen and water by low temperature combustion with hydrogen at a platinum surface. Pascal[5] states that nitrous oxide is reduced to nitrogen by sulfur dioxide, if the temperature and sulfur dioxide concentration are high. At this laboratory, Coblens and Bernstein[6] obtained almost complete reduction to ammonia by shaking the nitrous oxide with a solution of titanous chloride.

## Experimental

The nitrous oxide was prepared by the method of Victor Meyer[7] from pure sodium nitrite and hydroxylamine sulphate and collected in a gasometer over water which had been saturated previously with pure nitrous oxide. Its purity was determined by slow combustion with hydrogen in a Hempel combustion pipette L (Fig. 1) as described by Milligan. Six analyses starting with about 18 cc. of nitrous oxide gave a mean purity of 99.8%, with an average deviation from the mean of 0.2%.

### *Analytical Methods*

The ammonium salts were determined by Milligan's modification of Suler's[8] method. The method used for the determination of hydroxylamine in the presence of ammonium salts was reduction with a titanous salt solution as recommended by Milligan. Six analyses taking 0.026 — 0.077 g. of ammonia in the presence of 0.05 — 0.25 g. of hydroxylamine gave results on the average too small by 0.25 milligrams ± 0.06 milligrams corresponding to a relative error of — 0.7% ± 0.4%.

---

* Contribution from the Baker Laboratory of Chemistry at Cornell University.

[1] Armstrong: J. Chem. Soc., **32**, 56 (1877); Bancroft: J. Phys. Chem., **28**, 493 (1924); Dhar: J. Phys. Chem., **29**, 152 (1925).

[2] Winkler: "Lehrbuch tech. Gasanalyse," 3rd Ed., 190 (1901).

[3] Kemp: Chem. News, **71**, 108 (1895).

[4] Lunge: Ber. **14**, 2190 (1881).

[5] Pascal: "Synthesis and Industrial Catalysis," 348 (1925).

[6] Coblens and Bernstein: J. Phys. Chem., **29**, 750 (1925).

[7] Meyer: Ann., **175**, 141 (1875); Milligan: J. Phys. Chem., **28**, 544 (1924).

[8] Suler: Z. Elektrochem., **7**, 839 (1901).

Six analyses taking 0.1 — 0.2 g. of ammonia and 0.1 — 0.2 g. of hydroxylamine in the presence of large amounts of stannous chloride gave results for ammonia on the average too small by 0.3 milligram ± 0.1 milligram, corresponding to a relative error of 0.2% ± 0.1%. The results for hydroxylamine showed an average error of 0.2 milligrams ± 0.2 milligrams, corresponding to a relative error of 0.1% ± 0.1%.

The strength of the solution of titanous chloride was determined by precipitation with ammonium hydroxide and bromine water and ignition to titanic oxide[1]. The solution was found to contain 20.6 per cent $TiCl_3$. All

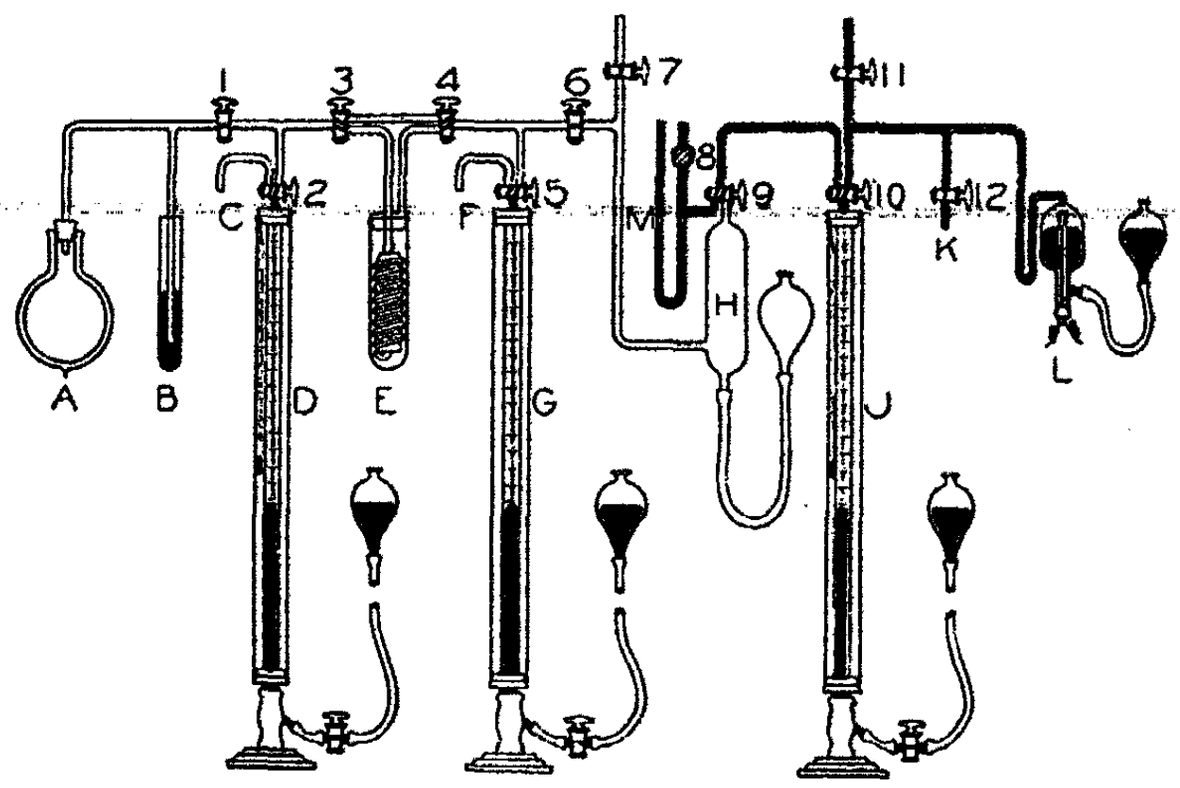



FIG. 1

of the solutions of titanous chloride used in the subsequent experiments were prepared by diluting this solution with the proper amount of water.

The solution of stannous chloride was prepared by boiling a large excess of pure tin with concentrated HCl until hydrogen was no longer liberated, adding small amounts of water from time to time to replace that lost by boiling. After filtration the solution was kept in a stoppered bottle in contact with pure tin. The strength of the solution was determined by adding an excess of iodine and titrating the excess with sodium thiosulphate[2]. The solution was found to contain 0.3705 grams of $SnCl_2$ per cc. In preparing the solutions for use in the experiments, a slight excess over the theoretical amount of this approximately standard solution[3] was diluted with the proper amount of water and the resulting solution standardized with iodine as before.

[1] Treadwell and Hall: Vol. II, 100 (1911).

[2] Hallett: J. Soc. Chem. Ind., 35, 1087 (1916).

[3] It was impossible to keep the stannous chloride solution without some oxidation of the stannous chloride to stannic chloride.

*Apparatus and Manipulation*

The apparatus used in these experiments is shown in Fig. 1. Carbon dioxide snow[1] was placed in the liter unsilvered Dewar flask, A, surrounded by a cotton jacket to control the rate of evaporation of the snow. The pressure on the system was regulated by means of the large test tube, B, containing mercury. The reducing agents were placed in E which is a modification[2] of a Friedrichs[3] spiral wash bottle. The tubes C, F, and K served as a means of introducing gases into the apparatus and as a channel through which the burettes were cleaned. All of the burettes used were calibrated at 20°C. Atmospheric pressures were determined by means of a standard, high-grade barometer fitted with a vernier. The large tube H was filled with concentrated sodium hydroxide solution. The $CO_2$ used to wash out the gases was absorbed by the NaOH in this tube. The final combustion was made in the Hempel pipette L and the hydrogen introduced through K. The manometer M was used as an indicator for bringing the gas in the burette J to exactly atmospheric pressure.

About 100 grams of carbon dioxide snow was placed in the flask A and the carbon dioxide allowed to pass into the bottle E and through the by-pass between stopcocks 3 and 4 and out through stopcock 7. The apparatus was washed out in this manner until the gas bubbling into H when stopcock 7 was closed, was completely absorbed by the sodium hydroxide solution. This showed that all of the air had been washed out of the solution in E as well as out of the entire apparatus. To accomplish this required usually from forty to eighty minutes.

To test the accuracy of the apparatus the bottle E was filled with distilled water and the apparatus washed free from air as previously described. Nitrous oxide was introduced into the burette D and measured at 20°C. and atmospheric pressure. The gas was then passed back and forth between D and G through E and returning through the by-pass between stopcocks 3 and 4. The gas was then finally passed into H and the carbon dioxide from the flask allowed to flow through E by opening stopcock 1. During the passing of the nitrous oxide back and forth through E stopcocks 1, 6 and 7 were closed and the tube connecting 6 and 7 with H was filled completely with the solution of sodium hydroxide by raising the level-bulb attached to H. The carbon dioxide was able to wash out all of the nitrous oxide from the water and the sodium hydroxide solution, since nitrous oxide does not form a stable compound[4] with either. The time required to wash out all traces of the gas was between 15 and 20 minutes. After all of the carbon dioxide had been absorbed by the sodium hydroxide, the gases remaining in the top of H were drawn into the burette J, the tube between stopcocks 9 and 10 having been previously filled completely with mercury. The mercury in the pipette L was

[1] Milligan: J. Phys. Chem., 28, 544 (1924).
[2] Milligan: Ind. Eng. Chem., 16, 889 (1924).
[3] Friedrichs: Z. anal. Chem., 50, 175 (1911).
[4] Milligan: J. Phys. Chem., 28, 544 (1924).

forced to the entrance of the tube K into the horizontal tube, and the volume of the horizontal tube between the entrance of K into this tube and the tube joining stopcocks 10 and 11 was determined and a correction applied. The hydrogen, having been purified and measured at 20°C. and atmospheric pressure, was passed into L. The spiral was then heated and the gas from H, having been likewise measured in burette J was passed into the pipette and determined as previously described.

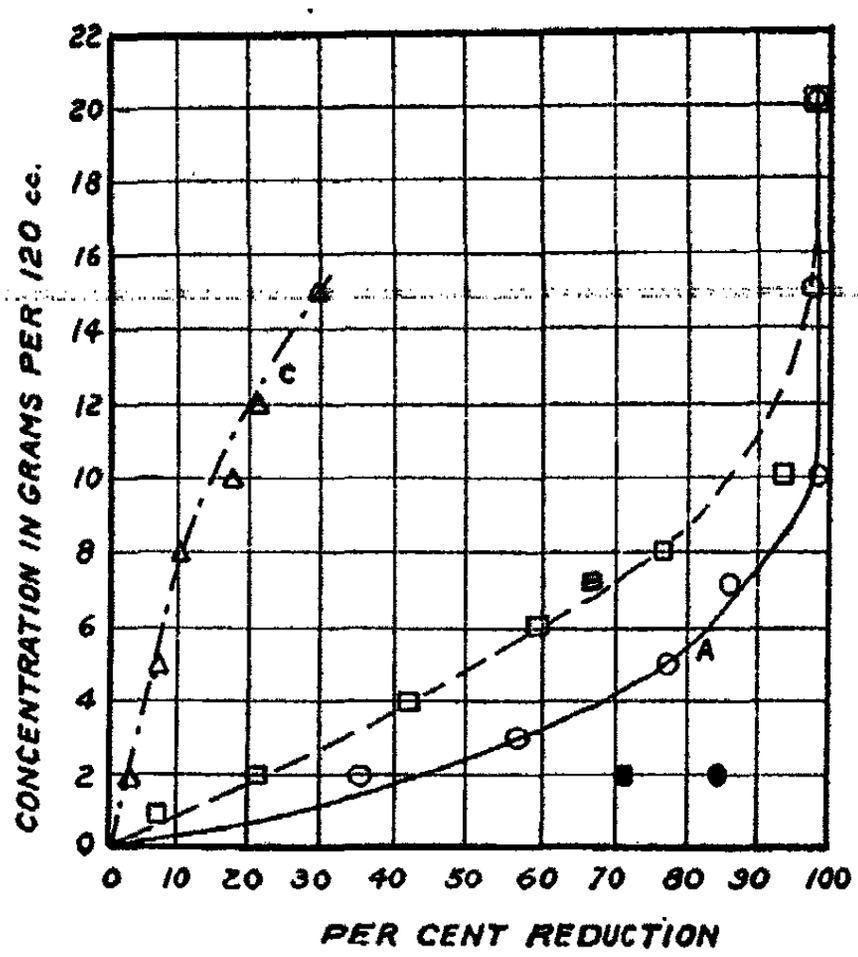



FIG. 2
The Reduction of Nitrous Oxide:
Variation of the Concentration of Reducing Agent at Constant Temperature
Curve A = Titanous Chloride
Curve B = Stannous Chloride
Curve C = Sodium Sulfite
Note—Solid black points are for a longer time of contact.

Four determinations taking about 20 cc. of nitrous oxide gave theoretically correct results while two determinations on 18 and 30 cc. of nitrous oxide gave results too small by 0.2 cc., corresponding to relative errors of 1.1% and 0.65%.

*The Reduction of Nitrous Oxide by Titanous Chloride*

The nitrous oxide was passed through solutions of titanous chloride and the residual gas analyzed by combustion, as previously described. The temperature was kept constant by almost completely immersing the wash bottle E in a water bath. A large beaker fitted with a siphon arrangement and inlet tube was found to serve the purpose adequately. The temperature was measured by means of a thermometer which had been calibrated against a standard thermometer certified by the Bureau of Standards. After passing

the gas through E a definite number of times (see table) and washing the residual gas into H with carbon dioxide, the solution in E was divided into two parts and analyzed for ammonia and hydroxylamine. The result of these determinations are shown in Table I and Fig. 2, Curve A. All of the measurements were made at 20°C. and atmospheric pressure. Experiment No. 8 shows the results of increasing the time of contact. In this, and all the other groups of experiments using titanous chloride as the reducing agent, the only product found was ammonia. Any nitrogen formed would have been definitely indicated by the combustion data on the residual gas. If hydroxylamine were formed it would have been detected in the analysis of the solution. On examining Table I it can be seen that the amount of ammonia found was sufficiently near the theoretical amount to warrant the conclusion that no other products were formed, or if other products were formed, they were not the final products of the reduction. The fact that the difference between the theoretical amount and the experimental amount is nearly constant further warrants this view, since it is not likely that the amount of a substance formed would remain constant under such varying conditions.

TABLE I

The Reduction of Nitrous Oxide with Titanous Chloride:
Variation of the Concentration of Titanous Chloride.

Temperature 20°C.
Volume of HCl (Sp. Gr. 1.17)—0.5 cc.
Volume of solution—120 cc.
Number of passages of gas—10 in all except No. 8 where was 45.
Time of contact—120 min. in all except No. 8 where was 540 min.

| Expt. No. | $TiCl_3$ G | $N_2O$ taken Mg. | $N_2O$ reduced Mg. | $NH_3$ calc. Mg. | $NH_3$ found Mg. | Per cent reduction |
|---|---|---|---|---|---|---|
| 1 | 2 | 34.7 | 12.0 | 9.3 | 9.0 | 34.7 |
| 2 | 3 | 35.7 | 20.2 | 15.6 | 15.1 | 56.4 |
| 3 | 5 | 35.4 | 27.2 | 21.1 | 20.8 | 77.0 |
| 4 | 7 | 36.1 | 30.7 | 23.8 | 23.4 | 85.2 |
| 5 | 10 | 35.7 | 35.0 | 27.1 | 26.6 | 98.0 |
| 6 | 15 | 36.4 | 35.4 | 27.4 | 27.0 | 97.1 |
| 7 | 20 | 36.1 | 35.4 | 27.4 | 27.3 | 98.0 |
| 8 | 2 | 35.5 | 29.8 | 23.1 | 22.9 | 84.0 |

From the preceding group of experiments it can be readily seen that 10 grams of titanous chloride in 120 cc. of solution is the most favorable concentration and was used for the next series of experiments to establish the effect of varying the temperature. These determinations were carried out as before, all of the other factors except the temperature being kept constant. The results are shown in Table II and Fig. 3, Curve A. Experiment No. 9 shows the effect of increasing the time of contact.

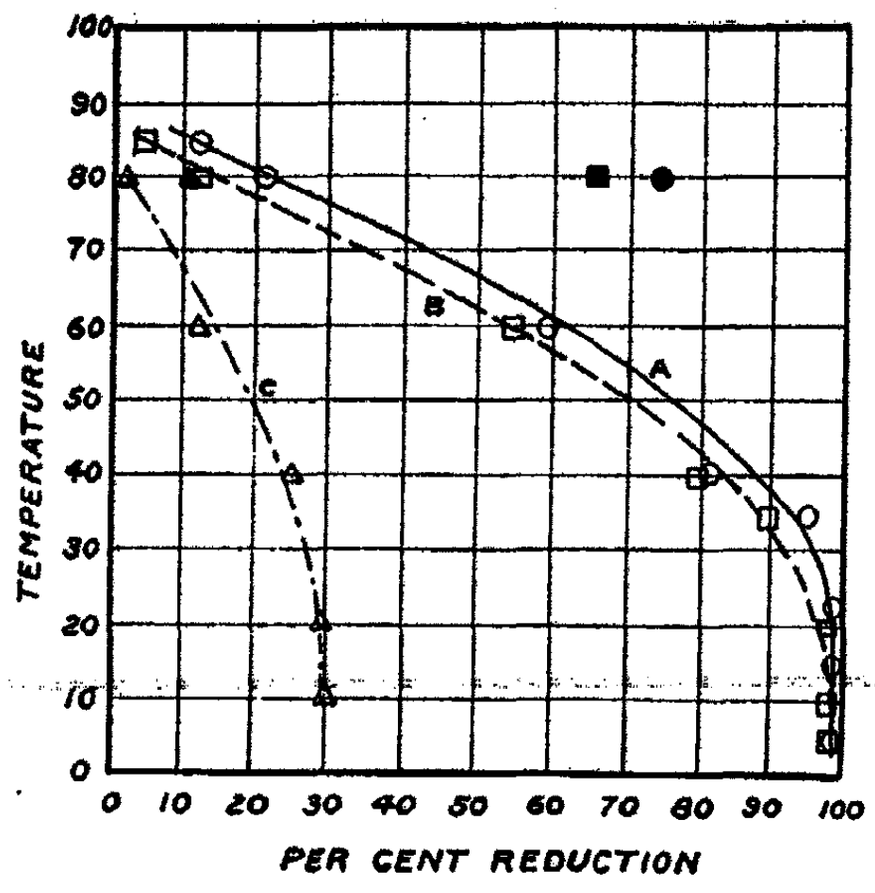



FIG. 3

The Reduction of Nitrous Oxide:
Variation of the Temperature with Constant Concentration of Reducing Agent.
Curve A = Titanous Chloride
Curve B = Stannous Chloride
Curve C = Sodium Sulfite
Note—Solid black points are for a longer time of contact.

TABLE II

The Reduction of Nitrous Oxide with Titanous Chloride:
Variation of the Temperature.

Amount of $TiCl_3$—10 gr.
Volume of HCl (Sp. Gr. 1.17)—0.5 cc.
Volume of solution—120 cc.
Number of passages of gas—10 in all except No. 9 where was 45.
Time of contact—120 min. in all except No. 9 where was 540 min.

| Expt. No. | Temp. °C. | $N_2O$ taken Mg. | $N_2O$ reduced Mg. | $NH_3$ calc. Mg. | $NH_3$ found Mg. | Per cent reduction |
|---|---|---|---|---|---|---|
| 1 | 5 | 35.9 | 35.2 | 27.3 | 27.2 | 98.0 |
| 2 | 15 | 35.9 | 35.2 | 27.3 | 27.3 | 98.0 |
| 3 | 23 | 35.6 | 34.9 | 27.0 | 27.0 | 98.0 |
| 4 | 35 | 35.9 | 33.8 | 26.2 | 25.8 | 94.1 |
| 5 | 41 | 35.9 | 29.2 | 22.6 | 22.3 | 81.2 |
| 6 | 60 | 35.2 | 20.8 | 16.1 | 16.1 | 59.0 |
| 7 | 80 | 35.9 | 7.8 | 6.0 | 5.7 | 21.6 |
| 8 | 85 | 34.5 | 4.2 | 3.3 | 2.8 | 12.2 |
| 9 | 80 | 35.8 | 26.2 | 20.3 | 20.0 | 73.3 |

Using the same concentration of titanous chloride, as in the previous group, and a temperature of 20°C., the acid concentration was varied. Concentrated hydrochloric acid, specific gravity 1.17, was used. The results obtained are shown in Table III and Fig. 4, Curve A. In experiment No. 8, an amount of sulphuric acid equivalent to 25 cc. of hydrochloric acid was used. In experiment No. 9, 25 cc. of hydrochloric acid was added and then neutralized with an equivalent amount of sodium hydroxide. In experiment No. 10, a piece of platinized platinum foil was used as a catalyst. The foil was placed at the mouth of the entrance tube into E.

TABLE III

The Reduction of Nitrous Oxide with Titanous Chloride: Variation of the Acidity.

Amount of $TiCl_3$—10 gr.
Temperature—20°C.
Volume of solution—120 cc.
Number of passages of gas—10.
Time of contact—120 min.

| Expt. No. | Vol. HCl Sp. gr. 1.17 Cc. | $N_2O$ taken Mg. | $N_2O$ reduced Mg. | $NH_3$ calc. Mg. | $NH_3$ found Mg. | Per cent reduction |
|---|---|---|---|---|---|---|
| 1 | 2 | 36.3 | 35.3 | 27.3 | 27.0 | 97.1 |
| 2 | 5 | 35.6 | 33.5 | 25.9 | 25.6 | 94.0 |
| 3 | 10 | 35.3 | 28.5 | 22.1 | 22.1 | 80.8 |
| 4 | 15 | 36.0 | 25.3 | 19.6 | 18.9 | 70.3 |
| 5 | 25 | 35.5 | 7.0 | 5.5 | 5.1 | 19.8 |
| 6 | 35 | 35.8 | 0.0 | 0.0 | 0.0 | 0.0 |
| 7 | 50 | 35.5 | 0.0 | 0.0 | 0.0 | 0.0 |
| 8 | (1) | 35.5 | 7.8 | 6.0 | 5.7 | 22.0 |
| 9 | (2) | 36.2 | 19.2 | 14.8 | 14.8 | 52.9 |
| 10 | 25(3) | 35.3 | 11.3 | 8.7 | 8.4 | 32.0 |

1—7.48 cc. $H_2SO_4$ the equivalent of 25 cc. HCl used.
2—25 cc. HCl neutralized with NaOH.
3—Platinized platinum used as catalyst.

*The Reduction of Nitrous Oxide by Stannous Chloride*

In all of the experiments using stannous chloride, hydroxylamine was the only product formed. The results of varying the concentration of stannous chloride at constant temperature and time of contact are shown in Table IV and Fig. 2, Curve B. Experiment No. 8 shows the effect of increasing the time of contact.

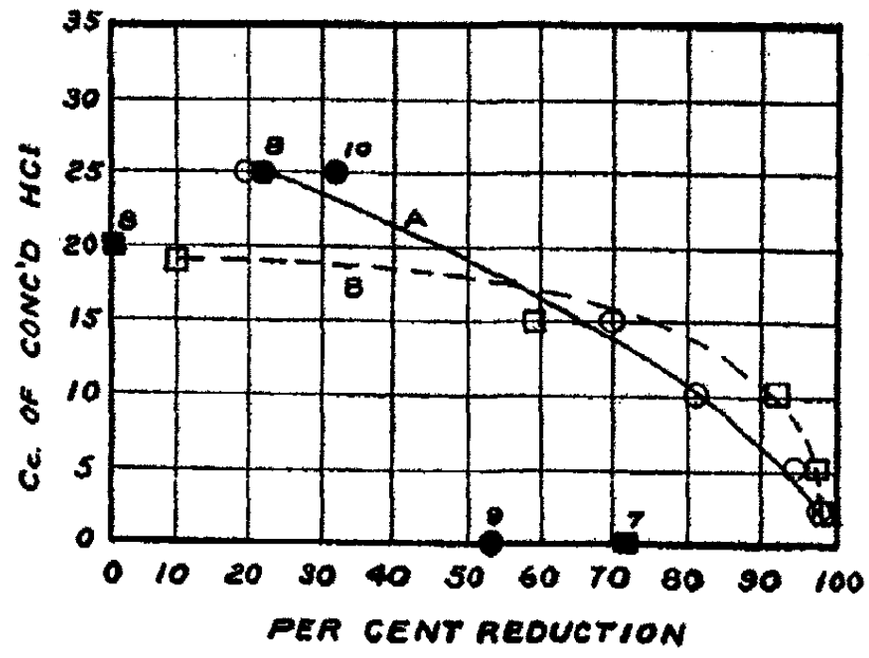



FIG. 4

The Reduction of Nitrous Oxide:
Variation of the Acid Concentration at Constant Temperature and Reducing Agent Concentration.

Curve A = Titanous Chloride
Curve B = Stannous Chloride

Note—For the conditions of the experiments shown by the solid black points see the corresponding experiment in Tables III and VI.

## TABLE IV

### The Reduction of Nitrous Oxide with Stannous Chloride:

Variation of the Concentration of Stannous Chloride.

Temperature—20°C.
Volume of solution—120 cc.
Number of passages of gas—10 in all except No. 8 where was 45.
Time of contact—120 min. in all except No. 8 where was 540 min.

| Expt. No. | $SnCl_2$ G. | $N_2O$ taken Mg. | $N_2O$ reduced Mg. | $NH_2OH$ calc. Mg. | $NH_2OH$ found Mg. | Per cent reduction |
|---|---|---|---|---|---|---|
| 1 | 20 | 35.8 | 35.1 | 52.6 | 53.3 | 98.0 |
| 2 | 10 | 35.4 | 32.9 | 49.5 | 50.0 | 93.0 |
| 3 | 8 | 36.1 | 27.6 | 41.5 | 41.6 | 76.5 |
| 4 | 6 | 35.6 | 21.2 | 31.8 | 32.1 | 59.4 |
| 5 | 4 | 35.3 | 14.8 | 22.2 | 22.2 | 42.0 |
| 6 | 2 | 35.5 | 7.4 | 11.1 | 10.8 | 20.8 |
| 7 | 1 | 35.9 | 2.5 | 3.7 | 3.4 | 6.9 |
| 8 | 2 | 35.5 | 25.1 | 38.0 | 38.5 | 71.3 |

The temperature was then varied, Table V and Fig. 3, Curve B. The effect of increased time of contact is shown in experiment No. 9.

TABLE V

The Reduction of Nitrous Oxide with Stannous Chloride: Variation of the Temperature.

Amount of $SnCl_2$—20 gr.
Volume of solution—120 cc.
Number of passages of gas—10 in all except No. 9 where was 45.
Time of contact—120 min. in all except No. 9 where was 540 min.

| Expt. No. | Temp. °C. | $N_2O$ taken Mg. | $N_2O$ reduced Mg. | $NH_2OH$ calc. Mg. | $NH_2OH$ found Mg. | Per cent reduction |
|---|---|---|---|---|---|---|
| 1 | 5 | 36.3 | 35.6 | 53.4 | 53.8 | 98.0 |
| 2 | 10 | 35.6 | 34.9 | 52.3 | 52.7 | 98.0 |
| 3 | 20 | 35.9 | 34.9 | 52.3 | 52.4 | 97.0 |
| 4 | 35 | 35.7 | 32.2 | 48.3 | 49.0 | 90.1 |
| 5 | 40 | 35.4 | 28.7 | 43.0 | 43.2 | 81.0 |
| 6 | 60 | 35.4 | 19.5 | 29.2 | 29.1 | 55.0 |
| 7 | 80 | 35.6 | 4.6 | 6.9 | 6.4 | 12.9 |
| 8 | 85 | 35.3 | 1.8 | 2.7 | 2.3 | 5.0 |
| 9 | 80 | 35.3 | 23.3 | 34.9 | 35.1 | 66.0 |

In Table VI and Fig. 4, Curve B, is shown the effect of varying the acid concentration at constant temperature and concentration of reducing agent. In experiment No. 7, 20 cc. of hydrochloric acid was neutralized with sodium hydroxide. Experiment No. 8 shows the effect of adding a quantity of sulphuric acid equivalent to 20 cc. of hydrochloric acid.

TABLE VI

The Reduction of Nitrous Oxide with Stannous Chloride: Variation of the Acidity.

Amount of $SnCl_2$—20 gr.
Temperature—20°C.
Volume of solution—120 cc.
Number of passages of gas—10
Time of contact—120 min.

| Expt. No. | Vol. HCl Sp. gr. 1.17 Cc. | $N_2O$ taken Mg. | $N_2O$ reduced Mg. | $NH_2OH$ calc. Mg. | $NH_2OH$ found Mg. | Per cent reduction |
|---|---|---|---|---|---|---|
| 1 | 2 | 35.9 | 35.2 | 52.8 | 53.1 | 98.0 |
| 2 | 5 | 35.5 | 34.5 | 51.7 | 52.2 | 97.0 |
| 3 | 10 | 36.2 | 33.4 | 50.1 | 50.3 | 92.2 |
| 4 | 15 | 35.1 | 20.7 | 31.1 | 31.5 | 59.0 |
| 5 | 18 | 35.6 | 3.5 | 5.3 | 5.0 | 9.9 |
| 6 | 20 | 35.6 | 0.0 | 0.0 | 0.0 | 0.0 |
| 7 | (1) | 35.3 | 25.1 | 37.6 | 37.8 | 71.0 |
| 8 | (2) | 36.5 | 0.0 | 0.0 | 0.0 | 0.0 |

1—20 cc. HCl neutralized with NaOH.
2—6 cc. $H_2SO_4$ the equivalent of 20 cc. HCl used.

*The Reduction of Nitrous Oxide by Sulphurous Acid*

A solution of sulphurous acid containing 0.0431 grams per cc. was used and 29 per cent reduction to nitrogen was obtained. No further experiments were performed with sulphurous acid due to the fact that the carbon dioxide and nitrous oxide drive the sulphur dioxide from solution and thereby change the concentration. Sodium sulphite was used instead of sulphurous acid.

*The Reduction of Nitrous Oxide by Sodium Sulphite*

Sodium sulphite reduces nitrous oxide to nitrogen. The results of varying the concentration of sodium sulphite are shown in Table VII, and Fig. 2, Curve C. Experiment No. 7 shows the result of increased time of contact upon the reduction. Using a concentration of 15 grams of sodium sulphite in 120 cc. of solution, the effect of temperature was studied Table VIII, Fig. 3, Curve C. The effect of increased time of contact is shown in experiment No. 6. No acid was used in these experiments as sulphur dioxide is formed with a corresponding decrease in the concentration of the sodium sulphite.

TABLE VII

The Reduction of Nitrous Oxide with Sodium Sulphite:
Variation of the Concentration of Sodium Sulphite.

Temperature 20°C.
Volume of solution—120 cc.
Number of passages of gas—10 in all except No. 7 where was 45.
Time of contact—120 min. in all except No. 7 where was 540 min.

| Expt. No. | $Na_2SO_3$ G. | $N_2O$ taken Mg. | $N_2O$ reduced Mg. | $N_2$ calc. Mg. | $N_2$ found Mg. | Per cent reduction |
|---|---|---|---|---|---|---|
| 1 | 2 | 35.5 | 1.1 | 0.7 | 0.7 | 3.0 |
| 2 | 5 | 35.5 | 2.4 | 1.6 | 1.6 | 6.9 |
| 3 | 8 | 35.6 | 3.9 | 2.5 | 2.5 | 10.9 |
| 4 | 10 | 35.8 | 6.4 | 4.0 | 4.0 | 17.8 |
| 5 | 12 | 36.2 | 7.8 | 4.9 | 4.9 | 21.6 |
| 6 | 15 | 35.4 | 10.6 | 6.7 | 6.7 | 30.0 |
| 7 | 15 | 35.7 | 30.0 | 18.9 | 18.9 | 84.0 |

*E. M. F. and Conductance Measurements*

For reasons which are given in the theoretical division of this paper, it was found necessary to make a series of e.m.f. determinations upon the solutions of the reducing agents used, and upon a saturated solution (20°C.) of nitrous oxide, containing varying amounts of hydrochloric acid. These determinations were made by means of a calomel electrode against a platinum electrode in the case of the solutions of the metallic salts, and against an electrode of platinum black in the nitrous oxide experiments. A Leeds and Northrup

## TABLE VIII

### The Reduction of Nitrous Oxide with Sodium Sulphite: Variation of the Temperature.

Amount of $Na_2SO_3$—15 g.
Volume of solution—120 cc.
Number of passages of gas—10 in all except No. 6 where was 45.
Time of contact—120 min. in all except No. 6 where was 540 min.

| Expt. No. | Temp. °C. | $N_2O$ taken Mg. | $N_2O$ reduced Mg. | $N_2$ calc. Mg. | $N_2$ found Mg. | Per cent reduction |
|---|---|---|---|---|---|---|
| 1 | 10 | 36.4 | 10.6 | 6.7 | 6.7 | 29.1 |
| 2 | 20 | 37.0 | 11.0 | 7.0 | 7.0 | 29.8 |
| 3 | 40 | 35.5 | 8.9 | 5.8 | 5.6 | 25.0 |
| 4 | 60 | 35.6 | 4.2 | 2.7 | 2.7 | 11.9 |
| 5 | 80 | 35.8 | 0.7 | 0.67 | 0.45 | 2.0 |
| 6 | 80 | 35.5 | 3.9 | 2.5 | 2.5 | 11.0 |

## TABLE IX

### Voltage Measurements of Solutions of Titanous Chloride, Stannous Chloride, Sodium Sulphite and Nitrous Oxide, in Solutions containing varying Amounts of Hydrochloric Acid.

| Cc. HCl | Volts | Corrected reading[1] |
|---|---|---|
| **Titanous Chloride** 10 grams, in 120 cc. of solution | | |
| 2 | 0.270 | +0.023 |
| 10 | 0.230 | −0.018 |
| 15 | 0.207 | −0.041 |
| 20 | 0.189 | −0.059 |
| **Stannous Chloride** 20 grams, in 120 cc. of solution | | |
| 2 | 0.057 | −0.191 |
| 10 | 0.081 | −0.167 |
| 15 | 0.112 | −0.138 |
| 20 | 0.119 | −0.129 |
| **Sodium Sulphite** 12 grams, in 120 cc. of solution | | |
| 0 | 0.035 | −0.213 |
| **Nitrous Oxide** Saturated solution at 20°C. 120 cc. solution | | |
| 0 | 0.599 | +0.847 |
| 2 | 0.603 | +0.851 |
| 10 | 0.611 | +0.859 |
| 15 | 0.625 | +0.873 |
| 20 | 0.641 | +0.889 |

[1] By subtracting 0.2475, the value of the calomel electrode.

Type K potentiometer was used in making the measurements. Results are given in Table IX. The values obtained are in agreement with those of B. Neumann[1]. In order to refer the values to a normal hydrogen electrode, it was necessary to add the value of the calomel electrode to the voltages obtained with the solutions of nitrous oxide since the calomel electrode is negative with respect to platinum black in this solution. The solution was kept saturated with nitrous oxide by bubbling the gas through the solution during the experiment.

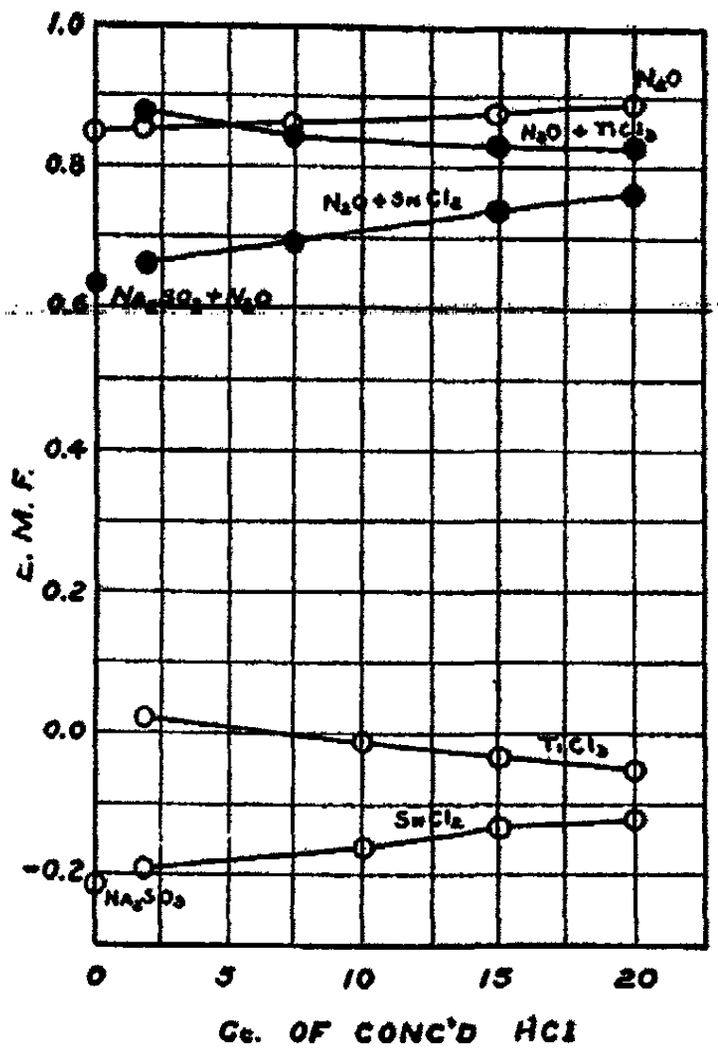



FIG. 5
E. M. F. Measurements
Note—Solid black points are derived by taking the algebraic sum of the experimentally determined values.

In order to determine the change in conductivity of distilled water when saturated with nitrous oxide, 100 cc. of distilled water was placed in a large test tube and the conductivity measured. Table X, experiment No. 1. The water was then saturated with pure nitrous oxide by bubbling the gas through the solution and the conductivity again measured. Table X, experiment No. 2. C is the conductivity in reciprocal ohms of the solution between the electrodes. Leeds and Northrup apparatus was used throughout. The specific conductivity of the distilled water used was about $2.0 \times 10^{-6}$. The results obtained showing an increase in conductivity would indicate that $(NOH)_2$ was formed (See discussion).

[1] Neumann: Z. physik. Chem., 14, 193 (1894).

TABLE X

Conductivity Measurements

| Expt. No. | Temp. °C. | C | ΔC |
|---|---|---|---|
| 1 | 25.22 | $1.6 \times 10^{-6}$ | — — — |
| 2 | 25.18 | $2.1 \times 10^{-6}$ | $5 \times 10^{-6}$ |

## Discussion

From the preceding experimental work it has been shown that, with all of the reducing agents used, the percentage reduction for a definite time of contact, (1) increases with an increase in concentration of the reducing agent, (2) decreases with a rise in temperature and, (3) in the case of titanous chloride and of stannous chloride, decreases with increased acid concentration. The experimental work also shows that the only effect of these variables is to change the percentage reduction and never the nature of the final reduction product with a given reducing agent.

It would be natural to expect in the reduction of a gas by liquid reagents that no reduction would take place, except with gas which dissolves in the liquid. In the reduction with stannous chloride the only product obtained is hydroxylamine, which can only be explained on the assumption that hydration of nitrous oxide occurs, which we believe takes place with the formation of hyponitrous acid.

$$N_2O + H_2O = (NOH)_2$$

On this basis it is possible to explain all of the results obtained. A direct reduction of nitrous oxide without the addition of water would give an unsymmetrical product and only a fifty percent yield of hydroxylamine.

Since in every case with a given reducing agent the final product is always the same, the reducing power of the agent employed must govern the nature of the product and the quantity of the product obtained must depend upon the velocity at which the total process of reduction occurs. The total process of reduction takes place in two steps: (1) the dissolving of the $N_2O$ with the formation of $(NOH)_2$ and (2) the reduction of the $(NOH)_2$ formed, by the different reducing agents. It is highly improbable that these two reactions will take place at the same rate under varying conditions and the velocity of the total reaction will be dependent upon the rate at which the slower reaction occurs.

In all of the experiments where the concentration of the reducing agent was varied, the acid concentration was very low or zero and the temperature was kept at 20°C. Unless then, the concentration of the reducing agent itself has some effect, the first reaction in the process should take place at constant speed, and the total velocity of the reaction will depend upon the speed of the second reaction. Since the speed of a reaction is proportional to the active mass of the reactants, it would be expected that an increase in the concentration of the reducing agent would increase the velocity of the re-

action. Also, an increase in the time of contact should increase the total amount of reduction which occurs. The curves (Fig. 2) show that this is true.

It has already been stated[1] that the decrease in the reduction of NO with $SnCl_2$ at high temperatures is probably due to the decreased solubility. Since nitrous oxide is only sparingly soluble at high temperatures, any increase in the temperature will decrease the amount of $N_2O$ that would be dissolved when equilibrium is reached in the first reaction. This would decrease the concentration of $(NOH)_2$ and result in a decreased percentage of reduction for a given time of contact. Increased time of contact would give increased reduction. The curves (Fig. 3) show that results of this nature were found.

The decreased reduction with increased acidity might be due to any of the following causes: (1) A decrease in the velocity of the reduction of $(NOH)_2$ because of (a) a decrease in the concentration of the $Ti^{+++}$ of $Sn^{++}$ ions due to the repression of the ionization by HCl or (b) a decrease in the reducing power of the $TiCl_3$ and $SnCl_2$ with increased acidity. (2) The acidity of the solution decreasing either the rate of attainment of equilibrium in the formation of $(NOH)_2$, or the equilibrium concentration of $(NOH)_2$.

Experiments No. 9, Table III and No. 7 Table VI show that it cannot be due to decreased ionic concentration. In these experiments, hydrochloric acid was added and then neutralized with sodium hydroxide.. The amount of reduction in these cases was much greater than when the equivalent amount of the HCl was present, although the concentration of the $Cl^-$ ion was approximately the same in both cases.

The e.m.f. measurements of the reducing power of titanous chloride decrease with increased quantities of HCl, whereas those for stannous chloride increase under the same conditions (Table IX, and Fig. 5). The case of titanous chloride is what we would expect, while that of stannous chloride at first seems anomalous. Goldschmidt and Ingebrechtsen[2] have shown that the increased reducing power of stannous chloride on nitro bodies with increased acidity is due to the formation of $HSnCl_3$. Since, however, the rate of reduction of $N_2O$ by either $TiCl_3$ or $SnCl_2$ decreases with increased acidity, the change in the reducing power of the solution is not the essential factor.

The controlling factor must be that the increased acidity decreases the rate at which equilibrium is attained in the formation of $(NOH)_2$. If this is the case, then, an equivalent amount of some other acid would have the same effect. This was proved by the use of an equivalent amount of sulphuric acid in experiment No. 8, Table VI and experiment No. 8, Table III. The slightly increased reduction can be accounted for by the difference in the ionization of the acids. Also the presence of some catalyst like platinized platinum should increase the amount of reduction by increasing the rate at which equilibrium in the first reaction is attained. This was found to be the case as

[1] Bancroft: J. Phys. Chem., 28, 488 (1924).
[2] Goldschmidt and Ingebrechtsen: Z. physik. Chem., 48, 435 (1904).

shown by experiment No. 10, Table III, and shows that it is the rate of formation of $(NOH)_2$ which is affected by the acid, and not the equilibrium concentration of $(NOH)_2$.

Since the reducing power of titanous chloride decreases and that of stannous chloride increases with increased acidity it would seem probable that the same reduction product should not always be obtained under all of the conditions under which the experiments were performed. However, as the voltage measurements show, the oxidizing power of the nitrous oxide increases with increased acidity. The total effect of the reaction must be represented by the algebraic sum of these two measurements which is shown by the curves (Fig. 5). It is seen that the total reducing power in the case of titanous chloride and nitrous oxide decreases rapidly at the start and then remains practically constant. In the case of stannous chloride the total reducing power increases rapidly at the start but later the rate of increase decreases. This is probably due to the formation of large amounts of $HSnCl_3$ with increased concentration of HCl.

$$\frac{(HSnCl_3)}{(SnCl_2) \times (HCl)} = K$$

The rate of change of reducing power of stannous chloride solutions will naturally decrease as the concentration of HCl increases.

Since the above mentioned curves do not intersect at any point in the region of the values used in these experiments and since the reducing power of sodium sulphite is less than that of either stannous chloride or titanous chloride, the fact that only one primary reduction product is obtained with each reducing agent is readily explained.

With higher concentrations of hydroxylamine in the presence of an excess of stannous chloride, other experimenters have found[1] that ammonium salts may result. Stannous chloride is therefore capable of reducing hydroxylamine to ammonia, but the low concentrations of hydroxylamine developed in the solutions of this work probably account for the fact that no ammonia was found.

From the fact that the reduction of nitrous oxide to ammonia, hydroxylamine, or nitrogen is dependent upon the reducing power of the salt used, the following is suggested as the mechanism of the reactions.

$$N_2O + H_2O = H_2N_2O_2$$
$$H_2N_2O_2 + 2H = 2\,H_2O + N_2$$
$$H_2N_2O_2 + 4H = 2\,NH_2OH$$
$$H_2N_2O_2 + 8H = 2\,NH_3 + 2H_2O$$

This view was also advocated by Milligan and Gillette.

[1] Milligan and Gillette: J. Phys. Chem., 28, 744 (1924).

## Summary

The results of these experiments may be summarized as follows:

1. Nitrous oxide is reduced by aqueous solutions of titanous chloride, stannous chloride and sodium sulphite, with the formation of ammonia, hydroxylamine, and nitrogen respectively.

2. The rate of reduction of nitrous oxide by aqueous solutions of these salts decreases with increase in temperature.

3. The rate of reduction of nitrous oxide by aqueous solutions of titanous chloride and stannous chloride decreases with increased acidity.

4. The rate of reduction of nitrous oxide by aqueous solutions of titanous chloride is catalyzed by platinized platinum.

5. The rate of reduction of nitrous oxide by aqueous solutions of titanous chloride, stannous chloride and sodium sulphite increases with increase in concentration of the reducing agent.

6. The probable mechanism of the reduction of nitrous oxide has been suggested.

# A COMPARATIVE STUDY OF TWO KINDS OF COLORED ROCK SALT*

BY T. E. PHIPPS AND WALLACE R. BRODE

## Introduction

Two kinds of colored halite were investigated, the deep-blue naturally occurring variety,—hereafter called "Stassfurt blue halite",—and halite colored by heating in contact with alkali metal vapor at high temperatures,—hereafter called "sodium-colored halite". The blue color of certain Stassfurt halites attracted the attention of Sir Humphry Davy in 1818, and though many researches into the cause of the color have been undertaken since that time[1] a satisfactory explanation is still lacking. The theory which seems to have found most support is the one suggested by Zsigmondy,[2]—that the color is due to colloidal particles of free metal in the halite. This explanation has been accepted by many colloid chemists, notably Siedentopf[3] and Svedberg.[4] Siedentopf studied the Stassfurt blue salt with the ultramicroscope and published patterns of what he believed to be particles of sodium in the halite lattice. Siedentopf's evidence was questioned by Spezia,[5] who failed to find any trace of alkalinity to indicators in water solutions of the blue salt. One or two other investigators agree with Spezia as to the non-alkalinity of such solutions.

Ordinary colorless halite can be colored[6] by heating it in contact with sodium vapor to temperatures above 650°C. This is done most easily by sealing up cubes of rock salt with sodium in an iron crucible with a high-temperature cement and heating in an electric furnace for an hour or more. The colors obtained with different heat treatments will be discussed later in this paper. Siedentopf[7] sealed crystal and metal up in a glass tube, and heated to a temperature 50° to 80° below the boiling point of the metal (680°C. for sodium and 590°C. for potassium). At lower temperatures the vapor pressure of the metal was too low and at higher temperatures he states that the metal distills out of the crystal again and the glass is attacked. Higher temperatures can be used with the iron crucible; on the other hand, temperatures too near the melting point of the halite are not desirable, since only an amber or pale straw coloration is obtainable under these conditions. It is conceded by all investigators that crystals colored in this manner contain free sodium, visible ultramicroscopically, and that their water solutions are alkaline.

---

*Contribution from the chemical laboratory of the University of Illinois.

[1] A complete summary may be found in Mellor: "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", 2, pp. 530 et seg. (1922).

[2] "Zur Erkenntnis der Kolloide," p. 58 (1905).

[3] Physik. Z., 6, 855-864 (1904).

[4] "Colloid Chemistry," p. 67 (1924).

[5] Centr. Min. 1909, 394-404.

[6] For references see Mellor: "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 2, pp. 530 et. seq.

[7] Siedentopf: Physik. Z. 6, 855-864 (1904).

In general the two types of colored halite behave quite differently toward heat, the Stassfurt blue fading out at about 300°C, whereas the artificial color persists (though faintly) up to the melting point. Nevertheless it is possible to prepare artificially colored crystals which match Stassfurt blue crystals fairly closely both as to visual tint and depth of color; hence it is not surprising that many investigators have supposed that the color is due to the same cause in both cases.

Two lines of study occurred to the authors: (1) an accurate comparison by means of the hydrogen electrode of the alkalinities of water solutions of the two types, and (2) a comparative spectrophotometric study of the two types over the ranges of temperature where color changes occur.

### *A. Study of the Alkalinity of Water Solutions of the Two Types of Colored Halite.*[1]

After several attempts to adapt the Hildebrand and other types of hydrogen electrode to the problem, the electrode shown in Fig. 1 was designed. The Pyrex electrode vessel is of the captive hydrogen type, and combines features of the Clark and of the Bailey vessels. It has the following advantages: (1) it comes to quick equilibrium, (2) it can be stirred simply and effectively by tilting back and forth a few times, thus eliminating complicated mechanical stirring, (3) after the first few rapidly performed steps it is protected from further contamination by the $CO_2$ of the air, (4) the electrode is easily replaceable, and (5) the trap connection to the saturated KCl calomel half-cell gives steady boundary conditions between the two liquids. The operation of the electrode is as follows:

The vessel (Fig. 1) is completely filled with conductivity water, and while it is held in the position shown in Fig. 1, it is about half filled by downward displacement with purified hydrogen led in through C. A weighed crystal is dropped into the bend, and the ground glass stopper D is seated so as to completely exclude the air. Equilibrium is then quickly obtained between hydrogen, solution, and electrode by one or two minutes of vigorous shaking. Then, with the arm A vertical as in Fig. 1, the stopper D. is removed and connection is quickly made with the saturated KCl calomel electrode (Fig. 2) by slipping the arm B over F and tightly engaging the rubber stopper G,—the arm A still being kept vertical. This puts a slight pressure upon the hydrogen, and when H is opened to the atmosphere, the solution runs up into the trap about half-filling it and resting upon the denser saturated solution of KCl below. The arm A is then turned to a horizontal position (shown in Fig. 2) by rotating the stopper G about its axis.

The E. M. F. of the combination is measured by a Leeds and Northrup Students' Type Potentiometer. Ordinarily, steady readings are obtained within two or three minutes. At the end of the run the hydrogen electrode is

[1] This work was done in part by Mr. G. C. Mason. Mason: Thesis for the Degree of Bachelor of Science, Univ. of Illinois (1924).

disconnected at G, the total volume of the solution is measured, the strap E is flushed out with saturated KCl and another run is begun.

Measurements were made upon solutions of (1) Stassfurt blue halite, (2) samples cleaved from the colorless portions of large Stassfurt blue specimens, (3) colorless crystals from Navarre, Michigan, (4) crystals from both Stassfurt and Navarre, colored artifically in sodium vapor. Utmost care was taken in the choice of samples of the artifically colored salt for alkalinity tests, to exclude those into which metal might have penetrated by following faults or cleavages or otherwise than by diffusion into the lattice. A large part of any given colored crystal was dissolved away, and only the center, which must appear crystal clear and free of faults, was used for an alkalinity test. Table I gives results representative of more than a hundred such measurements.

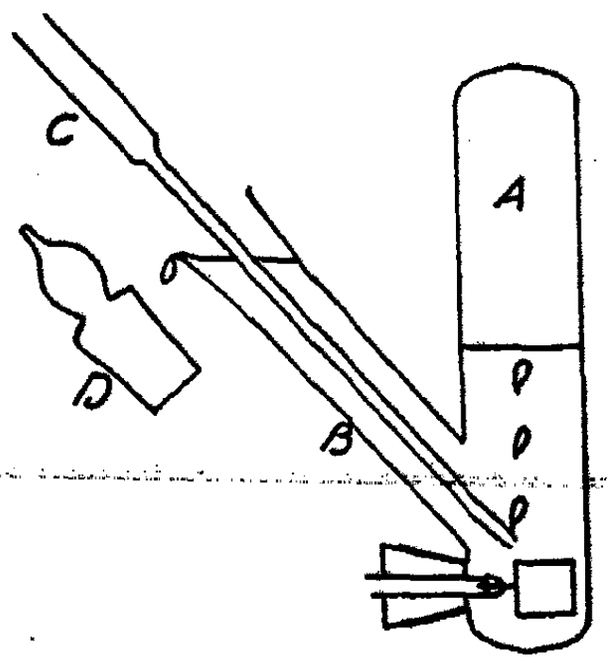



FIG. 1

TABLE I

| Dissolved salt | Color | $P_H$ of solution | Normality of free sodium in crystal |
|---|---|---|---|
| Sodium-colored Halite (Navarre) | | | |
| 1 | Blue | 8.38 | $5.2\times10^{-4}$ |
| 2 | Pink | 7.62 | $1.6\times10^{-4}$ |
| 3 | Pink | 8.81 | $2.3\times10^{-3}$ |
| 4 | Green | 7.94 | $1.5\times10^{-4}$ |
| Halite (Navarre) | | | |
| 1 | Colorless | 5.87 | Zero |
| 2 | " | 6.07 | " |
| 3 | " | 6.09 | " |
| 4 | " | 6.02 | " |
| 5 | " | 6.05 | " |
| 6 | " | 6.04 | " |
| Halite (Stassfurt) | | | |
| 1 | Colorless | 6.04 | Zero |
| 2 | " | 6.07 | " |
| Halite (Stassfurt blue) | | | |
| 1 | Blue | 6.04 | Zero |
| 2 | " | 6.05 | " |
| 3 | " | 6.04 | " |
| 4 | " | 5.98 | " |
| 5 | " | 6.04 | " |

Solutions of the colorless crystals and of the Stassfurt blue crystals gave practically identical $P_H$ values, while the solutions of the artificially colored crystals invariably gave markedly alkaline solutions,—sometimes 0.001 N or greater. Calculation showed that the maximum concentration of free sodium which (because of limitations of the method) might be conceded to be present in the Stassfurt blue crystal is of the order of magnitude $1 \times 10^{-3}$ N, or one-hundred-millionth normal. In view of the fact that Kraus has stated that the dilute solution of sodium in liquid ammonia whose *very faint blue* is still just visible, has a concentration of $2.5 \times 10^{-5}$ or one-forty-thousandth normal, it seems highly improbable that the color in the case of a *deeply colored* Stass-

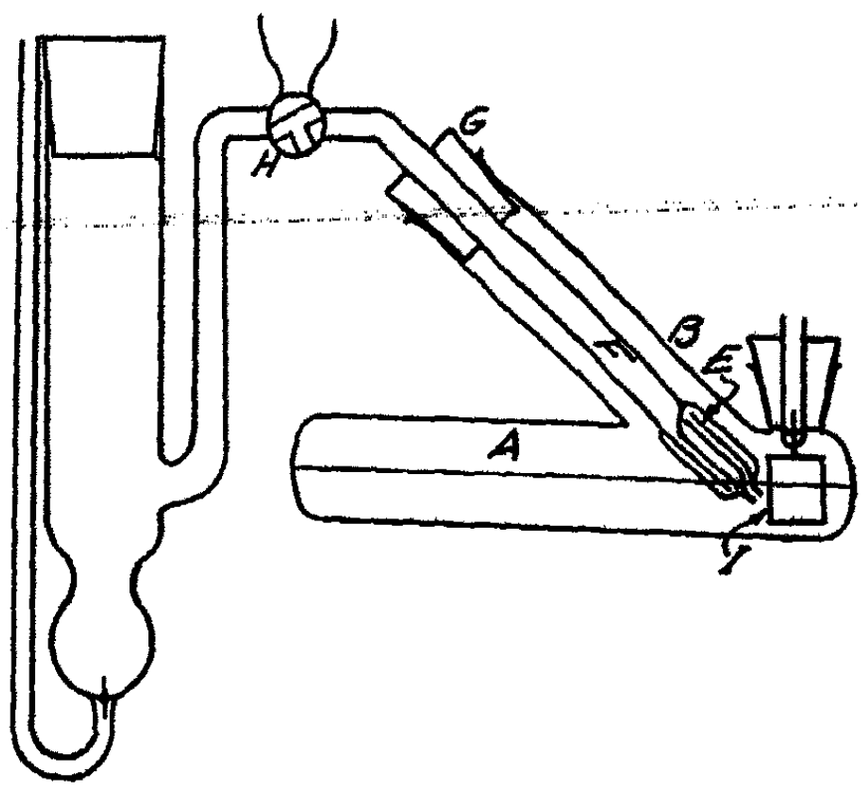



FIG. 2

furt crystal could be due to free sodium. There is no case on record, so far as the authors know, where coloring matter in concentrations less than one-forty-thousandth normal has been observable.

Clark[1] has pointed out the difficulties which attend the accurate determination of $P_H$ values in unbuffered solutions of salts like KCl in the neutral range; and the uncertainty involved in the "salt error" is well recognized. In this case, however, where we are seeking only comparative data as between solutions of Stassfurt blue and solutions of sodium-colored halite, all such effects may be assumed to cancel. Though the normalities calculated in column 4 can be relied upon to give only the order of magnitude of the free sodium in the sodium-colored crystals, we feel confident that the $P_H$ values in column 3 have a definite comparative value.

Artifically colored crystals were heated just below their melting point, and were found to give alkaline solutions still. Since sodium will dissolve in *molten* NaCl to give a bluish melt, it was hardly to be expected that heating

[1] "Determination of Hydrogen Ions," 2nd edition, p. 269 (1922).

artificially colored halite to its melting point would expel the sodium. Stassfurt blue crystals after being decolorized by heat were found to give the same $P_H$ values in solution as before.

The results of this part of the investigation seem conclusive against the colloidal metal theory of the color in Stassfurt blue halite. One investigator[1] has stated that *some* Stassfurt blue halite shows alkalinity, implying that most of it does not. Whether or not the blue color is found in some samples which give alkaline solutions, the significant fact remains that a random sample of the characteristic blue Stassfurt halite gave no trace of alkalinity as tested

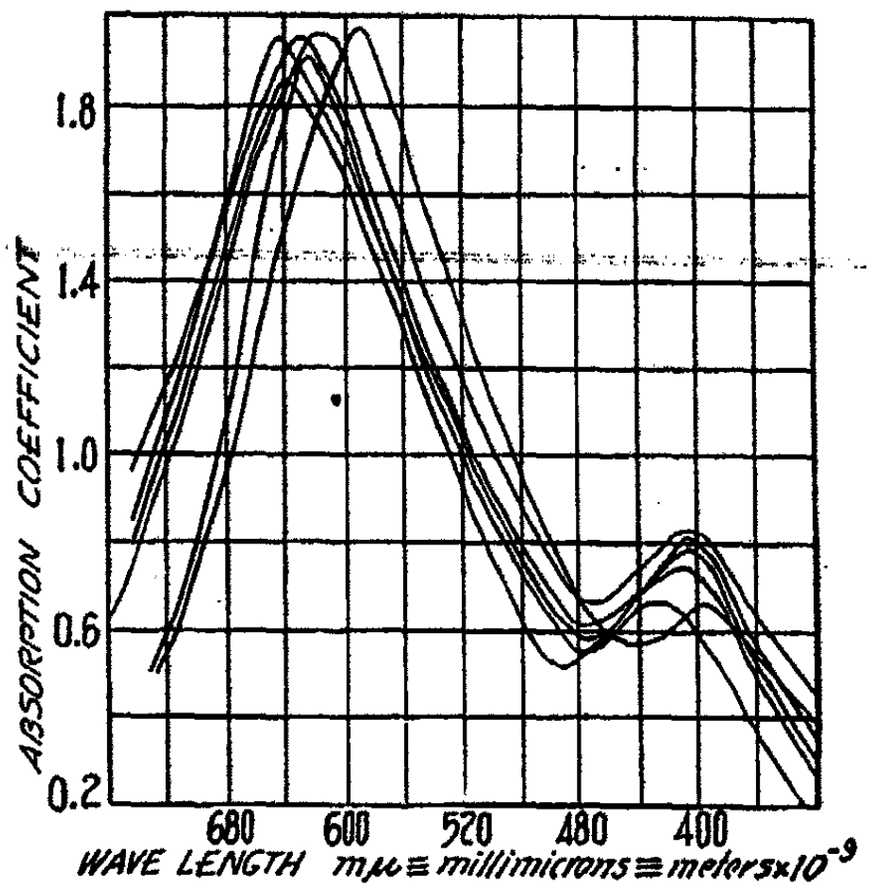



FIG. 3

by the hydrogen electrode; whereas under identical conditions artifically colored crystals of approximately the same depth of color, known to contain sodium, showed marked alkalinity in solution.

*B. Spectrophotometric Study of the Two Types of Colored Halite*

This study was made with a Keuffel and Esser Spectrophotometer. A horizontal, tubular, electrically-heated furnace with end windows of mica was designed to fit into the optical path of the instrument between the light source and the main optical system. The temperature could be raised slowly or rapidly at will, or could be kept constant within less than five degrees. A special holder for the crystal to be examined and for the colorless standard was designed for the furnace. Temperatures up to 350°C were measured with a mercury thermometer introduced laterally into the furnace through a porcelain tube. A chromelalumel thermocouple was used for higher temperatures.

[1] Cornu: Neues Jahrb. Min. Geol. 1, 22-58 (1908).

Fig. 3 shows the absorption curves obtained at room temperature for several different samples of Stassfurt blue halite. Two absorption bands are noted, one in the green at 524 mμ, and another more intense band in the red at 640-660 mμ. It is noteworthy that the vibration centers of the bands, though not quite constant, vary within a narrow range only, and the ratio between the intensities of the two bands in all cases is approximately constant.

Fig. 4 shows the progressive shift of the maximum of the principal band which resulted when a Stassfurt blue crystal was slowly heated from room temperature up to 320°C. The maximum first shifts toward the yellow, and at the same time begins to drop. Then, still dropping, it moves back toward

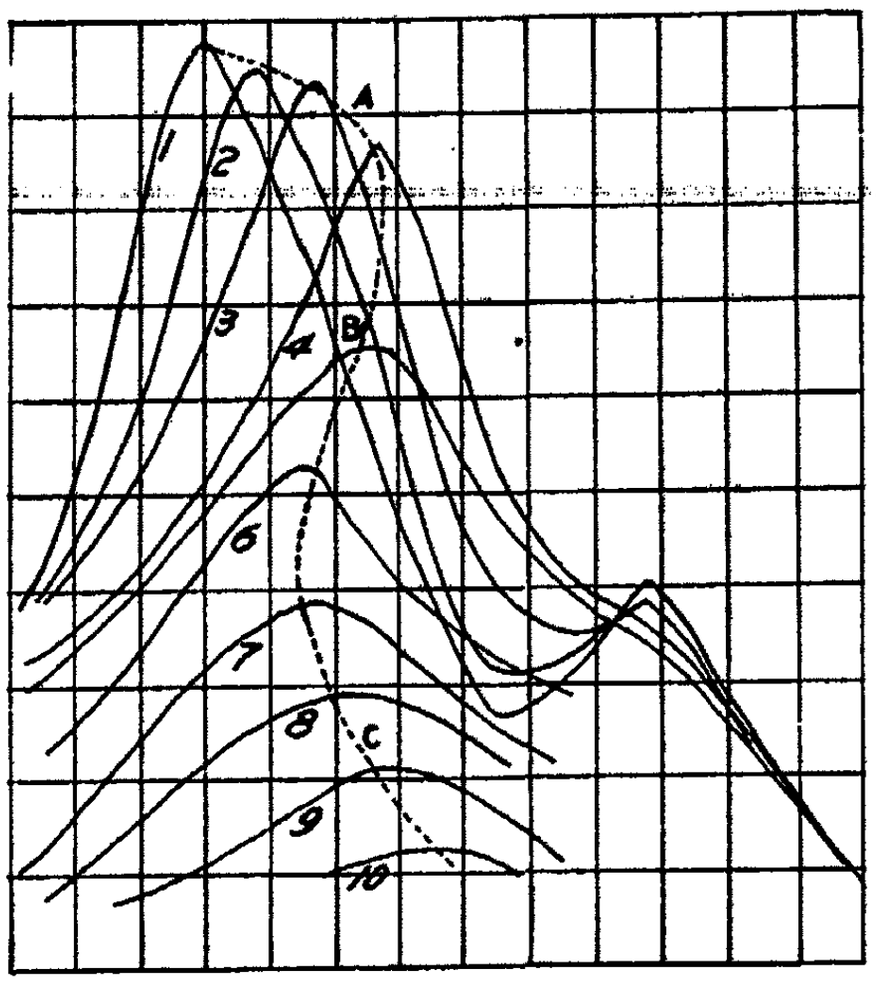



FIG. 4

the red, and finally back again into the yellow before completely fading out. The S-shaped dotted line indicates the movement of the maximum.

Fig. 5 shows the progressive shift of the maximum which resulted when a Stassfurt blue crystal was thrust directly into a furnace at 241°C and heated rapidly to 307°C. The maximum quickly shifts without appreciable change intensity to the neighborhood of 589 mμ( ±2 mμ). Then it stops its lateral shifting and drops, maintaining a nearly constant peak at 589 mμ. The behavior toward heat of the Stassfurt blue halite as shown in Figs. 4 and 5 has been checked a number of times and in all cases rapid heating caused the principal band to shift to 589 mμ, followed by rapid fading. In all cases of slow heating there was a shifting of the maximum back and forth between red and yellow, usually in an S-shaped course as shown in Fig. 4. In no case did the band shift further toward the shorter wave-lengths than 589 mμ.

Figs. 6 and 7 show the absorption curves for several samples of rock salt artificially colored with sodium. These crystals show surprising colors and color combinations with varying heat treatment. Often when first removed from the crucible in which they were colored they show a metallic bronze, yellow, brown, green, or smoky gray color, but upon being heated to low redness in air, secondary pink and purplish-blue colors usually appear. It seems probable that the first smoky or cloudy appearance is due to colloidal masses of metal, and that the secondary color development is due to dispersion of the colloidal aggregates by heat. Two principal types of color are evolved by the secondary heating, a purplish-blue and a deep pink. The purplish-blue color (Curves 1, 2, 3, 4, and 5, Fig. 6) exhibits a single broad band having

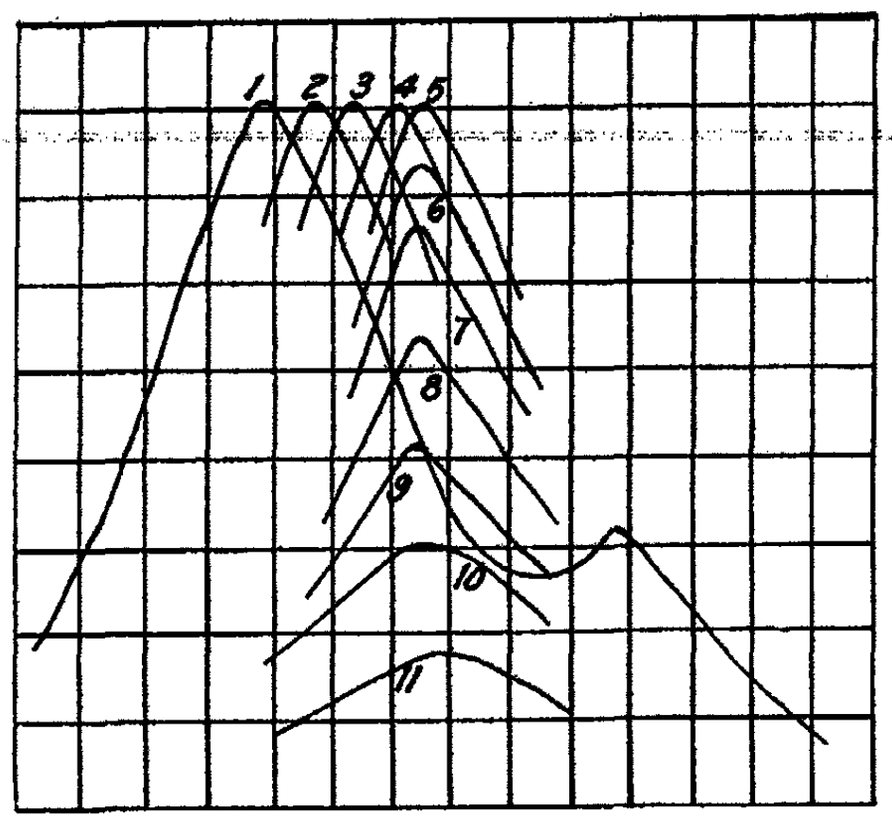



FIG. 5

its vibration center in the vicinity of 589 mμ, with a possible secondary inflection in the green in some cases (Curves 3 and 4, Fig 6), reminding one somewhat of the secondary band in the green at 524 mμ for the Stassfurt blue crystals. The vibration center of the principal band is not definite. Nevertheless in all of the crystals studied it lay between 560 mμ and 620 mμ. Curve No. 6 (Fig. 6) which crosses the other curves in the unusual way was obtained from a greenish colored crystal got by suddenly cooling from about 650°C during the operation of coloring.

The other type of color produced by secondary heating is a fine clear pink. Fig. 7 shows absorption curves for this type. The sharpness and intensity of these bands suggest that there is a single definite vibration in this case. It is also interesting to note that when potassium metal is used in coloring halite the same band (No. 3) is obtained as for pink sodium-colored halite. Absorption curves of this pink type are characterized by a sharp intense band at 552 mμ.

It is possible to produce side by side in the same crystal a pink and a purple-blue region merging into each other, by sudden cooling of one edge of a crystal during the secondary heating operation. Usually the pink region will be found deeper in the crystal and the blue next to the surface, though sometimes one meets with a reversal of this order. In general the progression of colors with rising temperature is (1) purplish-blue (2) deep pink (3) amber and (4) pale straw (just below the melting point of the crystal). These are the colors obtained in a cold crystal by heating it to successively higher temperatures and cooling it periodically. When hot a crystal will usually show a color one or two steps lower in the series than when cold; for example a crystal which

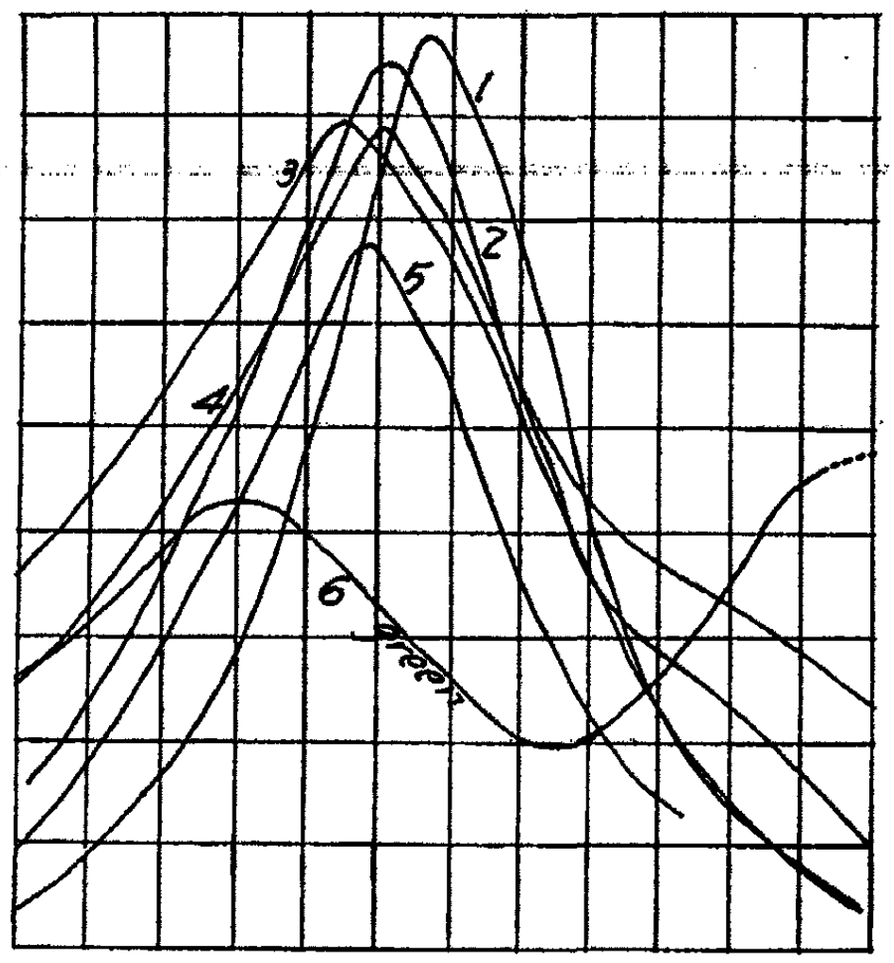



FIG. 6

will show a pink when cold will look purple when hot, and one which is amber when cold will look pink or purplish-pink when hot. The series seems to be irreversible. Thus when a purplish-blue crystal has been heated sufficiently to cause it to show pink when cold, the purple tint when cold cannot be restored by any heat treatment or other treatment. On the other hand, by carefully heating a purple crystal, a part only of the purple modification can be converted into the pink, and beautiful magenta shades can be produced by the blending. The amber color which is obtained by heating sodium-colored crystals to high temperatures matches visually the amber color produced in colorless crystals by exposure to radium emanation. However, we have made no accurate comparison of these two colors.

Fig. 8 shows the effect of heat upon the absorption of a single purple sodium-colored crystal. The band narrows and intensifies to a fairly sharp

peak at 589 mμ, and then on fading the peak shifts over toward the shorter wave-lengths (apparently approaching 552 mμ). At the same time the curve shows a secondary inflection at or near 589 mμ, showing the continued presence of a small number of vibrators of this original frequency even at the higher temperature. The sequence of curves with rising temperature, beginning with No. 1 at 310°C, is readily followed in Fig. 8.

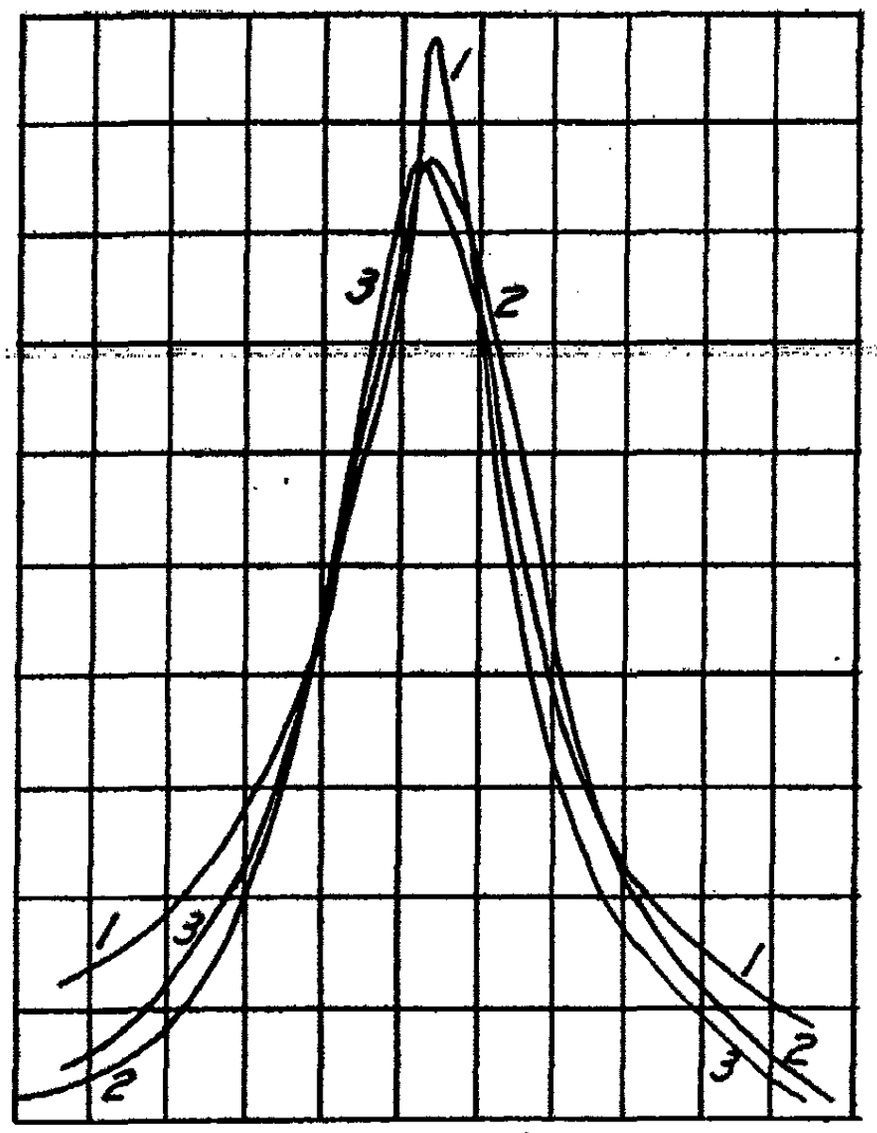



FIG. 7

Fig. 9 shows the effect of heat upon a typical pink sodium-colored crystal. The band moves from 552 mμ over to 589 mμ, maintaining its sharp well-defined character. Then it fades, and during the fading the band appears to shift back and forth between 552 mμ and 589mμ.

A brief comparison of the effect of ultra-violet light upon Stassfurt blue and sodium-colored halite was attempted. Crystals of the two types were exposed side by side for two hours at a distance of 12 inches from a quartz mercury vapor lamp. The sodium-colored crystal (purplish-blue initially) was changed to a pale straw color visually identical with that got by heating such a crystal to a high temperature, and with that produced in a colorless crystal by radium emanation. There was no effect whatever upon the Stassfurt blue. The fading of the latter seems therefore to require vibration of the lattice produced only by temperature.

## Discussion

The recurrence of 589 mμ (Figs 4 and 5), the wave-length of the D-line of sodium, as the wave-length at which fading occurs in all Stassfurt blue crystals suggests at once the possibility that the Stassfurt blue may be due to an abnormality in the constraint upon the valence electron at various points in the halite lattice, and that the fading of the color with heat may come from the return of the electron to its normal constraint. If this is the

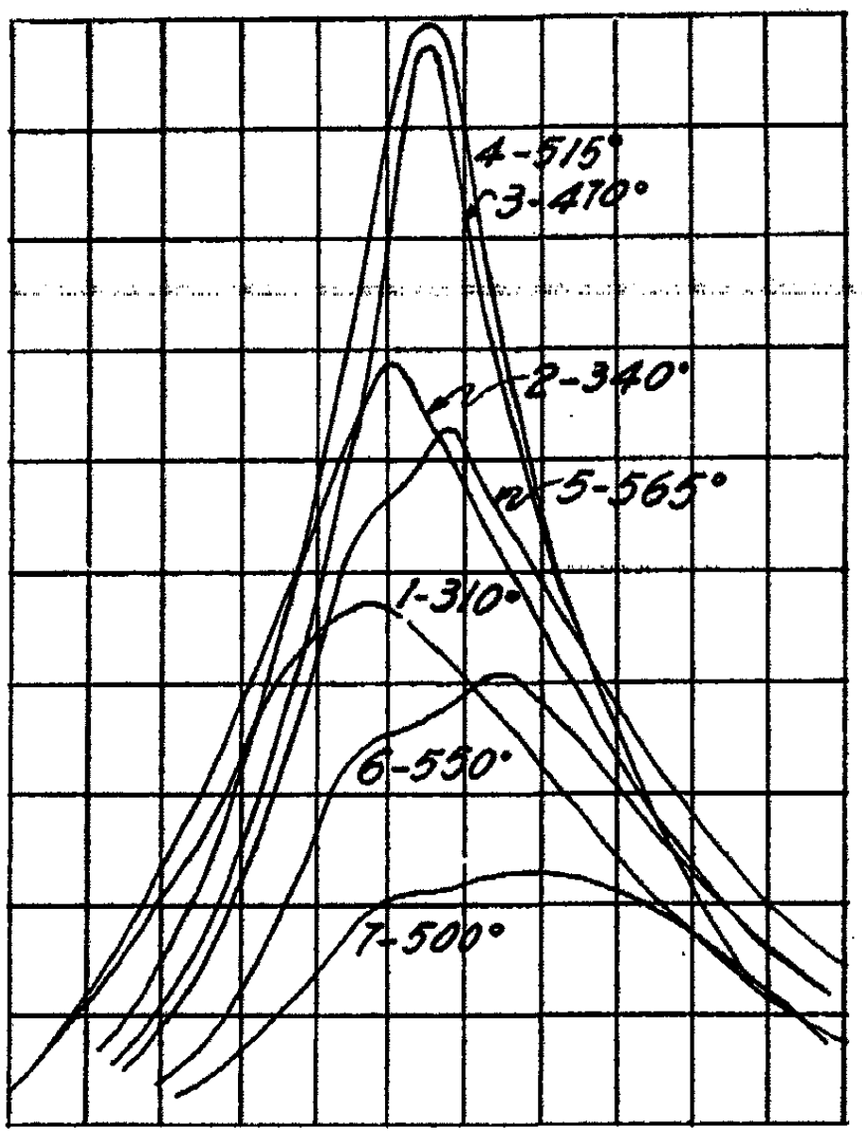



FIG. 8

case we may expect the fading at 589 mμ to be coincident with the appearance or intensification of an absorption band beyond the visible part of the spectrum,—perhaps in the ultra-violet.

The theory that electronic displacement constitutes one cause for color in crystals has been clearly stated by Lind and Bardwell[1] and we quote here from the concluding paragraphs of their recent paper. "Certain groups of electrons are displaced by radiation from their normal positions and take up new metastable positions among the atoms. No displacement (or only secondary displacement) of the atom is involved. No change in the crystal lattice as revealed by X-Rays would be expected nor would there by any production

[1] J. Franklin Inst. 196, 375 (1923).

of colloidal particles. One or more groups of electrons may be involved. . . It appears to us probable that the color is due to the vibration of electrons in their abnormal positions. . . . Since the crystal is transparent, the color complementary to the one absorbed by the electronic vibration is transmitted. In the metastable positions, under less constraint, the electrons are also freer to take part in electrical conduction and in photo-electric emission under radiative stimulus, and can also return to their normal positions under this stimulus or by that of heat."

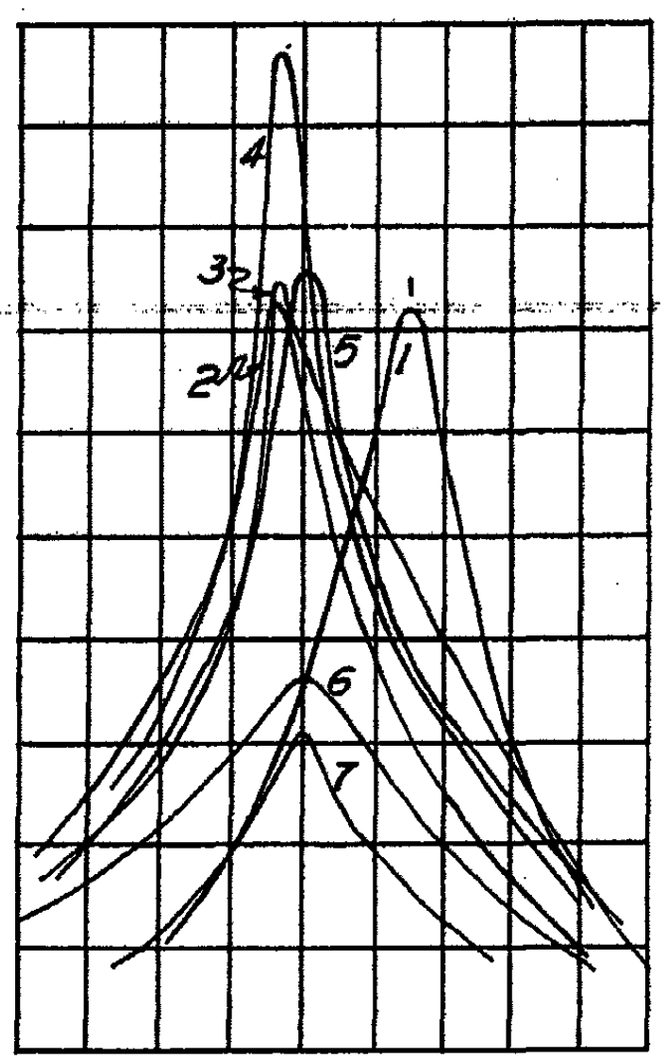



FIG. 9

Without committing ourselves finally as to the exact nature of the Strassfurt blue color, we may seek a general explanation for the rather complex shiftings of the maximum of the principal band with different rates of heating, as shown in Figs. 4 and 5. We shall make the following assumptions: (1) the primary cause of color in the principal band exists in two modifications which we shall call the "650" and the "589". The "650" is stable at room temperatures as low as 190°C undergoes slow transition into the "589". At 300°C the transition is very rapid. We shall speak of the "rate of transition" of the "650" into the "589", and this will be measured by the rate of lateral shifting of the principal band. The rate of transition depends upon the temperature only. (2) The "589" changes into a colorless modification. We shall speak here of a "rate of fading" and this will be measured by the rate at which the principal band drops. If the cause of the color is indeed the electron as suggested above, and if the fading at 589 mμ is coincident with the appearance

or intensification of an absorption band in (say) the ultra-violet, then the rate of fading may be determined by the rate at which the electron at the 589 "level" can acquire radiation of the critical frequency necessary to translate its absorption into the ultra-violet. This radiation may come largely from the spectrophotometer light source, or it may be radiation to which the crystal gives rise by virtue of its own temperature.[1] We shall assume then that the slow step which decides the rate of fading is the acquiring of this critical frequency, and that this depends mainly upon temperature and upon radiation from the light source of the spectrophotometer.

With these assumptions in mind, we conclude that with rapid heating (Fig. 5) the transition rate is very much greater than the fading rate, so that all of the "650" changes to the "589" before an appreciable fraction of the "589" can fade. The result is that the peak moves rapidly from 650 m$\mu$ to 589 m$\mu$ without appreciable dropping (fading). The rate of dropping at 589 m$\mu$ is then determined by the rate at which the critical fading frequency is acquired.

With slow heating (Fig. 4), we shall distinguish the following stages as designated by letters on the S-curve:

(A) In this range the transition rate is somewhat greater than the fading rate. During this interval perhaps 75 percent of the "650" undergoes transition, and of this fraction perhaps only 10 percent fades. The maximum of the band does not reach 589 m$\mu$ at this stage because of the considerable fraction (say 25 percent) of the "650" which remains unchanged.

(B) The transition rate has fallen below the fading rate. All of the "589" produced in (A) fades and the maximum recedes toward the red where the remaining 25 percent (or less) of the "650" still resists transition.

(C) The temperature is now high enough to force transition of the residual "650", and a complete and rapid transition results. The fading rate is not sufficient instantly to remove all of the "589" thus produced. The result is that the band shifts completely over to 589 m$\mu$ and quickly fades out there.

In discussion we have been assuming that a certain fraction of the "650" requires a higher temperature for transition than the rest. Indeed this seems to be the case. In several cases a residual faint blue color has been noticed in a crystal which has been held at a temperature above 300°C for as long as 20 minutes. Everything points to the fact that the "650" is not characterized by a single definite frequency nor by a definite temperature of transition.

The purple sodium-colored crystals (Fig. 6) are characterized by rather broad absorption bands which seem to be the resultant of more than one vibration frequency. It seems probable that in such crystals there is present a small fraction of vibrators absorbing at 552 m$\mu$, and a larger fraction absorbing at 589 m$\mu$. To explain curves of the type of No. 1 (Fig. 8) with its minimum lying well beyond 589 m$\mu$ toward the red, we must suppose that

[1] Experiment showed that a crystal heated above 300°C in the dark for several hours will fade completely, in the absence of any incident radiation from the spectrophotometer light source or otherwise.

some vibrators are present which absorb in the orange red or red part of the spectrum. Perhaps the presence of undispersed colloidal particles of sodium in the purple crystal may account for this absorption in the red and for them broad indefinite character of the principal band. It is significant in Fig. 8 that the broad band with peak about 607 mμ upon heating *intensifies* and shifts to 589 mμ. This intensification of color points to a dispersion by heat of colloidal particles. The shifting to 589 mμ suggests the behavior of the Stassfurt blue crystals, except that the principal band in the Stassfurt blue shifted and dropped at temperatures below 300°C whereas the corresponding change in Fig. 8 occurred at temperatures 200° higher. A further difference is that in the case of Stassfurt blue the principal peak never shifted further than 589 mμ toward shorter wave-lengths, whereas in Fig. 8 the principal band of the sodium-colored crystals shifted at high temperatures well over toward 552 mμ.

In Fig. 7 we undoubtedly have a pure color. The sharpness and intensity of these bands suggests that there is a definite vibration here which might be considered as a resonance band. The identity of the absorption curves of sodium-colored and potassium-colored halite may be explained by supposing that there is an actual replacement of sodium by potassium in the lattice, or by supposing that the color is electronic and a function more of the lattice than of the parent alkali metal.[1]

The effect of increasing temperature upon sodium-colored halite (Figs. 8 and 9) is first to intensify the principal band while shifting it to 589 mμ, and then to fade the principal band while shifting it toward the green. There seem to be two definite vibration centers, at 552 mμ and at 589 mμ. With rising temperature first the 589 vibration is intensified and predominates; then at higher temperatures the 589 absorption band fades and is replaced by one at 552 mμ. It is possible that the change from purplish-blue to pink is due to a change in the crystal structure of NaCl at high temperatures. The fact that two colors predominate and that such complex color results can be obtained merely by variation of the heat treatment indicates that the color is dependent upon an inner equilibrium between two crystal forms in the halite lattice. The surprising change in slope of the temperature-conductance curve of NaCl (when log. specific conductance is plotted against reciprocal of absolute temperature)[2] in the neighborhood of 490°C points to a possible change in crystal form.

In conclusion, the Stassfurt blue is probably due to abnormality in constraint upon electrons which belong properly to the halite lattice. In sodium-colored halite on the other hand the coloring principle is foreign to the lattice, consisting of sodium which may coagulate into colloidal particles in voids of

[1] Gibson and Argo [Phys. Rev. 7, 33 (1916); J. Am. Chem. Soc. 40, 1345 (1918)] showed that sodium and magnesium gave blue solutions in liquid ammonia having identical absorption spectra. Also they showed that the absorption curves of Na, K, Ca, and Cs in methylamine are nearly identical. The color in all these cases was thought to be due to solvated electrons existing more or less independent of the parent atom.

[2] Data of v. Seelen: Z. Physik, 29, 125 (1924), corroborated by unpublished work of one of the authors.

the lattice, or may be dispersed in solid solution, depending upon the heat treatment. Here too the color is due to the electron, but the constraint upon it is distinctly different from that in the Stassfurt blue, being the resultant in a sense of the force of attraction of the parent metal atom and the dielectric forces of the lattice. The irreversible character of the color changes produced in sodium-colored halite at high temperatures suggests that there may actually be a warping of the lattice at high temperatures to accommodate the foreign sodium atoms, with the resulting formation of some subchloride structures in the crystal. X-Ray analysis might be expected to reveal such a condition.

## Summary

(1) Solutions of Stassfurt blue and of sodium-colored halite were tested for alkalinity in a special type of hydrogen electrode vessel here described. The former gave no measurable alkalinity. This throws serious doubt upon the theory that the Stassfurt blue color is due to colloidal sodium. Sodium-colored halite under the same conditions invariably showed marked alkalinity.

(2) Spectrophotometric data at room temperature and over wide ranges of temperature show that there is a distinct difference between the two colors.

(3) It is suggested that the Stassfurt blue is an electronic color, and a tentative explanation of the behavior of its absorption curves with heat is given.

(4) Speculation as to the nature of the two predominant colors in sodium-colored halite is indulged in.

# BLUE WOOD[1]

BY WILDER D. BANCROFT

In 1903 von Schrenk[2] published a bulletin on the 'bluing' and the 'red rot' of the western yellow pine, which turns out to be concerned with a question of structural color.

"Very soon after the attack of the bark beetles (*Dendroctonus ponderosae*) the wood of the pine turns blue. The color at first is very faint, but it soon becomes deeper. . . . Lines of color extend in from the bark toward the center of the tree, and increase rapidly in intensity until the colored areas stand in sharp contrast to the unaffected parts. The color appears in small patches at one or more points on the circumference of the wood ring. At first it is a mere speck, but this gradually spreads laterally and inward, eventually forming triangular patches on cross section. The color likewise spreads up and down the trunk from the central spot. As the time passes after the first attack of the beetles, several color patches may fuse. . . . The intensity of the color may vary considerably on the two sides of one and the same trunk. After a certain period of time the whole sapwood will have a beautiful light blue-gray color. The wood which adjoins the inner line of the 'blue' wood is of a brilliant yellow color which contrasts sharply with the blue outside and the straw yellow of the heartwood. . . .

"The blue color of the wood is due to the growth of a fungus in the wood cells. The staining of wood due to fungi has been known for many years, especially the form known as 'green wood' (*bois verdi*). In Europe this green coloration attracted the attention of foresters and investigators as early as the middle of the last century, and a number of descriptions and discussions appeared from time to time (particularly in France), in which an attempt was made to account for this phenomenon. A green dye was extracted from the wood, which at one time was thought to be valuable because of its absolute permanency. Various dicotyledonous woods showed the green color; among others, beech, oak, and horsechestnut. In spite of numerous investigations, the causes of the green color and its relation to the wood remained comparatively obscure until recently when Vuillemin[3] published an extended account showing that one form of the green color was due to the growth in the wood of one of the Discomycetes, *Heliotum aeroginosum*. . . . Without going into details, Vuillemin established the fact that the green coloring matter called xylindeine, is formed by the hyphae of *Helotium aeroginosum*, and that the presence of these green-colored hyphae gives the green color to the wood. The wood fiber itself remains colorless. The xylindeine is soluble in alkalies

[1] This paper is a necessary consequence of experiments supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Bureau of Plant Industry, Bull. No. 36 (1903).

[3] Bull. Soc. Sci. Nancy, (2) 15, 90 (1898).

and can readily be extracted. The wood fiber is not destroyed, but remains intact. . . .

"In Europe the blue color of pine wood was first noted by Hartig[1], who refers briefly to the fact that a fungus (*Ceratostoma piliferum* (Fr.) Fuckel) is the cause of bluing in coniferous wood, especially of pine trees which have been weakened by caterpillars, and of firewood. He states that the hyphae of this fungus, which are brown, grow rapidly into the trunk through the medullary rays and that they avoid the heartwood, probably because of its small water content. The blue color of coniferous wood in this country is probably caused by the same fungus referred to by Hartig, although it seems necessary to refer to it under a different name (*Ceratostomella pilifera* (Fr.) Winter)."

"The spores of the 'blue' fungus are probably blown about by the wind in countless thousands, and at the time of the beetle attack in July and August some of the spores lodge in the holes made in the bark of the living pine tree by the bark and wood-boring beetles. The atmosphere of these holes is kept constantly moist by the water evaporating from the trunk. In these holes the spores can germinate within a day after falling there. . . . The hyphae grow into the bark tissues and into the cambium, and from these they enter the cells of the medullary rays. . . . The hyphae are at first colorless, very thin-walled, and full of vacuoles and oil globules. . . . The older turn brown and with the first sign of the brown color in the hyphae the bluish coloration of the wood begins."

"So far as known to the writer, no attempt has ever been made to explain the nature of the blue color of coniferous woods. The color is a difficult one to define. A number of the writer's artist friends who were called into consultation pronounced it a blue gray, approaching Payne's gray. Freshly cut wood looks decidedly blue, but as the wood dries the color fades somewhat and dry wood is mouse gray. . . . There are two possible explanations as to the cause of the so-called blue color: (1) The wood may appear colored because of the presence of the colored fungus threads in the wood. The mass effect of such colored threads might make the wood appear colored. (2) The wood might be colored by a pigment or stain formed either by the fungus or as a result of the fungus growth in the wood, and this pigment might stain the walls of the wood fibers.

"The first explanation holds good for the 'green' wood. Here a pigment is formed in the hyphae and fruiting bodies of the fungus, and it is because of the presence of the green-colored bodies in the fungus threads, according to Vuillemin, that the entire wood looks green. Careful examinations made of the 'blue' wood by persons trained to observe colors, called into consultation by the writer have led to somewhat conflicting results, and it is therefore thought inadvisable in the present stage of the investigation to enter on a lengthy discussion of the color subject. A number of facts may be stated, however. Examinations of the wood fibers of sound and 'blue' wood showed that it was possible in most instances to distinguish between the sound and the

[1] "Lehrbuch der Pflanzenkrankheiten," 75, 106 (1900).

'blue' wood. The walls of the sound wood look somewhat darker (with a suggestion of purple) than the blued fiber. This method of examination, with high magnification, is a rather uncertain one, however, for the refraction caused by the containing liquids, which are purplish, and of light falling from a blue sky, is apt to show very faint traces of color which do not belong to the wood. It may be stated definitely that the fibers of the 'blue' wood show no indication whatever of any color element seen in the wood en masse.

"The hyphae constitute the only color element present in the 'blue' wood which could not be detected in the sound wood. These are present in the medullary rays and adjacent cells, as described above. These hyphae are pale reddish-brown, a color which may be obtained by taking a pale tinge of warm sepia. This color is very distinct and stands out in sharp contrast to the surrounding yellow wood fibers. How these brown hyphae could make a blue gray or a mouse gray it is difficult to understand, for no density of such a brown, even in combination with straw yellow (of the wood fiber) could possibly produce blue gray. It would therefore seem probable, or at least possible, that there is some pigment with a blue element in the 'blue' wood which is so faint that its detection in thin microscopic sections becomes almost impossible.

"All efforts to extract any color of a blue nature from the wood have so far failed. Extracts of blued wood with ether, alcohol, benzol, chloroform, alkalies, and acids gave evidence that changes of some sort had taken place in the wood fiber, for the extracts of sound and 'blue' wood differed materially in nearly every instance. No signs of any blue or blue-gray color were obtained."

Last year Mr. von Schrenk was good enough to call my attention to his bulletin and to send us a sample of 'blue' wood, suggesting that perhaps the color was a structural one and not a pigment color. The sample of wood was not as blue as some pieces. It was blue only in courtesy, Mr. von Schenk's mouse gray being a better description. The sample was examined by Mr. Mason of the Cornell Laboratory, who reports that the so-called blue is a poor form of the Tyndall blue. It has already been pointed out[1] that one can get blue-grays to grays by mixing graphite or lampblack with zinc oxide. Mr. Mason found that the color of the wood could be duplicated exactly by putting a very thin wash of India ink on the unchanged wood.

Some one, whose letter I have filed so carefully that I cannot at present lay my hands upon it, sent me a sample of really blue wood from somewhere on the Mississippi River. The color was a pigment color due to vivianite, a somewhat oxidized ferrous phosphate. Mr. Mason recognized the material as identical with the 'blue roots' described by Dudley[2] in 1890.

"While making the preliminary survey of the Cumberland river from Nashville to its mouth . . . Assistant Engineer C. A. Locke discovered some 'blue roots' embedded in a stratum of clay which had been exposed in the bank made by the erosion of the waters in cutting out the channel of the river. The

[1] Merwin: Proc. Am. Soc. Testing Materials, 17 II, 503 (1917); Bancroft: J. Phys. Chem., 28, 25 (1924).

[2] Am. J. Sci. (3) 40, 120 (1890).

locality was about two miles above Eddyville, Ky. The stage of the river was about six feet above low water mark, and the stratum containing the roots was about two feet above the surface of the water or eight feet above low water. The stratum is exposed therefore only for a limited season each year. . . .

"Four of these 'roots', more or less perfectly preserved, were handed to me. They were from one-half to two centimeters thick and six to twelve long. The blue mineral which has almost wholly replaced the woody fiber of the roots is of a deep blue color resembling cobalt-blue but somewhat darker, and of a duller hue. It is earthy and very friable. There is no evidence of structure, and the specimens seem to be casts of the original roots, formed gradually as decay proceeded."

The mineral was extracted and analyzed with the following result: water given off at 100°, 10.59%; water given off at 230°, 7.24%; alumina 17.74%; ferric oxide, 9.35%; ferrous oxide, 24.58%; lime, 0.59%; magnesia, 0.43%; $P_2O_5$, 27.71%; insoluble matter, 1.84%. "When the water was driven off at 100°, the residue had a dull green color resembling chrome oxide. After heating to 230° until all of the water was eliminated, the color was light brown. In a desiccator, over sulphuric acid, the mineral gradually lost water and for several days became green. This occurred more rapidly of course if the air in the desiccator was exhausted."

Dudley concluded that the ferrous iron in the mineral was combined with the phosphate to form vivianite, $Fe_3(PO_4)_2 . 8H_2O$. The balance of the material has the formula $Al_6Fe_2P_4O_{22} . H_2O$, "which resembles an almost dehydrated double molecule of turquoise, $Al_8P_4O_{22} . 10H_2O$, in which one molecule of $Fe_2O_3$ has replaced one of $Al_2O_3$. The mineral was so earthy and friable that sections could not be cut and therefore microscopic evidence is impossible."

The blue of the wood is therefore a structural color and the blue of the roots a pigment color.

*Cornell University*

19-50

# THE THERMIONIC PROPERTIES OF SOME MIXTURES USED AS CATALYSTS IN THE SYNTHESIS OF AMMONIA

BY C. H. KUNSMAN

The synthesis of ammonia from $N_2$ and $H_2$ in the presence of a catalyst is generally considered to be an example of chemical action on a surface, or surface catalysis. In order to obtain further information as to the nature of such surfaces, both their chemical and physical properties are under investigation at the Fixed Nitrogen Research Laboratory. What follows has to do entirely with one property of the surface, namely, the thermionic emission of charged particles as a function of the temperature of the surface. Since the temperature of the catalyst is such an important factor in the synthesis process, any information as to the nature of the catalyst surface that can be obtained under the same temperature conditions of operation of the catalyst will be especially valuable.

The ammonia catalysts studied were made by fusing a mixture of very pure artificial magnetite, with about 1% $Al_2O_3$ and about 1/2% of an alkali or alkaline earth salt, usually the nitrate, in a resistance furnace where the mixture itself furnishes the resistor[1]. The reduced mixture probably consists largely of metallic iron with the oxides of aluminum and an alkali or alkaline earth metal oxide which was introduced in the original mixture. The iron is usually considered the catalyst, and the added materials, the promoters.

The property of small amounts of an added material of greatly increasing the chemical activity of the mixture is quite common, and is not confined to ammonia catalysts. There are a number of instances where the alkalies are especially good promoters. For example, a small amount of an oxide of an alkali or an alkaline earth metal greatly enhances the catalytic activity of the iron-ammonia catalyst containing a refractory oxide. The "synthol" catalyst[2] consists of iron filings impregnated with a strong alkali, as KOH or $Rb_2CO_3$. Strong alkalies are also added as promoters in some water gas catalysts. It is very likely that the effect on the catalyst materials of the alkali promoter is specific and may indicate a common source of catalytic activity; so that any information that can be obtained from the ammonia catalyst mixture, in relation to the alkali promoter, may contribute to the knowledge of catalysis in general.

If the so-called "surface catalysis" is strictly a surface condition, we are very limited in our present choice of methods of investigation. The fact that the thermionic emission from hot surfaces is largely, if not entirely, a surface effect, and is so very sensitive to minute traces of foreign material on the surface, suggests its use in the study of "promoters" and "poisons" as applied to surface catalysis[3].

[1] Larson and Richardson: Ind. Eng. Chem., 17, 971 (1925).

[2] Fischer and Lessing: "The Conversion of Coal into Oils," (1925).

[3] Langmuir and Kingdon find the electron emission of tungsten to be increased by a factor of $10^{20}$ at 800°K, in presence of a layer of caesium, and to be decreased by a factor of $10^6$ in the presence of a layer of oxygen at 1500°K.

This paper will deal largely with the total positive thermionic emission from the surface of the catalyst mixture. The discussion of the exact nature of the emission and its possible bearings on catalysis will be considered at a later time.

## Thermionic Properties of Surfaces

Guthrie, in 1873, observed that a hot iron ball at atmospheric pressure emitted positive electricity. O. W. Richardson, in 1902, showed that the equation (1) $I = AT^{\frac{1}{2}} \epsilon^{-b/T}$, satisfied the emission of electricity by heated metals. In this equation, I is the saturation current, positive or negative, T the absolute temperature, A and $b$ constants, A representing the current emitted per unit area of hot surface. The $b$ constant can be expressed in the form $b = \varphi e/k$, where $\varphi$ is the equivalent work function in volts, $e$ the unit electric charge, $4.774 \times 10^{-10}$ e.s.u., and $k$ the Boltzman gas constant, $1.372 \times 10^{-16}$ ergs per degree. From the relation $b = \varphi e/k$, we find that $b$ in degrees kelvin can be expressed in volts by dividing $b$ by $1.16 \times 10^4$. $\varphi e$ is the work required to liberate a singly charged particle from the surface; where $\varphi$ is referred to as the equivalent voltage of the work function. Equation (1) will be used in a consideration of the experimental results, and the corresponding value of $\varphi$ will be thus obtained. Another method of determining the work function for the electron emission from hot surfaces is the calorimetric method. In this method the amount of cooling of the surface due to the vaporization of charged particles is measured.

## Apparatus and Method of Observation

The apparatus and technique employed in these studies are the same as employed in vacuum tube and similar low pressure work. The pumping system consisted of an oil pump connected in series with two mercury vapor condensation pumps. Observations were made at pressures of $10^{-6}$ mm. of Hg and less, on a well degassed system.

The total positive thermionic emission of the following mixtures containing the materials as given will be considered: No. 216—Fe, Al, Cs; No. 740—Fe, Rb; No. 920—Fe, K; No. 571—Fe, Na; No. 260—Fe, Mg; and No. 319—Fe, Al, Ca.

In the first experiments, the partially reduced catalyst granules were placed in a platinum basket (c) and mounted in a tube as shown in Fig. 1. P is the collecting cylinder surrounding the catalyst and tungsten filament. F was used to heat the cylinder to a red heat on degassing the system and to heat the catalyst to the proper temperature by electron bombardment. The process of degassing by electron bombardment is accomplished by raising F, which is earthed, to a sufficient temperature, 2300°C. with a positive potential of about 500 volts to the cylinder (P).

By means of a series of switches, the parts of the tube could be shifted from the heating system to the emission collecting system. Due to the large mass of catalyst granules in comparison to the size of the 6 mil tungsten filament, the filament would cool to below visible before the temperature of

the catalyst had appreciably changed. With this system on September 10, 1924, positive ion currents up to $6 \times 10^{-7}$ amp. at a temperature of about 500°C were measured from a Fe-Al-Cs oxide catalyst. The negative or electron emission at these temperatures was negligible, never more than 1/100 of the positive ion current.

Fig. 2 is a sketch of the next tube used. The essential feature is the enclosed spiral, tungsten filament $F_1$, which heated the enclosing platinum cylinder by radiation and the catalyst by conduction; thus enabling the catalyst to be heated at any temperature continuously. $F_2$ is a filament used for degassing the collector (P). $F_3$ is another tungsten filament so placed as to collect some of the positive ions or material vaporized from the catalyst. From this system, observation of the positive emission as a function of the temperature was made and found to obey Richardson's equation. By measuring the temperature of the hot catalyst by an optical pyrometer, and substituting in equation (1) approximate values of $\varphi_+$, the work function of the positive ions, were obtained. The unevenness of the temperature of the catalyst granules made precision measurements of $\varphi_+$ impossible.

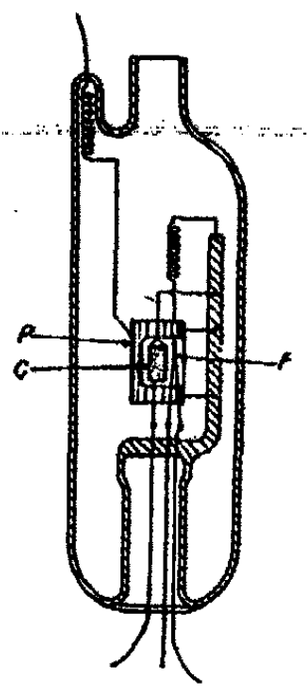



FIG. 1

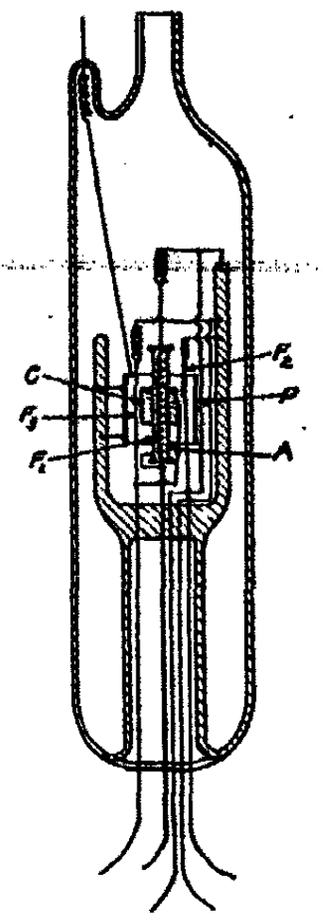



FIG. 2

### Nature of Positive Ions

Since the vaporization of positively charged particles took place from a mixture of partially reduced Fe, Al and Cs oxides at relatively low temperatures (below visible) one would no doubt first try to identify the charged particles with the caesium. The property of small traces of the alkali and alkaline earth metals or their oxides of greatly increasing the electron emission of platinum or tungsten, was used in this test[1].

The tungsten filament, $F_3$ (Fig. 2) was first raised to about 2400°C, so as to remove any impurities from the surface. A test showed that no electrons (currents less than $1 \times 10^{-10}$ amp.) were emitted at 900°C and below. However, after heating the catalyst for a short time and testing the emission from $F_3$, electron currents as large as $10^{-7}$ amp. were observed. At temperatures of the filament corresponding to an appearance of the surface of "just visible" and below, tests showed that at a given temperature the magnitude of this negative emission depended upon the length of the time the catalyst was hot, and also on the potential of $F_3$. For example, if $F_3$ was at a positive potential

[1] Davisson and Pidgeon: Phys. Rev., 15, 553 (1920); Langmuir and Kingdon: Science, 57, 58 (1923); Proc. Roy. Soc. 107A, 61 (1925).

with respect to C, the active material collecting on $F_3$, as measured by the electron emission, was very much smaller than when the filament was negative, with respect to C. This shows that most of the active material carries a positive charge. The increase in emission from $F_3$, when at a positive potential with respect to C, shows that neutral or negative charged particles may reach $F_3$. It is difficult to decide whether these particles come from the hot surface directly or from other parts of the tube after having lost their positive charges. However, the amount of uncharged atoms was relatively small in comparison to the positively charged atoms. Hence, we must conclude that at these temperatures the vaporization from the hot surface consists largely of positively charged atoms.

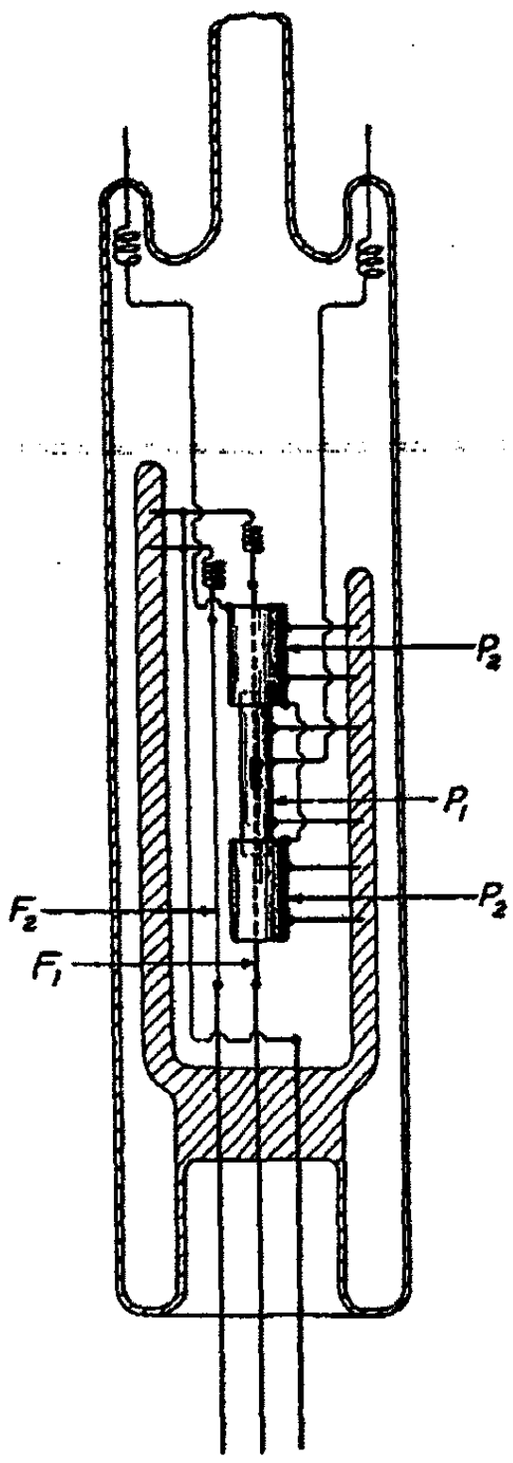


FIG. 3

The effect of caesium on increasing the electron emission on tungsten was investigated in a separate system in the presence of caesium vapor and gave results very similar to those observed for $F_3$, previously discussed. Quantitatively, the increase was in good agreement with the results reported by Langmuir and Kingdon. It would seem, therefore, that we are justified in concluding that the observed positive currents from a Fe-Al-Cs oxide mixture are largely due to positively charged Cs atoms.

### Coated Strip Apparatus

The coated strip form of anode has considerable advantages over the other forms of anodes previously described. It is quite simple to prepare and is very uniform in temperature. While the unreduced mixture can be coated, the reduced mixture can be coated more satisfactorily.

The process consists of grinding the mixture to a very fine powder (300 mesh or lower), similar to the preparation of a specimen for x-ray analysis by the powder method. The powder is then mixed with paraffin and heated until the paraffin melts. The platinum strip is then raised to a sufficient temperature to melt the paraffin. By passing a glass rod covered with the paraffin mixture back and forth over the strip, a uniform layer is obtained. The temperature of the platinum strip was then raised to about 900°C, for a sufficient time (a few minutes) to insure a firm attachment of material to the platinum. This process may be repeated a number of times until the desired

thickness of coating is obtained. For some mixtures it was found that a more satisfactory coating could be obtained if the process was carried out in an atmosphere of nitrogen. The coated filament should be mounted in place and the coating reduced by passing hydrogen over the surface, while at a dull red temperature.

A coated strip was mounted as $F_1$ in Fig. 3; The collector (P) is divided in 3 parts with separate leads to the middle and end parts. This enables the thermionic current to be measured from the middle section ($P_1$) which surrounds the part of the filament which is at a uniform temperature. Due to

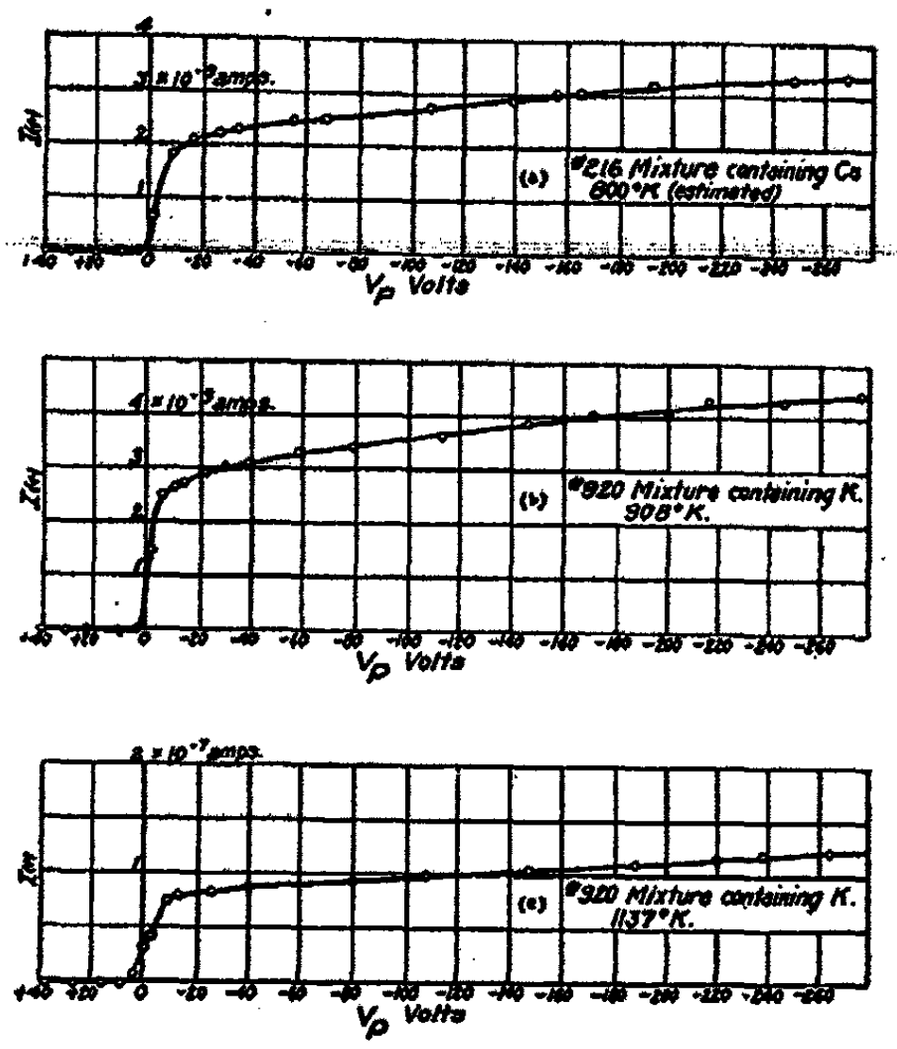



FIG. 4

the cooling effect of the leads, the ends of the filament are at gradually decreasing temperatures. $F_2$ is a tungsten filament used to degas the metal parts. Unless otherwise stated, the results which follow were obtained from coated strips.

## Experimental Results

If $F_1$, Fig. 3, is kept at a given temperature and the potential to the collector P varied from a positive through zero to a negative voltage, curves similar to those of Fig. 4 will be obtained. The negative current at these temperatures is practically zero in comparison with the positive currents. In Fig. 4 we have three curves for different temperatures:—(a) a caesium promoted catalyst at 800°K, and (b) and (c) a potassium promoted catalyst at 908°K, and 1137°K, respectively, as determined by an optical pyrometer. The reason the curves do not flatten out or show a saturation current at the

higher voltages is no doubt due to the roughness of the surface, so that the added voltage draws a few more ions to the collector. Curves of this type are quite reproducible after a steady state of the hot surface has been reached. The amount of the positive ion currents depends on the mixture and the previous heat treatment. The unreduced material gives some ions but many more are obtained from the reduced mixtures. In general, the magnitude of the positive ion current at a given temperature depends upon the alkali or alkaline earth metal or oxide which has been added as promoter. The temperature at which the first positive ion current, $1 \times 10^{-10}$ amp. is detected is lowest for a Cs promoted catalyst, followed by Rb, K, Na, Mg and Ca, with increasing temperatures. In the case of a Cs or a Rb promoted catalyst, appreciable positive ion currents are observed at temperatures where the surface was below visible in a very dark chamber.

In all of these tests, the pressure in the system enclosed by a liquid air trap was $10^{-6}$ mm. of Hg or lower, as measured by an ionization manometer. The system was being evacuated during the course of the experiment. However, no appreciable difference was observed in the results when the pumping system was separated from the test system by means of a mercury trap. Likewise, no increase in pressure was observed in the test system.

### Positive Emission—Power Curves

A very convenient method of representing the emission characteristics from a hot surface is shown in Fig. 5.

Dr. C. Davisson[1] has chosen the coordinates, so that, if the emission varies as a function of the temperature as given by equation (1), and the thermal radiation from the coated surface varies as the fourth power of the absolute temperature, a straight line relation exists between the emission from the surface and power supplied to the hot surface.

We have in Fig. 5, the observed positive ion emission from the surface plotted against the watts (amperes × volts) supplied to the hot anode. Straight line relations were obtained as shown by the curves. The observed points for the magnesium-promoted catalyst are shown as dots for increasing heating currents and dots encircled for decreasing currents. The corresponding temperatures for the mixtures for the curves of Fig. 5 were approximately as follows: Cs "below visible" to 1200°K; Rb "below visible" to 1180°K; K "dull red" to 1180°K; Na "dull red" to 1220°K; Mg "dull red" to 1190°K; Ca "red" to 1270°K. This is the order one would expect from the vapor pressure of these elements. Caesium vaporizes from the surface as positive charged Cs ions more rapidly and at lower temperatures than K.

It should be mentioned at this time that in the case of the alkali metals, if the temperature of the material is too high, there is a falling off of positive ions at these high temperatures, and the linear relation no longer holds and the curves for increasing and decreasing heating currents do not coincide.

[1] "Thermionic Vacuum Tubes", p. 82; van der Bijl: J. Optical Soc., 8, 79 (1924).

The plots, Fig. 5, represent the emission from approximately one square centimeter of surface. The surfaces of the respective anodes were as nearly the same as they could be made conveniently.

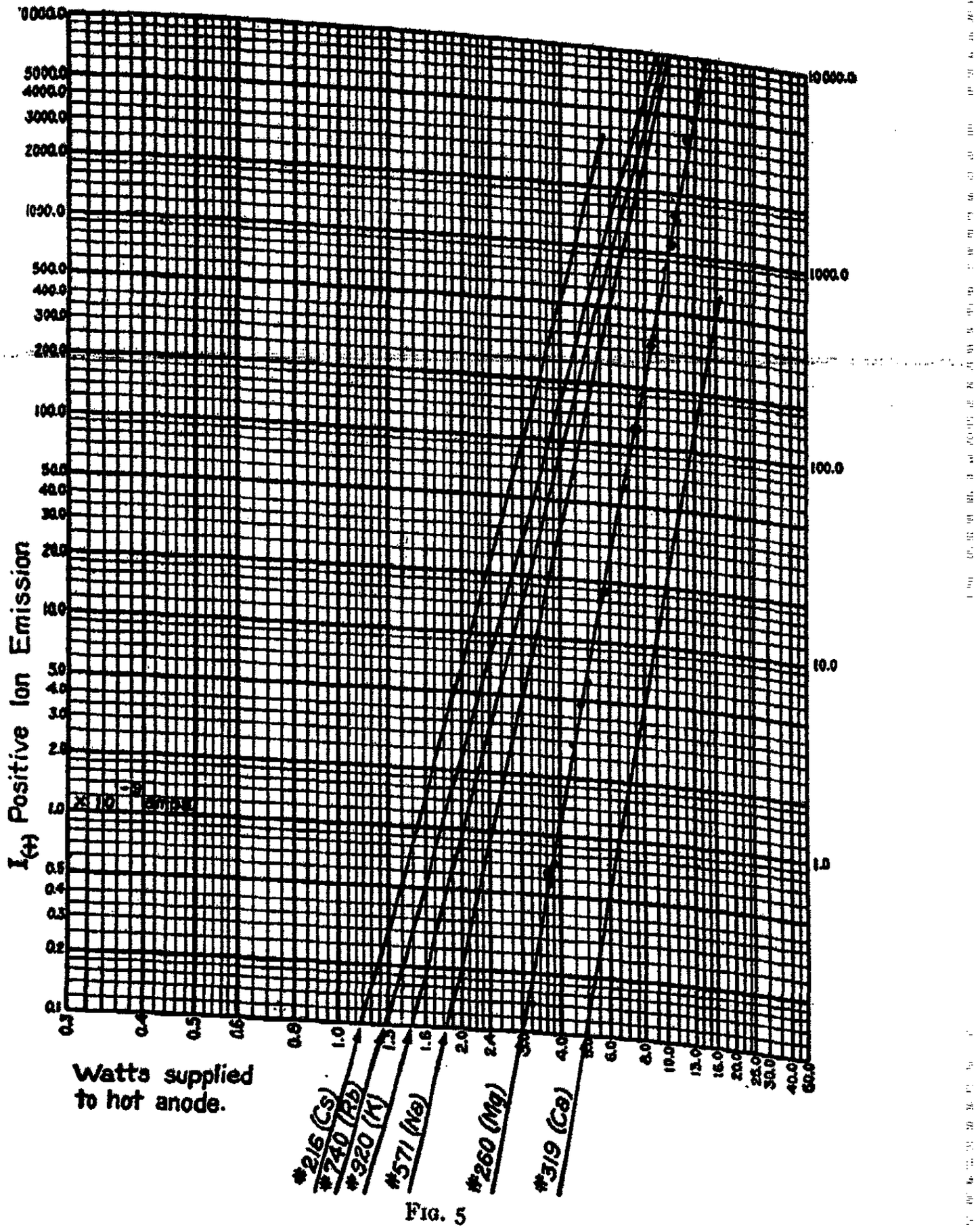



FIG. 5

**Determination of $\varphi_+$ for K and Cs**

Since a linear relation exists for the positive ion emission and the watts delivered to the coated strip, as shown by Fig. 5, we know that the equation (1) $i = AT^{\frac{1}{2}}\epsilon^{-b/T}$ holds through the corresponding range of temperatures. If the temperature is known, the constants A and b, or the equivalent $\varphi$, of

the equation can be evaluated. The accuracy with which $\varphi_+$ can be determined depends upon the measurement of the temperature T. As our chief interest is in a relative definition or comparison of the surfaces of the various mixtures in comparison to their chemical or catalytic activity, no great accuracy is claimed in these values of $\varphi_+$. The temperatures are as accurately determined as could be measured in a well darkened chamber by means of a Leeds & Northrup optical pyrometer, calibrated by the Bureau of Standards. The positive ion current $I_+$ could be very accurately determined for any temperature by a Leeds & Northrup high sensitivity galvanometer.

Equation (1) can be expressed in the form $\log i_+ = \text{const.} + 1/2 \log T - b/T$. In Fig. 6 and 7, the $\log i_+ / 1/2 \log T$ is plotted against $1/T$. The slope of the line is $-b \log \epsilon$, from which $\varphi_+$ is calculated[1].

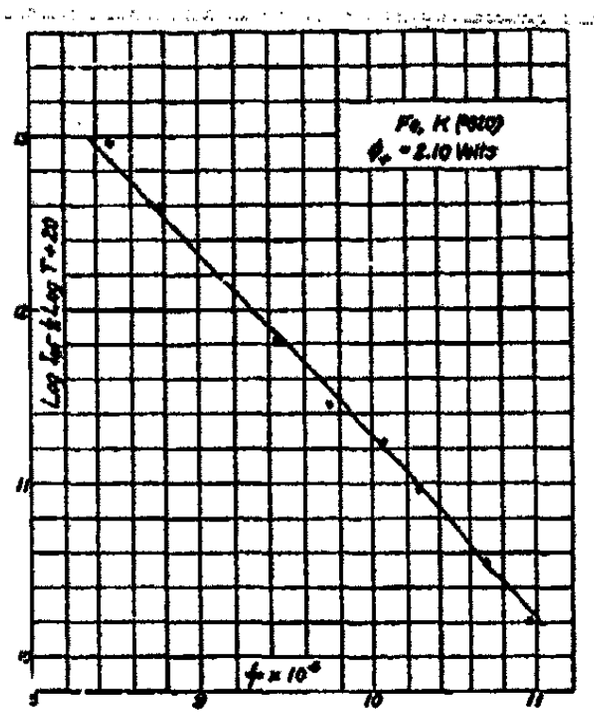



Fig. 6

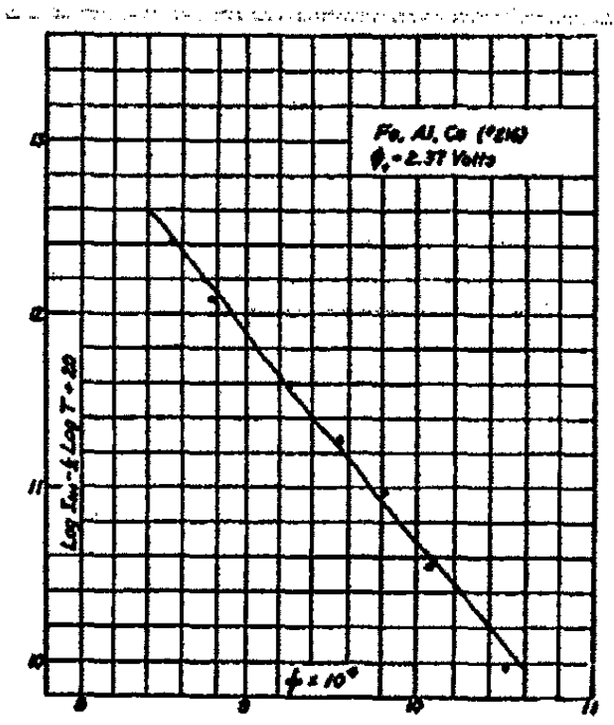



Fig. 7

$\varphi_+$ has been found to vary considerably with the mixture and gas treatment of the surface. However, after a preliminary heat treatment, consisting of glowing the filament for some time in a vacuum, consistent values of $\varphi_+$ are obtained which can be reproduced from one day to the next. Fig. 6 represents the curve from a K promoted catalyst. In this case, $\varphi_+ = 2.10$ volts, is the equivalent work function in volts for the vaporization of a positive potassium ion from the surface; Dr. H. A. Barton at Princeton, having found that this mixture emitted largely singly charged positive potassium ions[2]. Fig. 7 gives a similar curve for a Cs-promoted catalyst. From the magnitude of the effect of the vaporized atoms on increasing the electron emission of tungsten, we conclude this value of $\varphi_+ = 2.37$ volts is the work function in volts for the vaporization of positive Cs ions from the hot surface.

[1] Kunsman: Phys. Rev., 25, 892 (1925).
[2] Science, 62, 270 (1925).

## Structure of Mixture and Cause of Positive Ion Emission

The recent work of Wyckoff and Crittenden[1] gives us considerable information as to the structure of the mixtures under consideration. One effect of promoters, $Al_2O_3$ and an alkali metal or alkaline earth metal oxide, is to inhibit the growth of large crystals. An estimate of the size of the crystals in the reduced material is given as lying between $1 \times 10^{-6}$ cm and $1 \times 10^{-3}$ cm, where the dimensions are the average length of an edge of a crystal taken as a cube. Another interesting result is that the promoters do not show up in the form of a solid solution or give x-ray diffraction patterns; therefore, their exact form and structure in the mixture are not known. The conclusion drawn was that the promoters, $Al_2O_3$ and $K_2O$ exist in the reduced mixture as finely divided and uniformly distributed between the Fe crystals.

With this picture of the catalyst material, it is quite easy to see how a diffusion and vaporization from the surface may take place, as a function of the temperature; as it is now generally understood that diffusion takes place largely along interfaces between crystals[2]. With the small crystals there are ample channels for considerable diffusion at the lower temperatures. However, at the highest temperatures for some mixtures, a considerably less positive ion current was observed than would have been expected from Richardson's equation. This is no doubt due to the fact that the diffusion of alkali metal to the surface is too slow for what could vaporize from the surface at these temperatures, according to the vaporization equation.

The same explanation as advanced by Langmuir and Kingdon[3] for caesium in contact with hot tungsten, seems to explain why the alkali metal vaporizes from the surface as positive ions instead of neutral vapor. The electron "affinity" of the surface mixture is greater than the affinity between the alkali metal atom and its outer or conduction electron, so that when vaporization of the alkali metals takes place from the surface, the vaporization is in the form of positive charged ions, instead of neutral vapor. This was shown by experiments where the work function $\varphi_-$ for the electrons, gave values higher than $\varphi_+$ for the positive ions.

## Conclusions

1. The fused mixtures of iron oxide containing an alkali or alkaline earth metal oxide and in some cases aluminum oxide, are good emitters of positive ions. The reduced mixtures which are good catalysts for the synthesis of ammonia are considerably better emitters than the unreduced mixtures.

2. The negative or electron emission from the surfaces at these temperatures was very small in comparison to the positive ion emission.

3. The surface of the fused mixture may be defined in terms of $\varphi_+$, the equivalent work function in volts of the vaporized positive ions.

---

[1] J. Am. Chem. Soc., 47, 2866 (1925).
[2] Geiss and Liempt: Z. Metallkunde, 16, 317 (1924).
[3] Science, 57, 58 (1923); Proc. Roy. Soc., 107A, 61 (1925).

4. The catalyst mixture, and therefore, the catalyst surface, is changing at a rate depending on the temperature, due to the vaporization of the alkali which vaporizes in the form of positively charged ions.

5. The parts of the catalyst surface from which the vaporization of positive ions takes place may be considered active or volcanic centers.

Recent work done by Barton and Harnwell at Princeton, through the courtesy of Prof. K. T. Compton, on the mass spectrograph of the positive ions emitted will give further information as to the nature of these ions. The probable significance of positive ion emission in surface catalysis will be discussed in a later paper.

In conclusion, the writer wishes to acknowledge suggestions given and the interest shown in these studies by Dr. S. Karrer and other members of the Laboratory staff, and especially the careful work of Mr. R. A. Nelson in the construction of the apparatus and his assistance in the experimental work.

*Fixed Nitrogen Research Laboratory,*
*U. S. Department of Agriculture,*
*Washington, D. C.*
*December 12, 1925.*

# THE VISCOSITY OF AQUEOUS SOLUTIONS OF THE SILICATES OF SODA

BY V. R. MAIN

## Introduction

Solutions obtained by dissolving fusions of soda ash and sand in water have an ever increasing application in industry, and are sold under the names "soluble glass" and "waterglass". The properties of such solutions are dependent on the proportions of the constituents used in the fusion, that most commonly met with being approximately of the composition 3.3 parts of silica to one part of soda. Very little is known with certainty regarding their chemical constitution. From commercial "waterglass", by addition of caustic soda and alcohol, Vesterberg[1] obtained crystals of the definite salt sodium metasilicate with 9, 6, and 3 molecules of water, from which he also obtained the anhydrous salt $Na_2SiO_3$. No crystalline salt containing a higher proportion of silica has been obtained.

A brief account of the viscosity of solutions of sodium silicate fusions is given in an article by W. Stericker[2] on "The Colloid Chemistry of Silica and its Derivatives", in which figures are given indicating the colloidal nature of the solutions. The slope of the viscosity-concentration curves is dependent on the ratio $Na_2O:SiO_2$ of the solution, being more abrupt the higher the proportion of silica. Stericker attributes the difference to one of two causes, or possibly to a combination of both: "a) Peptization of the colloidal material, and b) Formation of a crystalline compound at the expense of the colloidal constituents."

He points out the importance of the rate of change of viscosity from a technical standpoint, as a measure of the 'rate of set' when the solutions are used as adhesives. Stericker states that the viscosity-ratio curve passes through a minimum when the ratio $Na_2O:Sio_2$ is between 1:2 and 1:3 for a given concentration (% total solids) of the solution. No reference is made to the Journals in this article, and the work does not appear to have been published elsewhere. As the author gives no details of the method or apparatus used in determining the viscosity values, and does not state at what temperature they were made, the results may only be compared in a general way with those set forth in the present paper.

## Materials

The present investigation was made with commercial samples of silicate of soda solutions provided by Brunner, Mond & Co. The analyses of these solutions are given in Table II. Traces of alumina and ferric oxide were found in the samples, insufficient, however, to affect appreciably the analysis figures.

[1] Proc. Eighth Int. Cong. Appl. Chem., 2, 225 (1912).
[2] Bogue's "The Theory and Application of Colloidal Behavior," 2, 563 (1924).

That these impurities exert a negligible influence on the viscosity measurements was satisfactorily demonstrated in the case of the solution of molar ratio $Na_2O:SiO_2 = 1:1$ where no difference in the viscosity was observed when a solution obtained by addition of caustic soda to a solution of higher ratio was compared with a solution of corresponding concentration prepared from crystals of sodium metasilicate free from impurity. The sample solutions provided vary in molecular ratio $Na_2O:SiO_2$ from 1:2 to 1:4.2. In addition to the solutions contained within this range, two others were investigated, one of ratio 1:1 and another of ratio ($Na_2O:SiO_2$) 2:1. These solutions were prepared by addition of the requisite amount of caustic soda to one of the solutions of higher silica content.

## Method and Apparatus

The primary object of the present investigation was to discover whether viscosity measurements would throw any light on the nature of the silicates in solution, and for this purpose absolute measurements were not essential. It was therefore decided to measure viscosity relative to that of the solvent (water). All the silicate solutions, whatever the value of the ratio $Na_2O:SiO_2$ have at low concentrations a viscosity coefficient very little greater than that of pure water. In view of this fact, the method of efflux was chosen for the determination of viscosity, as the one most suited to the requirements. For this purpose two types of instrument are available:—

(a) The Oswald Viscometer, particularly suited to relative measurement, in which the liquid flows through the capillary under its own hydrostatic pressure. A certain volume of liquid is run into the instrument from a pipette, and flows from a small capacity bulb on one limb of a U-tube, to a large reservoir situated below the first bulb on the opposite limb of the tube, the time of flow between two marks, one above the small bulb and the other below it on the capillary itself, being measured for each solution. The same pipette is used giving the same volume flow in each case, and the pressure forcing the liquid through the capillary is thus directly proportional to the density of the liquid flowing. In the case of the more viscous solutions, sufficient time must be allowed for the liquid to drain from the pipette. The time of flow was measured at least five times for each solution, and each set of five readings was repeated with a fresh sample of solution. This method serves as a check on the introduction of error by variation in the volume delivered by the pipette. The values of the time of flow were generally in agreement to one-fifth second, an allowable error in the operation of the stop watch. The maximum error produced in the viscosity value on this account is 1%. The instrument was calibrated by measurement of the time of flow for distilled water, and this value was checked from time to time to ensure that the capillary was not affected by continued contact with the 'waterglass' solutions. The densities of the solutions were measured by means of a capillary pyknometer, by comparison of the weights of equal volumes of the solutions with the weight of the same volume of water at the temperature of the experiment. For the calcula-

tion of the relative viscosity, the viscosity and the density of water at 25°C are taken as unity.

The relative viscosity of a solution measured in this way is given by $\eta = k\rho t$

where $\rho$ = density of the solution

and $t$ = time of flow of the solution.

The value of $k$ is the reciprocal of the time of flow for water. The instrument constants and the water values of the Ostwald instruments are tabulated below. Most of the measurements were made with the instrument A.

TABLE I

Instrument Constants

| Viscometer | Length of Capillary | Volume of flow | Time of Flow for water | Value of k |
|---|---|---|---|---|
| | l(cms.) | V(cc.) | $t_o$(secs.) | $1/t_o$ |
| A | 12.95 | 4.32 | 25.9 | .03861 |
| A | 12.95 | 4.32 | 26.2 | .03816 |
| B | 11.10 | 2.82 | 80.0 | .01250 |
| C | 9.65 | 3.28 | 37.1 | .02695 |

The second value of $t_o$ for the instrument A was obtained by using a second pipette delivering a slightly larger volume of liquid. Most of the results were obtained using this pipette.

(b) The Variable Pressure Type of Viscometer, developed by Ubbelohde, in which the liquid is forced through the capillary under an applied pressure of gas. This instrument has the advantages that the time of flow in the case of the more viscous solutions may be conveniently reduced and the density of the solution need not be accurately known. The two bulbs are of the same volume and shape and are placed one on each limb of the U-tube and at the same height. The apparatus is arranged as shown in Fig. 1.

The nitrogen cylinder A used to obtain the necessary pressure is connected with a large pressure reservoir B, from which a T-piece allows connection with a water-manometer C, and with the viscometer D, through a three-way tap E. The latter enables the viscometer to be connected with the rest of the apparatus, or to be opened to the air. The pressure is adjusted and the time required for the liquid meniscus to pass the constrictions $x$ and $y$ is measured. To facilitate the readings, the constrictions are marked. The viscometer, situated inside a thermostat, is constructed with the bulbs in the form of double cones, to facilitate the drainage of the more viscous solutions, and the entrances to the capillary are slightly trumpet-shaped for the same reason. The constrictions ($x$ and $y$) must not be too narrow, or a film of liquid forms across them which sets up a back pressure during the flow of liquid through the instrument.

A large aspirating bottle was the most suitable thing available as a pressure reservoir, and it was found that the manometer level fell through several millimetres during the flow. This fall is, however, accounted for by the change in gas volume in the apparatus due to the displacement of the liquid in the viscometer. The mean of manometer readings immediately before and after the observed flow is taken as the average pressure causing the flow. This is not necessarily the true average pressure, but corrections due to the density of the

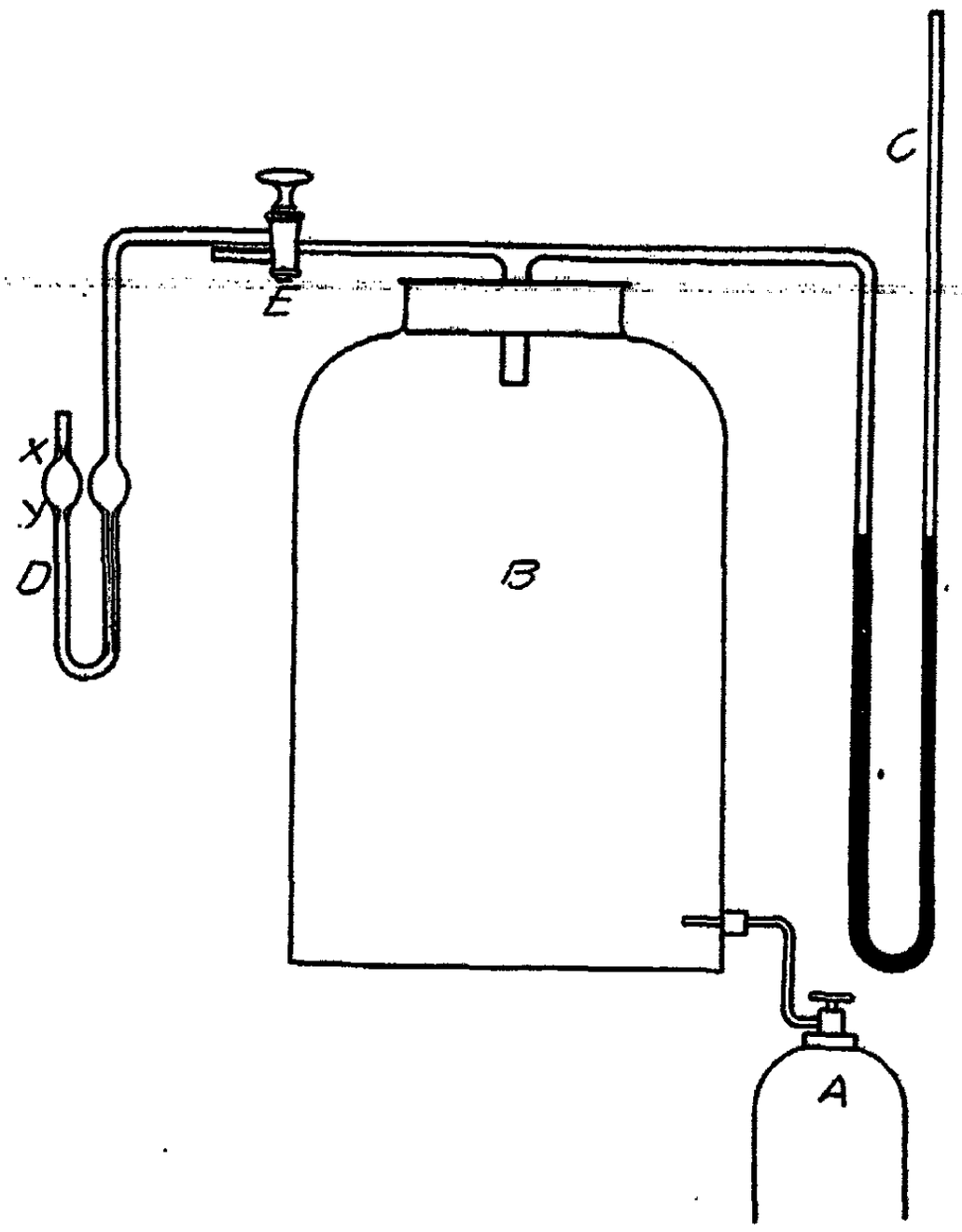



FIG. 1

solution when the bulbs in the viscometer are not at the same height, and the corrections for outside effects, are small, and as absolute measurements were not required, are not applied[1].

The method originally employed by experimenters using this type of instrument consisted in measuring the time of flow for each solution, at the same constant pressure. The viscosity of liquids, however, and more especially

[1] For these corrections see Bingham: "Fluidity and Plasticity," 298 (1922); Kendall and Monroe: J. Am. Chem. Soc., 39, 1787 (1917).

that of colloidal solutions, has been shown to be dependent on the rate of shear in the viscometer, and hence on the rate of flow, the volume flowing being constant[1].

It therefore seemed more satisfactory to compare the pressures required to cause all solutions to flow through the capillary at the same rate of flow, when the conditions in the capillary would be more nearly the same regarding shearing force, though the actual shearing which occurs in the solution is dependent on the latter. This method offers considerable experimental difficulty, the pressure requiring very fine adjustment. In the present investigation a series of values was obtained for each solution, the time of flow being measured for a large number of pressure values. An example of such a series is given in Table XIV.

The equation of Poiseuille with the later correction for the kinetic energy as the liquid leaves the capillary may be applied to these results, namely

$$\eta = \frac{\pi g p r^4 t}{8vl} - \frac{m\rho V}{8\pi l t}$$

where p = pressure producing flow
t = time of flow
r = radius of capillary
l = length of capillary
V = volume of liquid flowing
$\rho$ = density of solution
and m = a determined constant.

The equation may be written:—

$$\eta = Cpt - C'\rho/t$$

The values of C and C′ are then given by

$$C' = \frac{mV}{8\pi l} \text{ and } C = \frac{\eta_o t_o + C'\rho_o}{p_o t_o^2}$$

where the suffix o indicates measurements made for distilled water. The above method of calculating C, obviates the necessity of measuring the radius of the capillary (r), error in which is greatly increased in the value of C obtained directly, since C is proportional to the fourth power of the radius. The application of this formula is further discussed with particular reference to the results obtained at a later stage.

## Experimental

All determinations were made at a temperature of 25°C. in an air-thermostat provided with a glass door. The temperature was controlled by means of an electrical relay system, and was constant during a determination to 1/10°C. The thermometer was carefully checked by comparison with an accurate standard. Before use, viscometers were washed with caustic soda, chromic acid mixture, and distilled water, and were subsequently dried in an electric oven.

[1] Hatschek: Kolloid-Z., 8, 34 (1911); 13, 88 (1913); Garret: Diss. Heidelberg, (1903); Phil. Mag., 6, 374 (1903).

Solutions of different concentrations of each ratio were prepared by dilution of the sample, and concentration values are calculated in weight normality with respect to the sodium oxide content. After preparing a solution in this way, it is well shaken and is allowed to stand overnight. This precaution was taken to ensure a thorough mixing of the silicate solution with the water added. There is a tendency for the water to remain as a separate layer in the case of dilution of the more viscous samples. Mixing could be obtained by vigorous agitation of the containing vessel, but this caused a large number of small air bubbles to form in the solution which rise to the surface only very slowly.

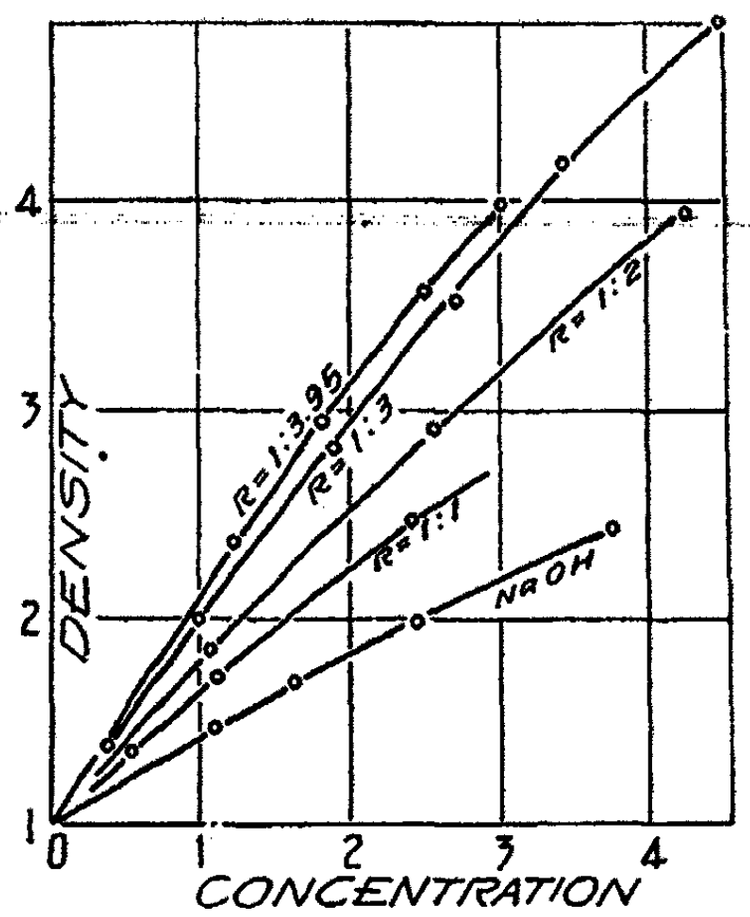



FIG. 2

Values were also obtained in the Ostwald viscometer for caustic soda solutions for purposes of comparison. No change in the viscosity of the solutions, which have been prepared as described, was observed over a period of several weeks.

TABLE II

Analysis of the Solutions

| Molecular Ratio $Na_2O:SiO_2$ | Percentage Analysis of Sample $Na_2O$ | $SiO_2$ | $H_2O$ |
|---|---|---|---|
| 1 : 2.0 | 18.50 | 36.00 | 45.50 |
| 1 : 2.5 | 13.80 | 32.90 | 53.30 |
| 1 : 3.0 | 9.06 | 26.44 | 64.50 |
| 1 : 3.3 | 9.50 | 30.50 | 60.00 |
| 1 : 3.8 | 7.16 | 26.26 | 66.58 |
| 1 : 3.95 | 6.45 | 24.88 | 68.67 |
| 1 : 4.2 | 5.29 | 21.51 | 73.20 |

## The Relative Density

The relative density of solutions at 25°C. was determined by means of a pyknometer, the volume of liquid in the instrument being each time adjusted to a mark etched on the capillary. Duplicate determinations were in agreement to within .01%.

The density-concentration curves exhibit slight concavity to the concentration axis. Examples of these are given in Fig. 2, the curves here reproduced being those for caustic soda solutions, and silicate solutions of ratios ($Na_2O$: $SiO_2$) 1:1, 1:2, 1:3 and 1:3.95. The values of density from which these curves are drawn are tabulated with the viscosity results in Tables IV to XIII.

From density-concentration curves, values are obtained by interpolation for the ratios investigated at the definite concentrations $1N_w$, $2N_w$ and $3N_w$,

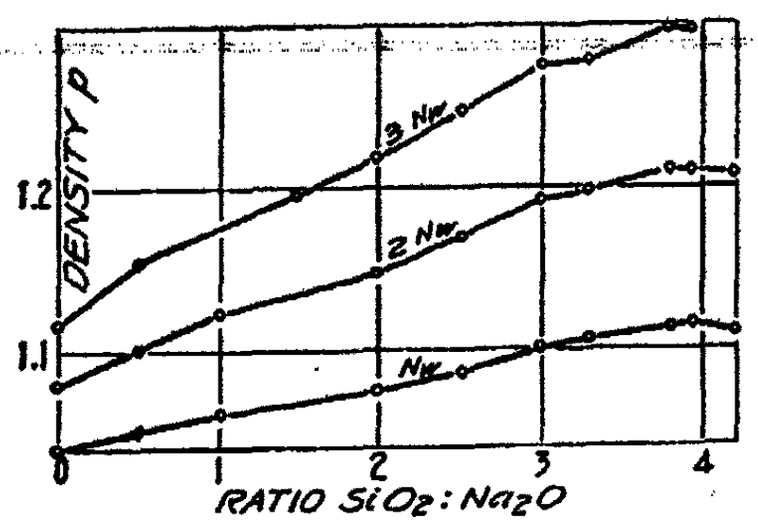



FIG. 3

the symbol $N_w$ representing weight normality of soda, or the number of gram *equivalents* of $Na_2O$ contained in 1000 gms. of water. These results appear in Table III and are represented graphically in Fig. 3.

The curves in this diagram represent the effect of addition of silica on the density of caustic soda solutions, the values on the density axis being those obtained for pure caustic soda solution.

TABLE III

Density-Ratio $SiO_2$:$Na_2O$

| Molecular Ratio. $SiO_2$:$Na_2O$ | Conc. $N_w$ | Density $\rho$ | Conc. $N_w$ | Density $\rho$ | Conc. $N_w$ | Density $\rho$ |
|---|---|---|---|---|---|---|
| NaOH | 1.0 | 1.040 | 2.0 | 1.080 | 3.0 | 1.116 |
| 1 : 2 | " | 1.052 | " | 1.101 | " | 1.150 |
| 1 : 1 | " | 1.062 | " | 1.123 | " | ——— |
| 2 : 1 | " | 1.075 | " | 1.147 | " | 1.217 |
| 2.5 : 1 | " | 1.085 | " | 1.168 | " | 1.247 |
| 3.0 : 1 | " | 1.099 | " | 1.190 | " | 1.274 |
| 3.3 : 1 | " | 1.105 | " | 1.195 | " | 1.276 |
| 3.8 : 1 | " | 1.111 | " | 1.208 | " | 1.296 |
| 3.95 : 1 | " | 1.113 | " | 1.207 | " | 1.295 |
| 4.2 : 1 | " | 1.109 | " | 1.205 | " | ——— |

With increasing content of silica the solutions exhibit a gradual rise in density until the ratio 1:4 ($Na_2O$:$SiO_2$) is approached, when the density shows no further rise, but in fact falls slightly when the proportion of silica is further increased. The maximum density value occurs in each case in the neighborhood of the ratio 1:4, but in the more concentrated solutions the maximum occurs at a value of the ratio where the silica content is slightly lower than that represented by this value.

No very certain interpretation can be given of this maximum, but it is known, and viscosity measurements show, that the solutions richer in silica are more colloidal in properties than those in which the proportion of silica is less, and that the colloidal properties are exhibited at lowers values of the ratio $SiO_2/Na_2O$ when the concentration is high. It seems possible therefore that the effect on the density may be due to a change in the hydration of the colloidal constituent.

## Relative Viscosity

Results obtained with Ostwald Instruments

TABLE IV

Viscosity of Caustic Soda

| Viscometer No. | Concentration $N_w$ | Time t(secs.) | Density $\rho$ | Viscosity $\eta$ |
|---|---|---|---|---|
| A. | 3.782 | 50.9 | 1.1423 | 2.219 |
| B. | 2.469 | 121.0 | 1.0959 | 1.658 |
| A. | 1.657 | 34.2 | 1.0687 | 1.395 |
| B. | 1.114 | 95.6 | 1.0464 | 1.250 |

TABLE V

Viscosity of Silicate Solution. Ratio $Na_2O$:$SiO_2$ = 2:1

| Viscometer No. | Concentration $N_w$ | Time t(secs.) | Density $\rho$ | Viscosity $\eta$ |
|---|---|---|---|---|
| A. | 6.033 | 139.5 | 1.2821 | 6.879 |
| A. | 2.801 | 49.6 | 1.1411 | 2.177 |
| A. | 2.130 | 41.2 | 1.1103 | 1.759 |
| A. | 0.940 | 31.1 | 1.0506 | 1.257 |

TABLE VI

Viscosity of Silicate Solution. Ratio $Na_2O$:$SiO_2$ = 1:1

| Viscometer No. | Concentration $N_w$ | Time t | Density $\rho$ | Visocsity $\eta$ |
|---|---|---|---|---|
| A. | 2.435 | 48.8 | 1.1458 | 2.158 |
| A. | 1.134 | 33.4 | 1.0705 | 1.381 |
| A. | 0.841 | 30.9 | 1.0529 | 1.256 |
| A. | 0.546 | 29.0 | 1.0352 | 1.159 |

TABLE VII

Viscosity of Silicate Solution. Ratio $Na_2O:SiO_2 = 1:2$

| Viscometer No. | Concentration $N_w$ | Time $t$ | Density $\rho$ | Viscosity $\eta$ |
|---|---|---|---|---|
| A. | 6.277 | 569.0 | 1.4083 | 30.531 |
| A. | 4.274 | 154.1 | 1.2948 | 7.616 |
| B. | 4.274 | 487.4 | 1.2948 | 7.889 |
| A. | 2.586 | 65.3 | 1.1900 | 2.966 |
| A. | 1.088 | 36.1 | 1.0845 | 1.494 |

TABLE VIII

Viscosity of Silicate Solution. Ratio $Na_2O:SiO_2 = 1:2.5$

| Viscometer No. | Concentration $N_w$ | Time $t$ | Density $\rho$ | Viscosity $\eta$ |
|---|---|---|---|---|
| A. | 6.114 | 1286.2 | 1.4450 | 71.483 |
| A. | 3.717 | 164.2 | 1.2938 | 8.171 |
| A. | 1.813 | 52.7 | 1.1543 | 2.340 |
| A. | 0.921 | 35.5 | 1.0815 | 1.477 |

TABLE IX

Viscosity of Silicate Solution. Ratio $Na_2O:SiO_2 = 1:3$

| Viscometer No. | Concentration $N_w$ | Time $t$ | Density $\rho$ | Viscosity $\eta$ |
|---|---|---|---|---|
| A. | 4.531 | 898.0 | 1.3868 | 47.532 |
| A. | 3.464 | 244.8 | 1.3177 | 12.312 |
| A. | 2.741 | 122.9 | 1.2507 | 5.867 |
| A. | 1.922 | 66.0 | 1.1816 | 2.977 |
| A. | 0.999 | 38.8 | 1.0994 | 1.628 |
| A. | 0.365 | 29.8 | 1.0379 | 1.180 |

TABLE X

Viscosity of Silicate Solution. Ratio $Na_2O:SiO_2 = 1:3.3$

| Viscometer No. | Concentration $N_w$ | Time $t$ | Density $\rho$ | Viscosity $\eta$ |
|---|---|---|---|---|
| A. | 5.108 | 3097.2 | 1.4231 | 1682 |
| A. | 3.785 | 529.0 | 1.3308 | 26.870 |
| A. | 2.758 | 145.6 | 1.2527 | 6.962 |
| B. | 1.851 | 207.2 | 1.1827 | 3.063 |
| B. | 1.157 | 133.0 | 1.1143 | 1.853 |
| B. | 0.542 | 98.8 | 1.0555 | 1.304 |

TABLE XI

Viscosity of Silicate Solution. Ratio $Na_2O:SiO_2 = 1:3.8$

| Viscometer No. | Concentration $N_w$ | Time $t$ | Density $\rho$ | Viscosity $\eta$ |
|---|---|---|---|---|
| A. | 3.469 | 3349.1 | 1.3353 | 170.69 |
| B. | 2.953 | 1583.3 | 1.2921 | 25.572 |
| A. | 2.953 | 496.1 | 1.2921 | 24.466 |
| A. | 2.543 | 217.6 | 1.2559 | 10.431 |
| B. | 2.061 | 348.4 | 1.2126 | 5.281 |
| A. | 1.044 | 43.8 | 1.1136 | 1.862 |

TABLE XII

Viscosity of Silicate Solution. Ratio $Na_2O:SiO_2 = 1:3.95$

| Viscometer No. | Concentration $N_w$ | Time $t$ | Density $\rho$ | Viscosity $\eta$ |
|---|---|---|---|---|
| A. | 3.030 | 2073.4 | 1.2989 | 103.582 |
| C. | 3.030 | 2970.4 | 1.2989 | 103.996 |
| A. | 2.530 | 307.0 | 1.2559 | 14.716 |
| A. | 1.852 | 96.6 | 1.1937 | 4.401 |
| A. | 1.247 | 52.1 | 1.1354 | 2.258 |

TABLE XIII

Viscosity of Silicate Solution. Ratio $Na_2O:SiO_2 = 1:4.2$

| Viscometer No. | Concentration $N_w$ | Time $t$ | Density $\rho$ | Viscosity $\eta$ |
|---|---|---|---|---|
| A. | 2.331 | 323.8 | 1.2362 | 15.395 |
| A. | 1.977 | 140.2 | 1.2044 | 6.494 |
| A. | 1.496 | 70.0 | 1.1589 | 3.120 |
| A. | 0.982 | 44.0 | 1.1075 | 1.874 |
| A. | 0.474 | 32.2 | 1.0541 | 1.305 |

These data are plotted in Fig. 8 and are considered in detail after presentation of the further results.

### Results obtained with Ubbelohde Instruments

A complete series of measurements of time of flow over a range of different values of pressure is given in Table XIV, and the remainder of the results are condensed into Tables XV to XXII, and are graphically represented in Figs. 4, 5, and 6, where values of the logarithm (of the applied pressure) are plotted as ordinates and the negative logarithm of the reciprocal of the time of flow as abscissae, the value of $1/t$ being proportional to the velocity of flow. These figures contain data chosen from a range of experimental values. The extreme values are presented in each case, and a convenient number of inter-

## TABLE XIV

Values obtained for 2.586 $N_W$ Solution. Ratio $Na_2O:SiO_2 = 1:2$ in Viscometer U 2.

| Manometer Readings. | Pressure p(cms.) | Time t(secs.) | | Log p | Log 1/t | Log $\alpha$ |
|---|---|---|---|---|---|---|
| 53.44 | 6.08 | 47.36 | 46.86 | 98 1/5 | 1.6708 | 1.9786 | 3.654 |
| 52.94 | 6.59 | 46.35 | | | | | |
| 52.50 | 7.09 | 45.41 | 44.91 | 99.1 | 1.6524 | 1.9961 | 3.654 |
| 52.00 | 7.60 | 44.40 | | | | | |
| 51.42 | 8.22 | 43.20 | 42.65 | 104 2/5 | 1.6289 | 2.0187 | 3.653 |
| 50.90 | 8.80 | 42.10 | | | | | |
| 50.01 | 9.70 | 40.31 | 39.80 | 111.3 | 1.5999 | 2.0465 | 3.651 |
| 49.51 | 10.22 | 39.29 | | | | | |
| 49.44 | 10.30 | 39.14 | 38.64 | 114 4/5 | 1.5870 | 2.0599 | 3.652 |
| 48.95 | 10.81 | 38.14 | | | | | |
| 48.37 | 11.43 | 36.94 | 36.38 | 121.9 | 1.5609 | 2.0859 | 3.652 |
| 47.81 | 11.99 | 35.82 | | | | | |
| 46.88 | 12.98 | 33.90 | 33.42 | 132 1/5 | 1.5240 | 2.1212 | 3.650 |
| 46.41 | 13.47 | 32.94 | | | | | |
| 46.41 | 13.46 | 32.95 | 32.30 | 136 | 1.5119 | 2.1335 | 3.650 |
| 45.96 | 13.91 | 32.05 | | | | | |
| 45.66 | 14.21 | 31.45 | 30.91 | 143 | 1.4901 | 2.1553 | 3.650 |
| 45.13 | 14.77 | 30.36 | | | | | |
| 44.38 | 15.57 | 28.81 | 28.32 | 155 3/5 | 1.4521 | 2.1920 | 3.649 |
| 43.89 | 16.07 | 27.82 | | | | | |
| 43.34 | 16.64 | 26.70 | 26.23 | 167.9 | 1.4188 | 2.2251 | 3.645 |
| 42.87 | 17.12 | 25.75 | | | | | |
| 42.42 | 17.59 | 24.83 | 24.38 | 180 3/5 | 1.3870 | 2.2567 | 3.648 |
| 41.99 | 18.06 | 23.93 | | | | | |
| 41.51 | 18.53 | 22.98 | 22.51 | 195.7 | 1.3524 | 2.2916 | 3.648 |
| 41.04 | 19.01 | 22.03 | | | | | |
| 40.35 | 19.76 | 20.59 | 19.95 | 220 2/5 | 1.3000 | 2.3432 | 3.647 |
| 39.71 | 20.40 | 19.31 | | | | | |
| 39.17 | 20.98 | 18.19 | 17.77 | 246 3/5 | 1.2497 | 2.3920 | 3.646 |
| 38.75 | 21.40 | 17.35 | | | | | |
| 38.07 | 22.11 | 15.96 | 15.37 | 278 | 1.1867 | 2.4440 | 3.634 |
| 37.49 | 22.72 | 14.77 | | | | | |
| 37.10 | 23.06 | 14.04 | 13.52 | 324.7 | 1.1310 | 2.5115 | 3.646 |
| 36.58 | 23.59 | 12.99 | | | | | |
| 35.89 | 24.32 | 11.57 | 11.04 | 399 | 1.0429 | 2.6010 | 3.647 |
| 35.36 | 24.85 | 10.51 | | | | | |
| 35.41 | 24.80 | 10.61 | 10.04 | 443 4/5 | 1.0017 | 2.6472 | 3.652 |
| 34.86 | 25.39 | 9.47 | | | | | |
| 34.76 | 25.50 | 9.26 | 8.53 | 525.9 | 0.9310 | 2.7209 | 3.655 |
| 34.04 | 26.24 | 7.80 | | | | | |

mediate points are inserted. All the intermediate values measured are not reproduced because they give rise to a large number of points lying close together on the figures, but the values not included lie equally well upon the curves.

The relation between the time of flow and the applied pressure producing the flow may be expressed by the equation

$$\text{Log } 1/t = n \log p - \log \alpha$$

where n and $\alpha$ are constants and are obtained graphically. The numerical value of Log $\alpha$ is given by the intercept on the Log $1/t$ axis, and the value of $n$ by the slope of the straight line to the Log p axis.

The relation between the time of flow $t$, and the pressure $p$, producing the flow, may be written

$$p^n t = \alpha$$

the Poiseuille equation representing linear or viscous flow is of the form $pt$ = constant, and is thus a special case of a general equation, characterised by the condition $n = 1$. If the value of $n$ is not unity, the conditions of flow do not satisfy Poiseuille's Law and the function measured by $Cp^n t$ where C is an apparatus constant, is not a true viscosity coefficient.

The values contained in the last column of Table XIV are calculated for each result, using the value of $n$ obtained graphically, and serve to show the agreement with the above law. The greatest deviation in the value of Log $\alpha$ neglecting the value 3.634 which is obviously due to an error in manipulation, is less than 0.3%.

TABLE XV

Ratio $Na_2O:SiO_2 = 1:1$

| No. of curve. | Viscometer No. | Concentration $N_w$ | Log$\alpha$ | n | $\alpha/\alpha_o$ |
|---|---|---|---|---|---|
| a. | U.2. | 2.435 | 3.496 | 0.986 | 2.649 |
| b. | U.2. | 1.133 | 3.272 | 0.981 | 1.581 |
| c. | U.2. | 0.702 | 3.200 | 0.960 | 1.340 |
| d. | U.2. | 0.505 | 3.166 | 0.960 | 1.239 |
| e. | U.2. | 0.202 | 3.136 | 0.960 | 1.156 |

TABLE XVI

Ratio $Na_2O:SiO_2 = 1:2$

| No. of curve | Viscometer No. | Concentration $N_w$ | Log$\alpha$ | n | $\alpha/\alpha_o$ |
|---|---|---|---|---|---|
| E. | U.2. | 6.277 | 4.677 | 0.996 | 40.179 |
| A. | U.3. | 6.277 | 3.177 | 1.001 | 28.840 |
| B. | U.3. | 4.274 | 2.631 | 1.020 | 8.204 |
| C. | U.2. | 2.586 | 3.657 | 1.003 | 3.837 |
| D. | U.2. | 1.088 | 3.370 | 1.011 | 1.982 |

TABLE XVII

Ratio $Na_2O:SiO_2 = 1:2.5$

| No. of curve | Viscometer No. | Concentration $N_w$ | Log$\alpha$ | n | $\alpha/\alpha_o$ |
|---|---|---|---|---|---|
| f. | U.6. | 3.717 | 3.436 | 1.000 | 8.531 |
| g. | U.6. | 1.813 | 2.862 | 0.953 | 2.275 |
| h. | U.6. | 0.921 | 2.618 | 0.907 | 1.297 |

TABLE XVIII

Ratio $Na_2O:SiO_2 = 1:3$

| No. of curve | Viscometer No. | Concentration $N_w$ | Log$\alpha$ | n | $\alpha/\alpha_o$ |
|---|---|---|---|---|---|
| n. | U.4. | 4.531 | 3.840 | 1.032 | 62.373 |
| o. | U.4. | 3.464 | 3.210 | 1.008 | 14.622 |
| p. | U.4. | 2.741 | 2.903 | 1.006 | 7.211 |
| q. | U.4. | 1.922 | 2.553 | 0.954 | 3.221 |
| r. | U.4. | 0.999 | 2.260 | 0.912 | 1.641 |
| s. | U.4. | 0.365 | 2.125 | 0.887 | 1.202 |

TABLE XIX

Ratio $Na_2O:SiO_2 = 1:3.3$

| No. of curve | Viscometer No. | Concentration $N_w$ | Log$\alpha$ | n | $\alpha/\alpha_o$ |
|---|---|---|---|---|---|
| F. | U.2. | 3.785 | 4.560 | 0.963 | 30.690 |
| G. | U.2. | 2.758 | 4.051 | 1.024 | 9.506 |
| H. | U.2. | 1.851 | 3.629 | 0.986 | 3.598 |
| I. | U.2. | 1.157 | 3.437 | 1.001 | 2.312 |

TABLE XX

Ratio $Na_2O:SiO_2 = 1:3.8$

| No. of curve | Viscometer No. | Concentration $N_w$ | Log$\alpha$ | n | $\alpha/\alpha_o$ |
|---|---|---|---|---|---|
| i. | U.5. | 2.953 | 3.482 | 1.013 | 35.237 |
| k. | U.5. | 2.543 | 3.108 | 1.009 | 14.894 |
| l. | U.5. | 2.061 | 2.778 | 0.993 | 6.966 |
| m. | U.5. | 1.044 | 2.408 | 1.034 | 2.972 |

TABLE XXI

Ratio $Na_2O:SiO_2 = 1:3.95$

| No. of curve | Viscometer No. | Concentration $N_w$ | Log$\alpha$ | n | $\alpha/\alpha_o$ |
|---|---|---|---|---|---|
| t. | U.5. | 3.030 | 3.900 | 0.882 | 92.257 |
| t. | U.1. | 3.030 | 3.810 | 1.004 | 117.22 |
| u. | U.5. | 2.560 | 3.250 | 1.004 | 16.406 |
| v. | U.5. | 1.852 | 2.730 | 1.001 | 6.237 |
| w. | U.5. | 1.247 | 2.387 | 0.950 | 2.831 |
| x. | U.1. | 2.862 | 3.355 | 0.977 | 41.115 |

TABLE XXII

Ratio $Na_2O:SiO_2$ = 1:4.2

| No. of curve | Viscometer No. | Concentration $N_w$ | Log$\alpha$ | n | $\alpha/\alpha_o$ |
|---|---|---|---|---|---|
| J. | U.6. | 2.331 | 3.734 | 1.010 | 16.943 |
| K. | U.6. | 1.977 | 3.354 | 1.010 | 7.063 |
| L. | U.6. | 1.496 | 2.989 | 0.956 | 3.048 |
| M. | U.6. | 0.982 | 2.751 | 0.938 | 1.762 |
| N. | U.6. | 0.474 | 2.600 | 0.920 | 1.245 |

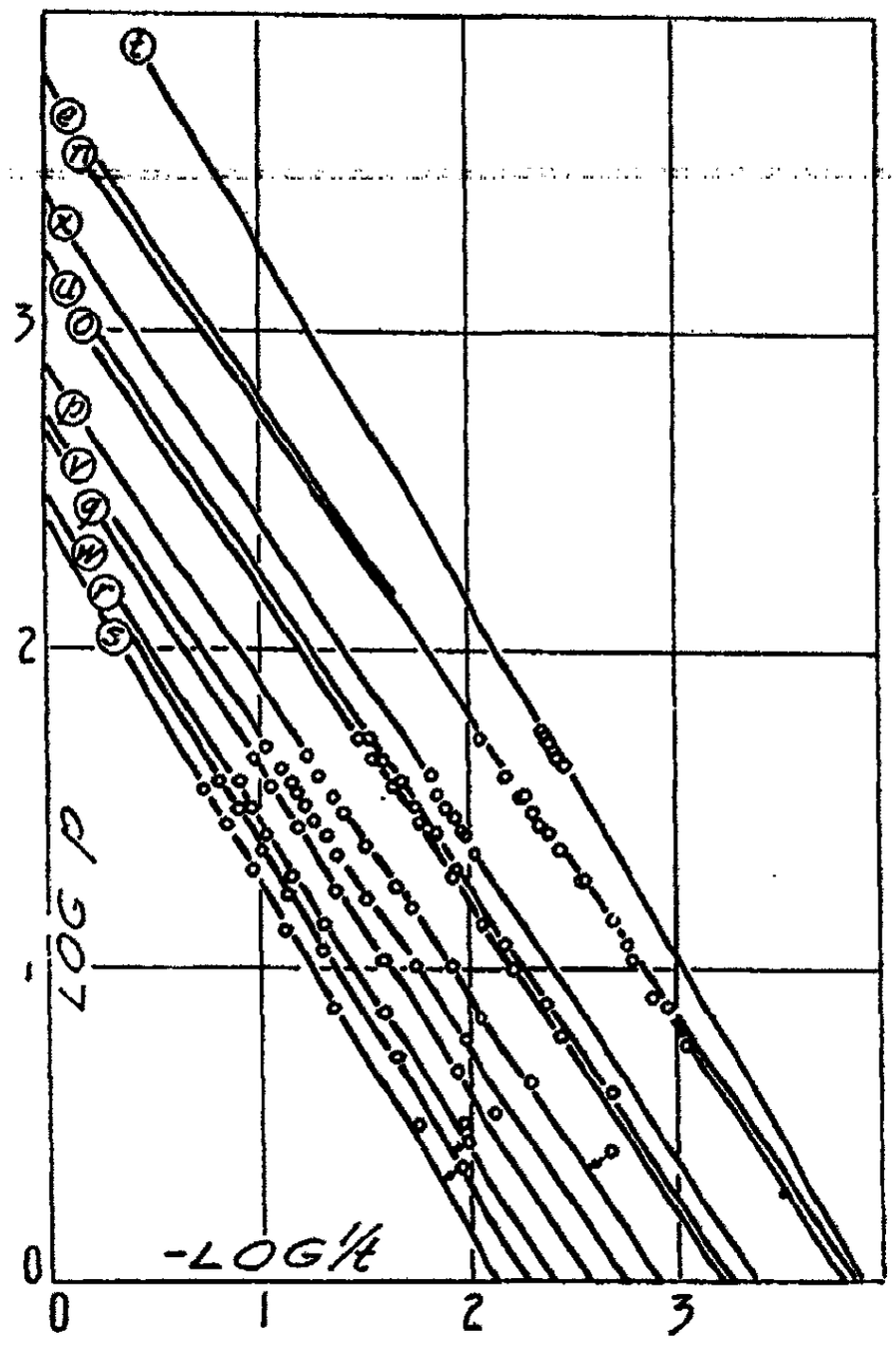



FIG. 4

The values of Log $\alpha_o$ from which the ratio $\alpha/\alpha_o$ given in the last column of Tables XI to XXII is calculated, are the values of the intercept on the Log 1/t axis of the straight line[1] representing the flow of water through the viscometer, and are obtained as calibration constants for each instrument.

[1] Obtained when − log 1/t is plotted against log p.

It will be seen from Figs. 4, 5, and 6, that for the more dilute solutions the extreme points lie somewhat off the straight line, and it is not certain that the straight line is here a true representation of the law of flow of the liquid. It should, however, be noted that the divergences are small and occur where (a) the pressure is very small and (b) with small values of time of flow; in both of these cases the experimental errors (a) in reading the manometer, and (b)

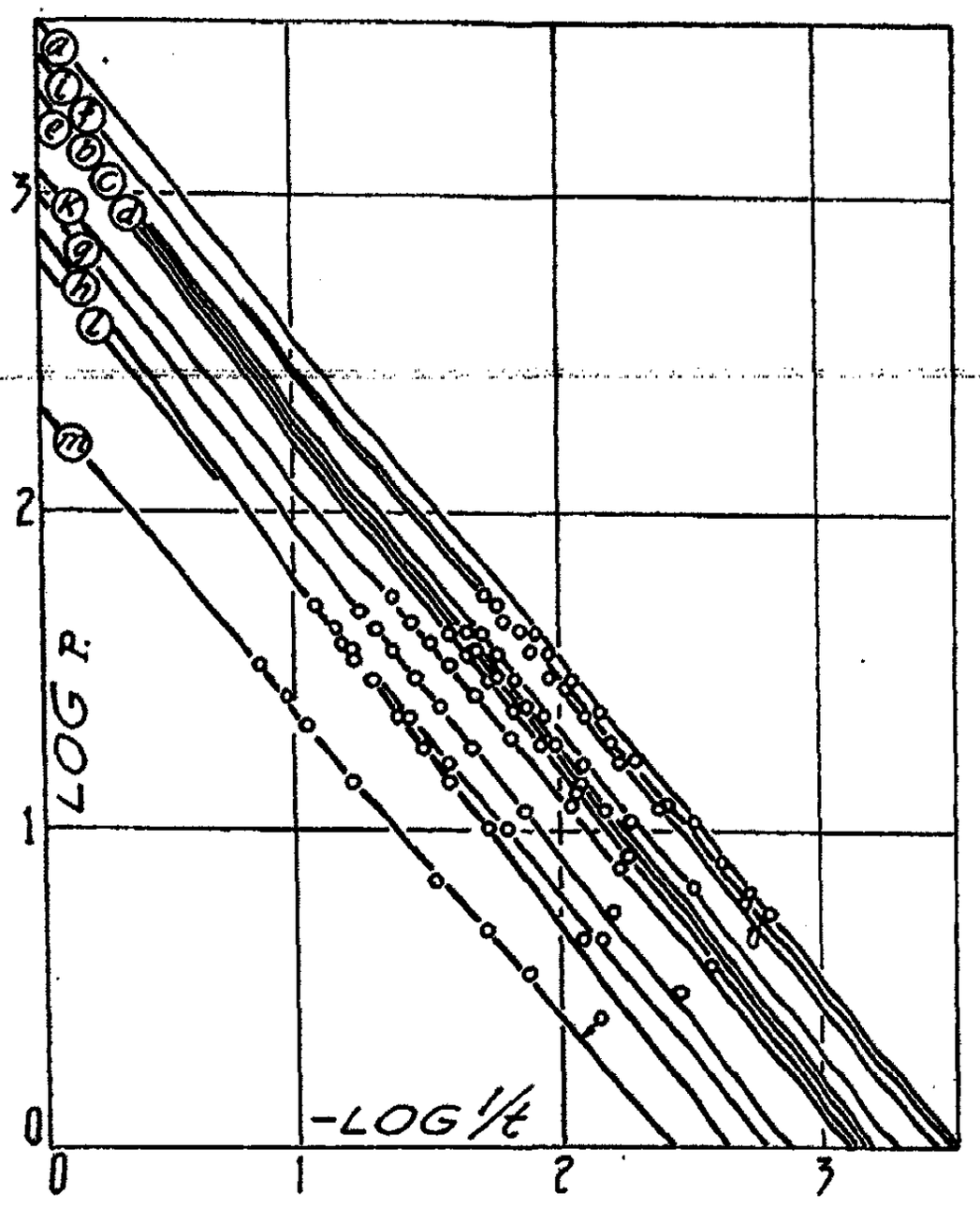



FIG. 5

in operation of the stop-watch, are greater than for values intermediate between the extremes. Also the divergence is only observed in the less viscous solutions with relatively small times of flow, when the effect of the kinetic energy correction (not applied in these results) is a maximum. It therefore seems justifiable to state that under the conditions of pressure employed the flow obeys the law expressed by the equation

Farrow[1], working on starch pastes, found that using the equation

$$V/t = kP^n$$

where V is the volume flowing in the $t$ under a pressure P, the value of N was independent of the instrument used, but changed from paste to paste and in-

[1] J. Textile Inst., 14, 11 (1923).

creased with increasing concentration, being always greater than unity. It is claimed that the value of N is an important property of the starch paste, as much so in fact as the value of the 'coefficient of flow', a term used in place of viscosity on account of the fact that N is not unity. The value of this coefficient was found to be dependent on the instrument used.

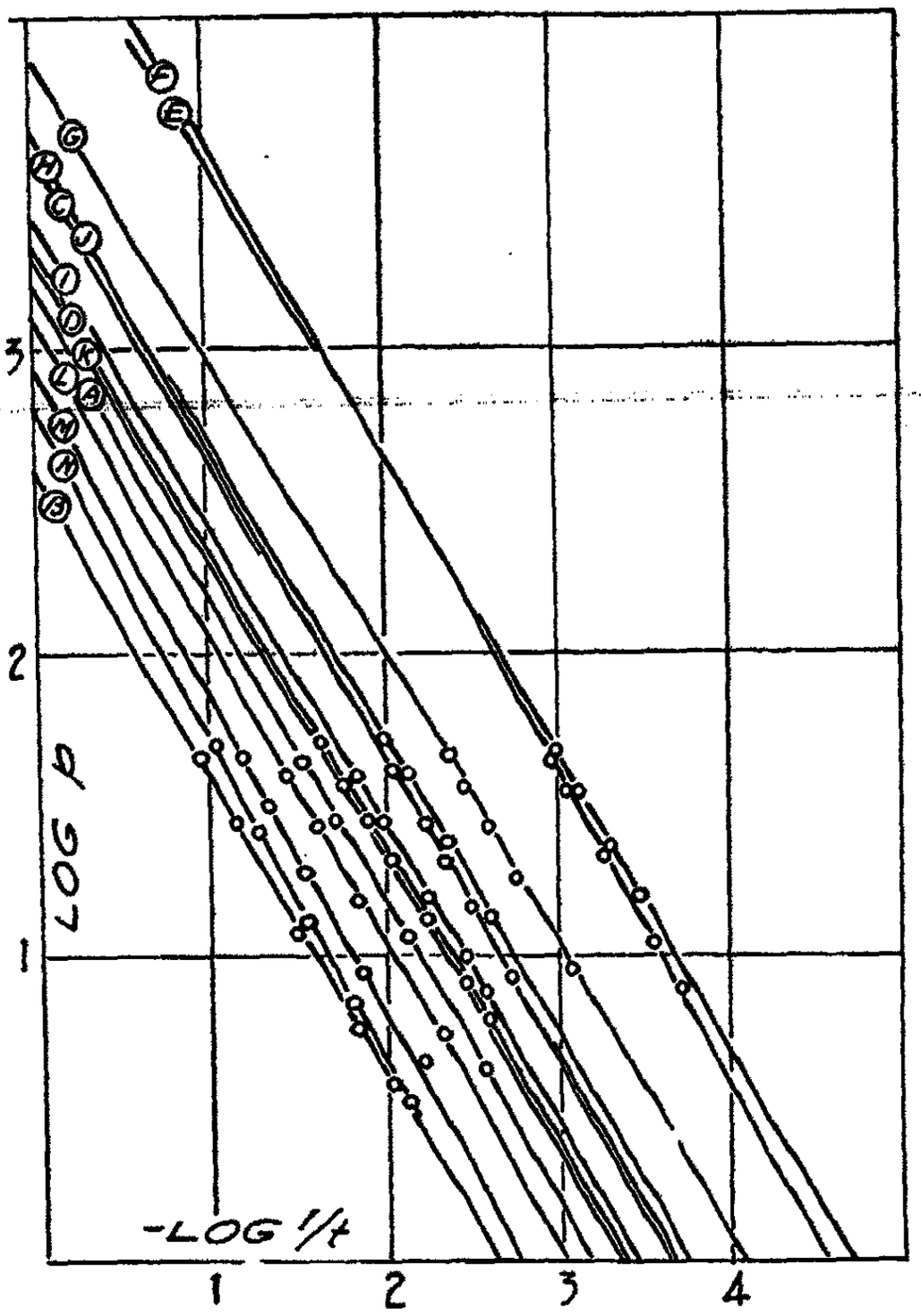



FIG. 6

The value of the exponent $n$ in the present investigation bears no relation to the nature of the solution examined, as in the case of the starch pastes. In fact, in the case of the ratio 1:1, the value of $n$ remains 0.960 though the concentration is increased from 0.2 to 0.7 $N_w$. In Table XX also, the value of $n$ remains almost constant though the concentration is almost trebled. Similarly, with increasing proportion of silica in the solutions, the value of $n$ does not change in any regular way, but shows only a divergence from a mean value. The value of the exponent is also independent of the instrument used,

showing a deviation from a mean value of about 2%. The same order of agreement in the value of $n$ is observed in the cases of changing concentration or of proportion of silica in the solution. The mean value of $n$ over the whole range is 0.979 which is very close to the condition $n = 1$ for viscous flow obeying Poiseuille's Law.

The exponent thus shows little variation with change of instrument and is unaffected by the varying composition of the solutions, being in general very nearly unity.

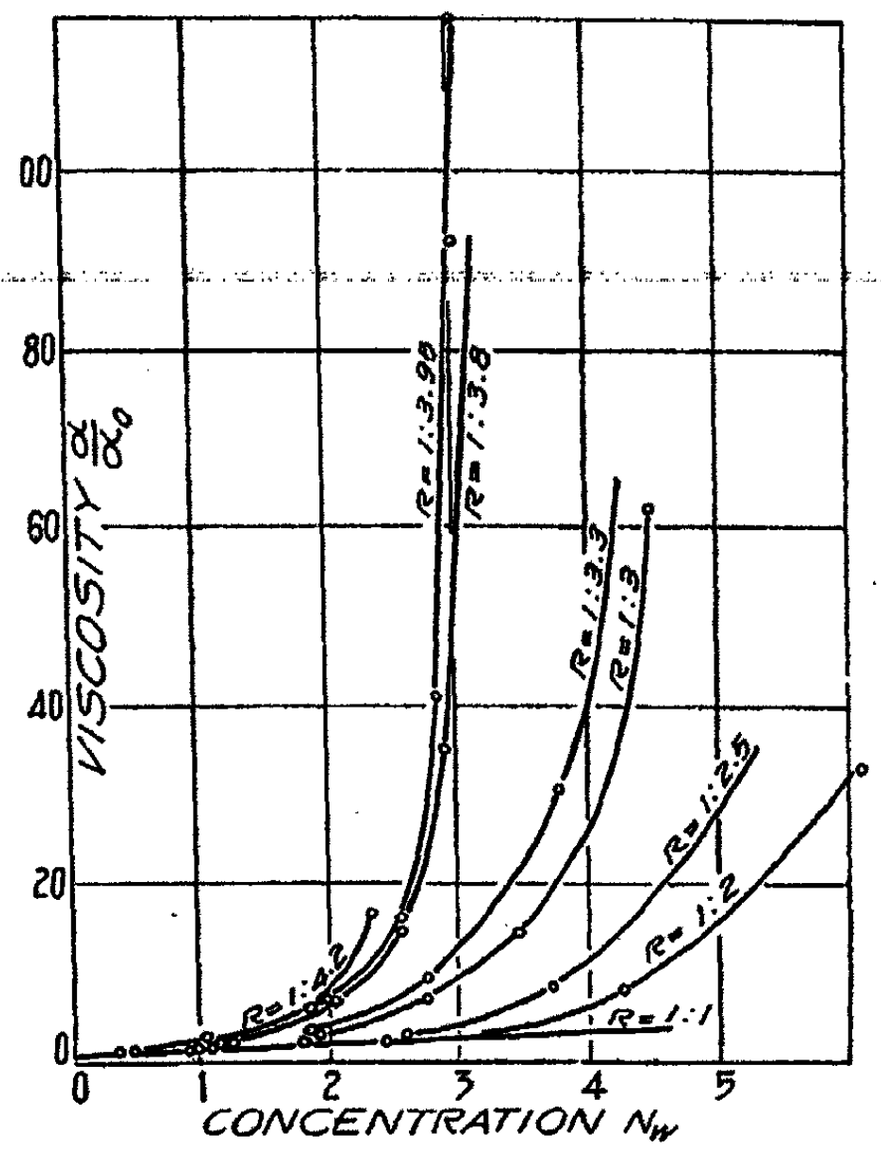



Fig. 7
Results with Ubbelohde Viscometers

The value of $\alpha$ obtained from the intercept on the negative Log 1/t axis is used as a measure of the viscosity. The equation expressing the viscosity of solutions measured in this type of instrument will now become

$$\eta = Cp^n t - C'p/t,$$

the second term being a correction for kinetic energy. The coefficient $\eta$ is not strictly a true viscosity coefficient, since the conditions are not those required by the Law of Poiseuille, but it is used as such in the expression of these results since $n$ is not greatly different from unity.

The corrective term is in general small compared with the first term, and the error introduced by neglecting the correction is not more than 2 or 3%, an

error of the same order as that incurred in the determination of the constants $n$ and $\alpha$ of the straight lines representing the flow. Moreover, the difference between values obtained for the same solution in two different instruments, irrespective of whether any correction is applied or not, is far greater than the correction to be applied. In view of these considerations it seemed superfluous to correct the values obtained in these instruments for kinetic energy at the capillary exit.

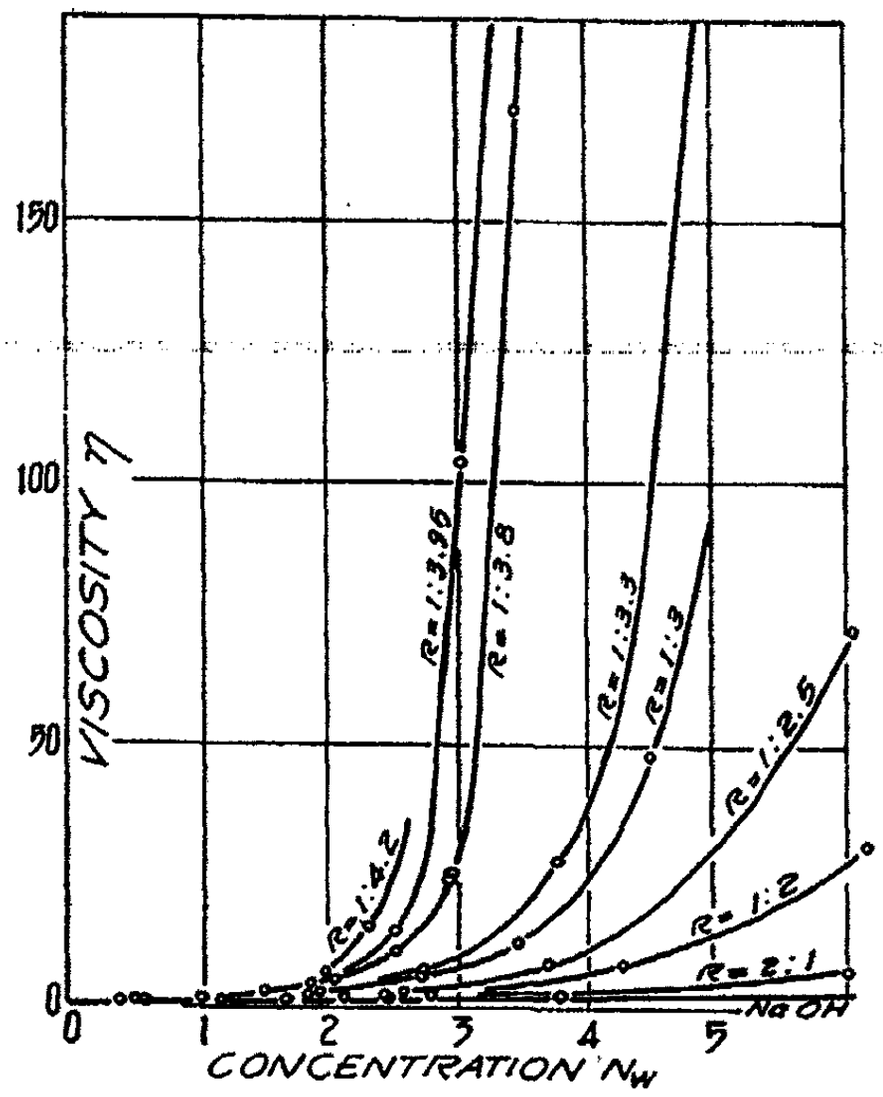



FIG. 8
Results with Ostwald Viscometer

The value of the viscosity coefficient relative to that of water at the same temperature, neglecting the kinetic energy correction, becomes:

$$\eta = \frac{p^n t}{p_o{}^{n_o} t_o},$$

where the values in the numerator are for the solution and those in the denominator for water. This ratio may be expressed as $\alpha/\alpha_o$ and the values of viscosity expressed in this way ($\alpha$ and $\alpha_o$ being obtained graphically in the manner already described) are given in the last column of Tables XV to XXII.

The values of $\alpha/\alpha_o$ taken as a measure of relative viscosity are represented in Fig. 7, each curve indicating the change of the function with increasing concentration for a solution of fixed ratio $Na_2O:SiO_2$. The concentration is expressed in weight normality with respect to the $Na_2O$ content of the solu-

tion, for reasons discussed later. Fig. 8 gives the results of determinations of relative viscosity made in the Ostwald type of instrument, the data from which these curves are drawn appearing in Tables IV and XIII. The two figures show certain differences apart from the fact that the values of $\alpha/\alpha_0$ (Fig. 7) lie, in general, above those of $\eta$ (Fig. 8) for the same value on the concentration axis, the difference varying with the instruments used, and with the viscosity of the solution investigated, the maximum differences being 20-25%. Thus, in the case of the measurements made with the Ostwald instrument, the curves showing the behavior of solutions of high silica content lie comparatively above those where the silica content is lower. The values of $\alpha/\alpha_0$, however, do not exhibit this characteristic at low concentrations. Here, however, different viscometers were used in the determinations of $\alpha$ and it has already been pointed out that the value of $\alpha/\alpha_0$ is dependent on the instrument used. This is sufficient to account for the discrepancy here observed, the difference between the values obtained in different instruments being in all probability due mainly to the different average rate of shear in the capillaries.

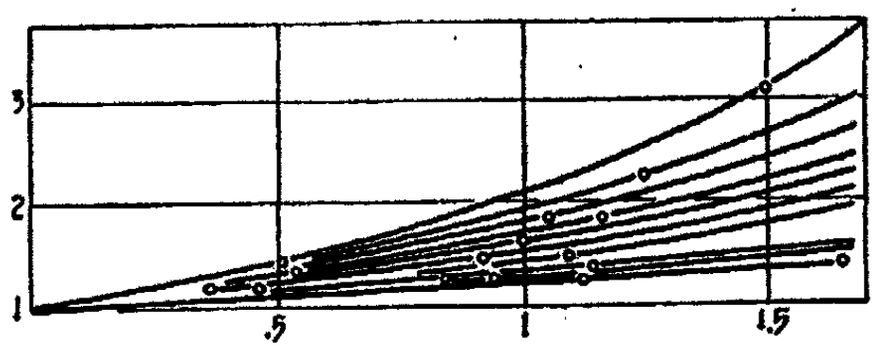



FIG. 8a

The curves of both figures, however, show the same general characteristics, and are typical of emulsoid or lyophile systems, where increase in concentration at low concentrations produces only a small increase in viscosity until a certain concentration is reached, when there is a very rapid rise in viscosity, and the latter is increased enormously by very small increase in concentration. The point at which this rapid increase in the slope occurs is dependent on the composition of the solution with regard to silica content. The ratios of high soda content show only a very gradual change of slope, and as the proportion of silica is increased the change of slope becomes more rapid until as the ratio 1:4 is approached, the curve rises very steeply and with small increases in concentration becomes almost vertical. Measurements made under these conditions become somewhat uncertain because very small changes in concentration exert an enormous influence on the viscosity, and the solutions at such concentrations evaporate very readily when exposed to the air, and consequently must be introduced into the instrument as rapidly as possible. Rapid transference from the containing bottle to the viscometer is difficult on account of the slow drainage from a pipette. The significance of the almost vertical portions of the curves would seem to indicate an ap-

proach to the gel state. In this connection work, as yet unpublished, on the preparation of silicate solutions by electrolytic methods carried out by R. W. Harman in this laboratory, may be mentioned, when a solution of low concentration and ratio approximately 1:5 was found to form a gel on standing for a few days.

At low concentrations the curves approach one another very rapidly. The lower portion of the curves of Fig. 8 are reproduced in Fig. 8a on a much larger scale, when they are still graded according to silica content, approaching the viscosity axis together at zero concentration, a value representing the viscosity of water.

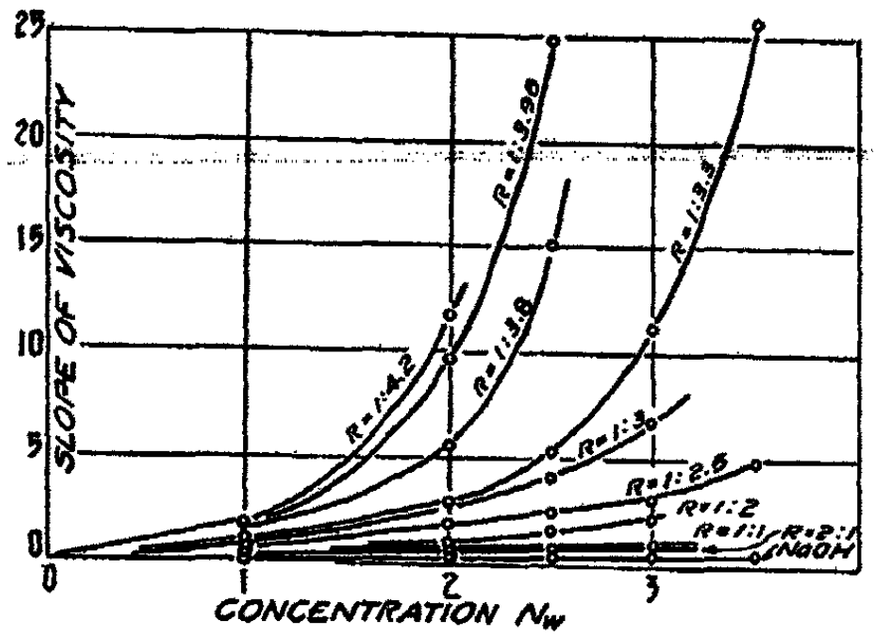



FIG. 9

The value of concentration at which the slope of the viscosity-concentration curve begins to change rapidly is much lower in the case of solutions containing a high proportion of silica than in those where the silica content is lower. This is well shown in Fig. 9, where the slope of viscosity is plotted against concentration. The slope rises in a normal manner until the concentration 1 $N_w$ is reached, when it begins to change more or less rapidly depending on the ratio $Na_2O$:$SiO_2$ of the solution. With ratio 1:4.2 at the concentration 1.5 $N_w$ the slope of the viscosity-concentration curve is 5, while with the ratio 1:2.5 a concentration of 3.5 $N_w$ is required to give the same slope, and a concentration of 2.5 $N_w$ for the ratio 1:3.3. There seems to be a very rapid increase in colloidal properties between the ratios 1:3.3 and 1:3.8, the curves for the latter being considerably higher than the ratios of lower silica content. With the solutions of ratio 1:1 and 2:1 the change of slope with increasing concentration is almost linear up to the highest concentrations investigated, and comparable with the curve for caustic soda solutions, though the actual values of the slope at given concentrations are higher. From this fact it is concluded that there is very little, if any, colloidal material present in the solutions until the ratio $Na_2O$:$SiO_2$ reaches the value 1:2.

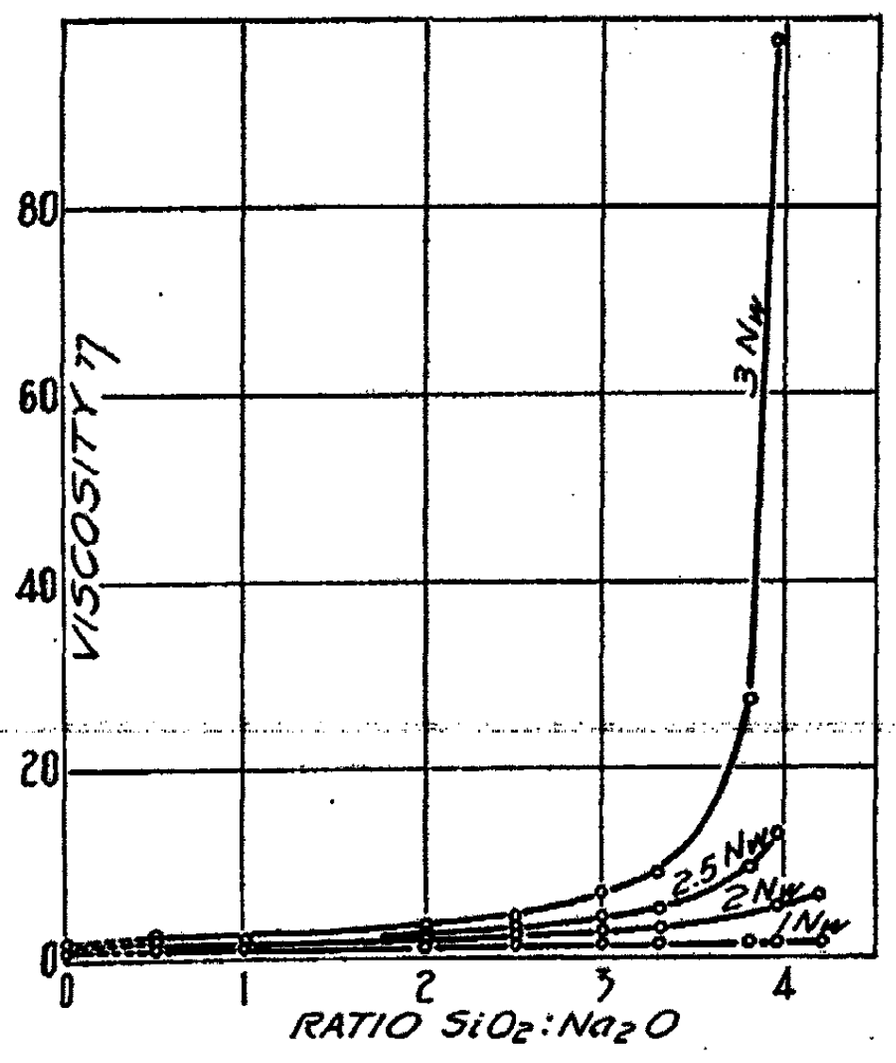



FIG. 10
Ostwald Viscometer

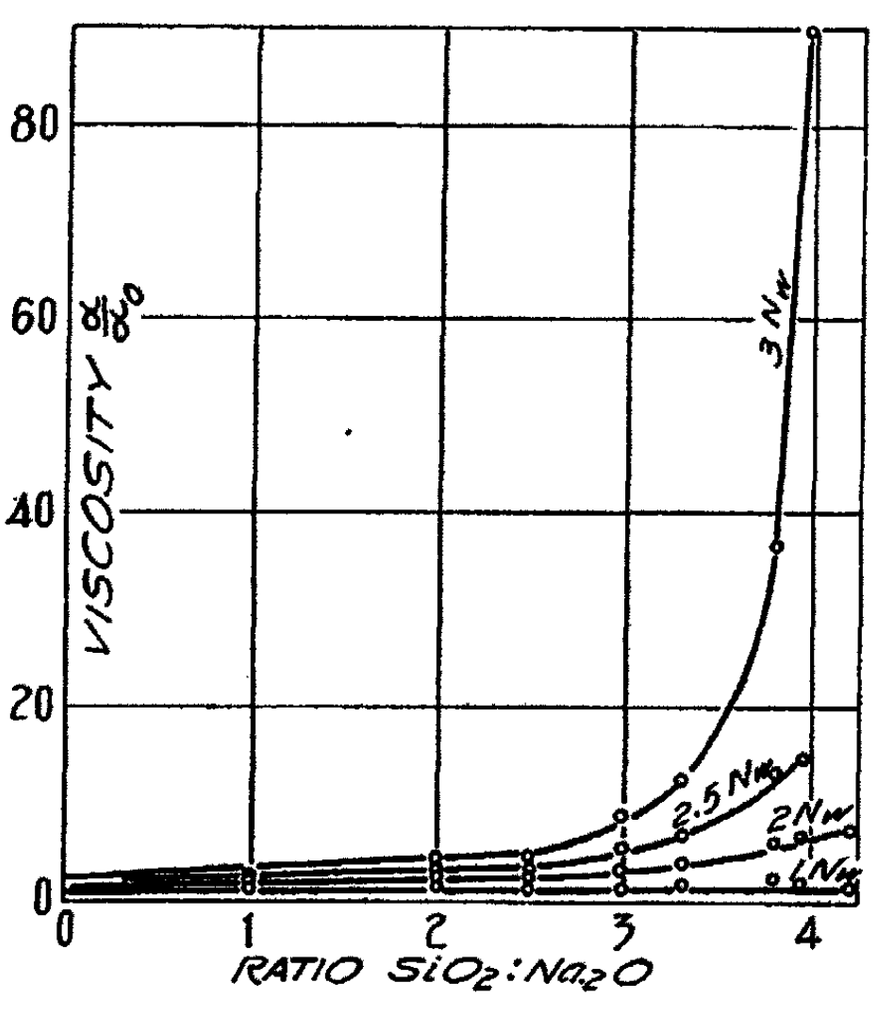



FIG. 11
Ubbelohde Viscometers

### The Effect of the Ratio $Na_2O$ : $SiO_2$ on the Viscosity

From the curves representing the relation between viscosity and concentration, values are obtained by interpolation, of the viscosity of the solutions at each ratio $Na_2O$:$SiO_2$ investigated, at concentrations ($N_w$, $_2N_w$, $_{2.5}N_w$ and $_3N_w$. The values so obtained are plotted as ordinates against the ratio $SiO_2/Na_2O$ as abscissae. The results are tabulated in Table XXIII and are graphically represented in Fig. 10. These curves show the influence of increasing silica content on the viscosity of solutions up to the ratio $Na_2O$: $SiO_2$ = 1:4.2. The values on the viscosity axis are those for pure caustic soda solutions.

TABLE XXIII.

| ratio $SiO_2$: $Na_2O$ | Conc. $N_w$ | Viscosity $\eta$ | $\alpha/\alpha_0$ | Conc. $N_w$ | Viscosity $\eta$ | $\alpha/\alpha_0$ | Conc. | Viscosity $\eta$ | $\alpha/\alpha_0$ | Conc. | Viscosity $\eta$ | $\alpha/\alpha_0$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Caustic | | | | | | | | | | | | |
| soda | 3.0 | 1.86 | — | 2.5 | 1.67 | — | 2.0 | 1.50 | — | 1.0 | 1.22 | — |
| 1:2.0 | " | 2.34 | — | " | 1.93 | — | " | 1.70 | — | " | 1.28 | — |
| 1.0 | " | — | — | " | 2.21 | 2.73 | " | 1.86 | 2.24 | " | 1.31 | 1.49 |
| 2.0 | " | 3.79 | 4.69 | " | 2.81 | 3.68 | " | 2.18 | 2.90 | " | 1.42 | 1.79 |
| 2.5 | " | 4.70 | 5.05 | " | 3.43 | 3.63 | " | 2.50 | 2.70 | " | 1.49 | 1.50 |
| 3.0 | " | 7.32 | 9.18 | " | 4.60 | 5.90 | " | 3.19 | 3.58 | " | 1.61 | 1.62 |
| 3.3 | " | 9.38 | 12.95 | " | 5.42 | 7.23 | " | 3.48 | 4.37 | " | 1.68 | 2.05 |
| 3.8 | " | 27.65 | 37 | " | 9.79 | 13.83 | " | 4.87 | 6.50 | " | 1.79 | 2.78 |
| 3.95 | " | 98 | 90 | " | 13.40 | 15.00 | " | 5.49 | 7.10 | " | 1.90 | 2.30 |
| 4.2 | " | — | — | " | — | — | " | 6.77 | 7.75 | " | 1.87 | 1.80 |

The values of $\alpha/\alpha_0$ taken as a measure of relative viscosity are plotted in Fig. 11, and give a curve of the same general type as that of Fig. 10 obtained by using the Ostwald type of Viscometer. If, however, the two curves are plotted on a larger scale as is done in Fig. 12, the values of the relative viscosity obtained in the Ostwald instruments still lie on smooth curves, but the values obtained in the pressure-type of instrument, while of the same general nature, though higher throughout, exhibit the minimum obvious from the above table between the ratios ($Na_2O$:$SiO_2$) 1:2 and 1:3.

It is between these two ratios that Stericker (loc. cit.) observed a minimum in viscosity, and in fact the dotted curves of Fig. 12 bear a very strong resemblance in form to his curves. Unfortunately, no significance can be attached to this minimum, which does not appear when the Ostwald viscometer is used, all measurements being made in the same instrument. The minimum may be due solely to the use of a number of instruments in determining the flow, and have no connection with the nature of the solutions themselves. In the higher concentrations the minimum disappears, as the values for the concentration $_3N_w$ (Table XXIII) indicate, which supports the view that it is due to the effect of unknown factors influencing the flow, the velocity of flow being much smaller at these higher concentrations in all the instruments used.

In considering the effect of ratio on the viscosity of the solutions, the reason for expressing concentration with respect to $Na_2O$ content becomes evident. If the concentration is expressed as total percentage of solids present, which at first sight seems the most reasonable mode of expression for viscosity measurements, and the values of viscosity at given concentrations are plotted against the ratio $SiO_2/Na_2O$, the curves obtained are irregular and very difficult to interpret. This is because the content of the solutions of different ratio is changing with respect both to soda and to silica. Thus a 30% solution of ratio $Na_2O:SiO_2 = 1:2$ contains 19.82 gms. $SiO_2$ and 10.18 gms. $Na_2O$, while a solution of composition $Na_2O:SiO_2 = 1:3.8$ of the same percentage content contains 23.57 gms. $SiO_2$ and 6.34 gms. $Na_2O$ per 100 gms. of solution.

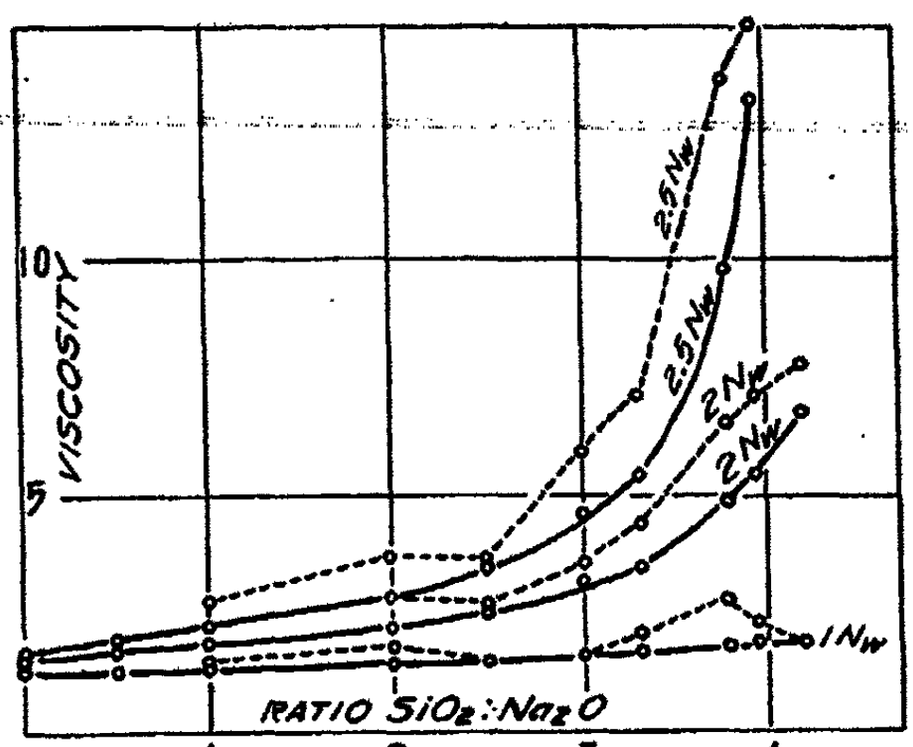



FIG. 12

If, however, as is done here, the concentration is expressed in normality with respect to one constituent, the concentration of that constituent remains constant as the ratio is increased. The equivalent content of soda is chosen rather than that of $SiO_2$ because solutions of corresponding $Na_2O$ content containing no silica may be used for viscosity measurement, and the values inserted in the curves which represent the effect on viscosity of addition of silica to a solution of caustic soda, the weight of $Na_2O$ per 100 gms. of water being constant throughout, for each curve considered separately.

At low concentrations the change of viscosity with increasing proportion of silica is not very great, and for concentrations up to $1N_w$ the viscosity-ratio curve is almost linear. At higher concentrations the viscosity is, of course, higher throughout, and the points lie on smooth curves exhibiting marked change of slope, as the proportion of silica is increased. When the concentration is $2N_w$ the slope changes gradually until the ratio 1:4 is approached, when a large increase in viscosity occurs with small increase in silica content. As the concentration is still further increased, the value of the ratio at which the

slope of the curve begins to increase sharply is less. Thus at $3N_w$ the curve bends up sharply at the ratio 1:3 ($Na_2O$:$SiO_2$). At all concentrations investigated no very rapid change of slope occurs in the viscosity-ratio curves until the ratio 1:2 is reached. Above this value the slope begins to increase more rapidly, the actual value of the ratio at which the change is most marked being dependent on the concentration of the solution. The higher the concentration the lower will be the value of the ratio at which this change is observed. The curve for the concentration $3N_w$ rises almost vertically as the ratio approaches 1:4, and it is doubtful whether a solution of such concentration could be prepared containing a higher proportion of silica and still have the properties of a fluid.

## Conclusions

These curves undoubtedly indicate a change in the colloidal nature of the solution as the proportion of silica is increased. Below the ratio $Na_2O$:$SiO_2$ = 1:1 the viscosity increase is normal, and at low concentrations at any rate the solutions are probably entirely crystalloidal, in which case they may be considered as solutions either of a series of definite salts or as a mixture of the known salt sodium metasilicate in solution with free caustic soda. Between the ratios 1:1 and 1:2 where the viscosity-ratio curve still shows little evidence of colloidal material, a salt of the composition $Na_2SiO_3$ may be present or the solution may be considered as containing the metasilicate together with non-colloidal silica acid. No definite conclusion as to the existence of definite salts in solution can be drawn from the measurement of viscosity alone, but it can be generally inferred that below the ratio 1:2 very little or no colloidal material is present in the solution under the conditions of concentration investigated.

While no very definite conclusion as to the exact nature of the colloidal constituents of these solutions can be arrived at, the rapid change in viscosity with increasing proportion of silica above the ratio 1:2 points to the probable formation of an aggregate in which the amount of silica increases in a manner analogous to the increase in the value of the ratio $SiO_2/Na_2O$ in the solution itself. This view receives support from the nature of the smooth viscosity-ratio curves discussed above, and from the fact that when the viscosity-concentration curves are considered, those for higher silica content show a rapid rise at lower values of concentration than is the case with the solutions of lower silica content. Thus if an aggregate of the type $(Na_2O.xSiO_2)_n$ were formed in the solution, in which the value of $x$ is in some way dependent on the actual ratio $Na_2O$:$SiO_2$ contained in the solution, the solutions containing a higher proportion of silica would be expected to have a considerably higher viscosity value, as the value of $x$ increased, and also to show the rapid rise in viscosity referred to, at a lower value of concentration, the size of the aggregate being greater. This change, however, would be greatly influenced by variations in the value of $n$. The typically lyophile or emulsoid properties of the solutions, as shown by the viscosity, would also suggest that if such aggregates

do exist they are largely solvated. Consideration of the effect of temperature on the viscosity also points to the probability of solvation.

The above remarks are not in any way intended as a quantitative explanation of the behavior of the solutions, viscosity considerations alone being insufficient to show the quantitative nature of the aggregate, or the form in which the silica is present.

### The Effect of Temperature on the Viscosity

If the idea suggested above regarding the formation of colloidal aggregates, the nature of which changes with change in silica content of the solution, is correct and the aggregates are associated largely with the solvent, it would be expected that the solutions of high silica content would have a far greater temperature coefficient than those in which the proportion of silica is less.

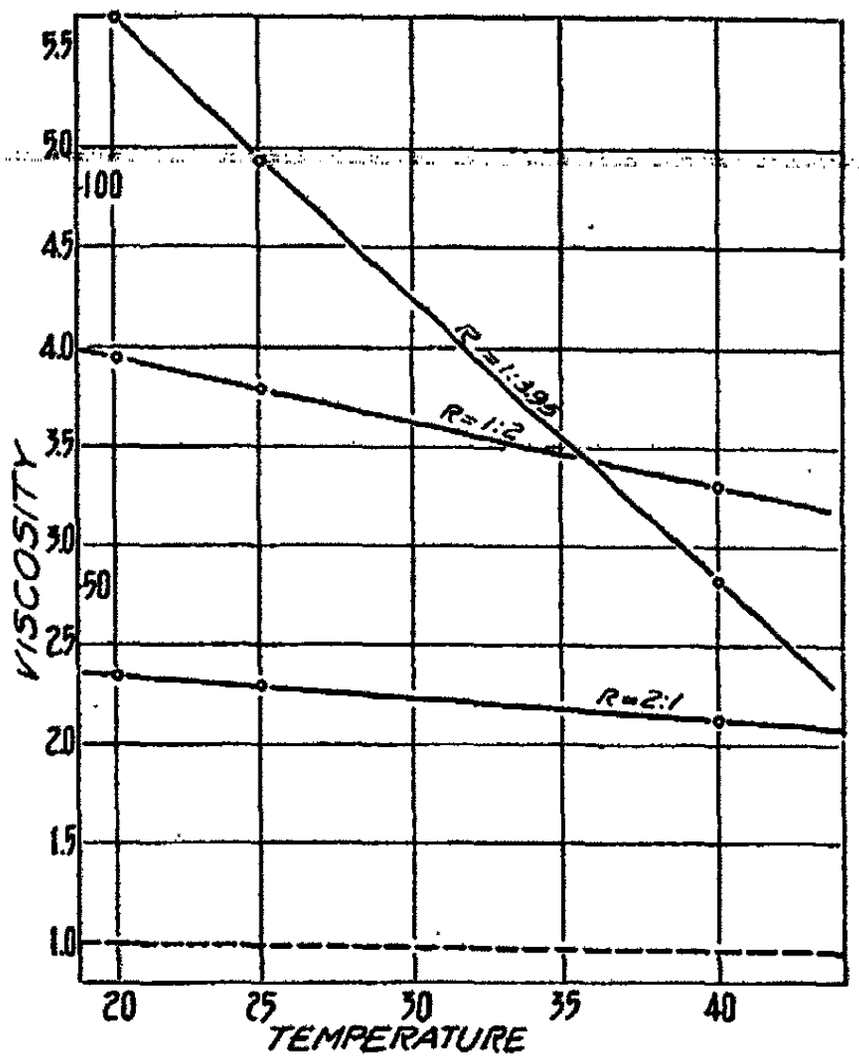



Fig. 13

The effect of temperature on the viscosity of these solutions has been investigated for three ratios $Na_2O:SiO_2$ 2:1, 1:2, and 1:3.95, at the concentration $3N_w$, which is well above that at which the colloidal properties for solutions of ratio greater than $Na_2O:SiO_2$ = 1:2 are first exhibited. Values for these solutions have been already given at 25°C., and further values were obtained in the Ostwald instrument at 20°C. and at 40°C. The times of flow for the solutions and for water were obtained at each temperature, and the

relative density of each solution at the corresponding temperature was obtained. The results of these measurements appear in Table XXIV, where the values in the fourth column are calculated relative to water at the same temperature. Thus at $T_c°$ the viscosity is given by $\eta_T = t\rho/t_o$ where t and $t_o$ are the times of flow of the solution and of water respectively at $T_c°$ and $\rho$ is the relative density. The maximum error in the series of measurements of time of flow is less than 0.5% in each case, which indicates that the temperature control was adequate. The figures here tabulated are plotted in Fig. 13, viscosity being plotted as ordinates and temperature in degrees centigrade as abscissae. The results for the ratio 1:3.95 are plotted on a much smaller scale than those for the other two ratios, the viscosity values being very much higher, and the effect of temperature greater.

TABLE XXIV

The Effect of Temperature on Viscosity

| Ratio $Na_2O:SiO_2$ | Temperature $T_c°$ | Rel .Density $\rho$ | Viscosity $\eta_o$ | Viscosity (calc.) |
|---|---|---|---|---|
| 2 : 1 | 20 | 1.1522 | 2.346 | 2.348 |
| | 25 | 1.1518 | 2.300 | 2.298 |
| | 40 | 1.1492 | 2.148 | 2.146 |
| 1 : 2 | 20 | 1.2194 | 3.946 | 3.947 |
| | 25 | 1.2190 | 3.800 | 3.790 |
| | 40 | 1.2169 | 3.327 | 3.319 |
| 1 : 3.95 | 20 | 1.2993 | 121.60 | 121.24 |
| | 25 | 1.2989 | 103.58 | 103.43 |
| | 40 | 1.2987 | 50.12 | 49.98 |

Over the range of temperature investigated, the relation between viscosity and temperature is well represented by a straight line, the slope of which increases in a marked way with increasing proportion of silica in the solution. In Fig. 13 the viscosity of water is represented by a straight line parallel to the temperature axis, the viscosity values being expressed in each case relative to that of water at the same temperature. The straight lines are represented by equations of the form:

$$\eta_T = -kT + C$$

or $\eta_T = \eta_o - kT$ where $\eta_T$ is the viscosity at the temperature $T_c°$ and $\eta_o$ is that at 0°C. The value of $k$ is obtained as the slope of the straight line to the temperature axis and is negative. The value of $\eta_o$ is obtained as the intercept with the viscosity axis. In the last column of Table XXIV values of viscosity are given, calculated from the above equation, the constants being obtained graphically. The agreement with the experimental values is very close, the difference being always less than 0.3%. The equations for the three solutions investigated may be written:

(a) For Ratio $Na_2O:SiO_2 = 2:1$ $\eta_T = \eta_o - 0.0101\ T$
(b) For Ratio $Na_2O:SiO_2 = 1:2$ $\eta_T = \eta_o - 0.0314\ T$
(c) For Ratio $Na_2O:SiO_2 = 1:3.95$ $\eta_T = \eta_o - 3.562\ T$

Further work is desirable on the influence of temperature on the viscosity of these solutions, but the results, though incomplete, show very definitely the marked increase in colloidal properties of the solutions above the ratio $Na_2O:SiO_2 = 1:2$. The temperature coefficient in passing from the ratio 1:2 to the ratio 1:3.95 shows a very large increase while the change in passing from the ratio 2:1 to the ratio 1:2 is in comparison very small, as is shown by the values of k. The large temperature coefficient of the solutions of high silica content, as shown by these measurements on the solution of ratio 1:3.95, may be explained on the assumption of the formation of a solvated colloidal aggregate. When the temperature is raised, the water held by the aggregate is freed, and a marked fall in viscosity of the solution results.

## Summary

The value found for the viscosity of a solution of silicate of soda is dependent on the instrument used for its measurement. Values obtained in an instrument of the Ostwald type are lower than those obtained in one of the variable pressure type. Using the latter, the flow is represented by the equation: $p^n t = \alpha$ and a measure of relative viscosity is given by the value of $\alpha/\alpha_o$, $\alpha_o$ being obtained for pure water.

Viscosity-concentration curves show the properties characteristic of lyophile sols, and the slope of the viscosity curve at a given concentration is dependent on the ratio $Na_2O:SiO_2$ of the solution, being greater for solutions containing a larger proportion of silica. Viscosity-ratio curves show the influence on the viscosity of additions of silica to caustic soda solutions, the viscosity being increased at first very slowly and then much more rapidly as the proportion of silica is increased above the ratio $Na_2O:SiO_2 = 1:2$ whilst the actual increase in viscosity for a given change of ratio is dependent on the concentration of the solution.

The effect of temperature on viscosity is represented by the linear equation $\eta_T = \eta_o - kT$. The value of the temperature coefficient is greatly influenced by the value of the ratio $SiO_2/Na_2O$, being higher, the greater the proportion of silica. Below the ratio 2 the change in $\eta_T$ is small.

It is concluded that solutions containing less silica than is represented by the ratio $Na_2O:SiO_2 = 1:2$ are, at normal concentrations, chiefly non-colloidal, and that when the proportion of silica is higher, a solvated colloidal aggregate is formed, the size and nature of which is dependent on the ratio $Na_2O:SiO_2$ and on the concentration of the solution.

In conclusion the author desires to express his thanks to Professor Donnan, under whose direction this investigation was made, for the interest he has shown in its progress.

*The William Ramsay Inorganic and Physical Chemistry Laboratories,*
*University College, London.*

# THE TRANSFERENCE NUMBERS OF HYDROCHLORIC ACID IN GLYCEROL-WATER MIXTURES*

BY WALTER W. LUCASSE

The transference numbers of an electrolyte can be calculated from the results of measurements of concentration cells without and with liquid junction. In a recent article[1] results have been published from measurements of cells of the type

$$H_2 \mid HCl \mid AgCl \mid Ag$$

in which the acid concentration was varied from 0.001 to 4M in solvents of one and five mole percent. glycerol in water. From these measurements it is possible to calculate the electromotive force of cells without liquid junction of the form

$$Ag \mid AgCl \mid HCl \mid H_2 \mid HCl \mid AgCl \mid Ag$$

In the present paper are given results of measurements of liquid junction cells of the type

$$Ag \mid AgCl \mid HCl\ (m) \mid HCl\ (0.01\ M) \mid AgCl \mid Ag$$

in solutions of one and five mole percent. glycerol at 25° ± 0.01. The acid concentration was varied from 0.01 to 1 M.

The hydrochloric acid and glycerol were the same as used in the previous study and the solutions and electrodes were made up in the same manner. The cell used was similar to that described in a previous investigation[2], the only change being that the capillary tube connecting the parts B and C was made in the form of a U-tube thus further decreasing the possibility of concentration changes in the solution around the electrode in part C due to diffusion.

The results are given in Table I, the values of the electromotive force being the mean of a number of readings taken over a period of several hours after the cell had been allowed to stand in the thermostat for about five hours. The variation in the readings was extremely small, seldom more than a few hundredths of a millivolt. Measurements were also made in each solvent with the electrolyte at 0.001, 0.002 and 0.005 M. The variations between duplicate determinations were found, however, to be large and from the cells without liquid junction it was seen that the type of electrode used is unreliable at low concentrations. The results of all measurements between 0.01 and 1 M are given with the exception of one at 0.02 M in the second series which was obviously in error. In the first series the values of the electromotive force at 0.1 and at 1 M are each the mean of two determinations, the average deviation from the mean being 0.14 and 0.08 mv., respectively. The

* Contribution from the John Harrison Laboratory of Chemistry of the University of Pennsylvania.

[1] J. Am. Chem. Soc., 48, 626 (1926).
[2] J. Am. Chem. Soc., 47, 743 (1925).

TABLE I

Results from Liquid Junction Cells
Ag | AgCl | HCl (m) | HCl (0.01 M) | AgCl | Ag

| | Solvent: | One mole | % glyc. | Solvent: | Five mole | % glyc. |
|---|---|---|---|---|---|---|
| m | E | log A | $t_+$ | E | log A | $t_+$ |
| (0.001) | | −0.0195 | 0.814 | | −0.0191 | 0.845 |
| ( .002) | | + .2792 | .817 | | + .2746 | .844 |
| ( .005) | | .6656 | .821 | | .6594 | .843 |
| .01 | 0.00000 | .9552 | .825 | 0.00000 | .9469 | .842 |
| .02 | .02812 | 1.2420 | .828 | .02846 | 1.2345 | .841 |
| .05 | .06511 | 1.6160 | .832 | .06530 | 1.6075 | .840 |
| .1 | .09259 | 1.9020 | .834 | .09433 | 1.8893 | .839 |
| .2 | .12090 | 2.1841 | .838 | .12165 | 2.1726 | .838 |
| .28 | .13507 | 2.3257 | .840 | .13574 | 2.3152 | .838 |
| .38 | .14811 | 2.4566 | .841 | .14894 | 2.4477 | .838 |
| .5 | .15994 | 2.5769 | .843 | .16057 | 2.5664 | .837 |
| .7 | .17565 | 2.7327 | .844 | .17671 | 2.7259 | .837 |
| 1.0 | .19306 | 2.9085 | .846 | .19422 | 2.9036 | .836 |

value at 1 M in the second series is the mean of two determinations, the average deviation from the mean being 0.07 mv. The concentrations are expressed in terms of formula weights per 1000 grams of solvent.

The method used in calculating the transference numbers was that employed by MacInnes and Beattie[1]. For a uni-univalent electrolyte the equation relating the activity of the electrolyte and the electromotive force of a cell without liquid junction is

$$d\,E = \frac{2\,R\,T}{F}\,d\ln a_{\pm} \qquad (1)$$

and for a cell with liquid junction

$$d\,E_t = t_+\,\frac{2\,R\,T}{F}\,d\ln a_{\pm} \qquad (2)$$

If the electromotive force be plotted against the logarithm of the geometrical mean activity a straight line will result from the first equation, of constant slope, $\frac{2\,R\,T}{F}$; while a curved line of variable slope, $t_+\,\frac{2\,R\,T}{F}$, will result from the second equation since $t_+$ is a variable. The ratio of the slopes of these lines at any given activity yields the cation transference number at the corresponding concentration. The values of the electromotive forces of the cells without liquid junction were related to the values of log $10^3\,a_{\pm}$ (=log A), obtained from the cells without liquid junction, by the empirical equation

$$E_t = a + b(\log A) + c(\log A)^2$$

The values of the constants *a*, *b* and *c* were determined by the method of least squares.

[1] MacInnes and Beattie: J. Am. Chem. Soc., 42, 1117 (1920).

For the one mole percent. solution the equation obtained was

$$E_t = -0.092528 + 0.096289\ (\log A) + 0.00066196\ (\log A)^2 \qquad (3)$$

and thus the slope of the curve was

$$\frac{d\,E}{d\ (\log A)} = 0.096289 + 0.0013239 \log A$$

Dividing by the constant slope of the curve without transference (1) gave for the variation of the transference number

$$t_+ = 0.8139 + 0.01119 \log A \qquad (4)$$

The mean deviation, positive and negative, of the observed values from those calculated by equation (3) was 0.11% of the total electromotive force.

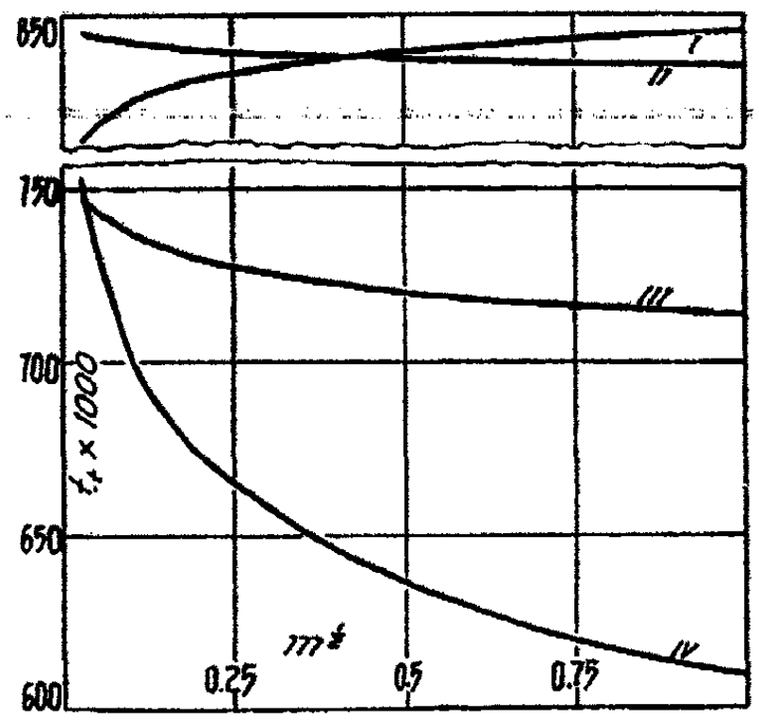



FIG. 1

The Cation Transference Numbers of Hydrochloric Acid: I in one mole percent glyc., II in five mole per cent glyc., III in fifty mole per cent alcohol, IV in absolute alcohol.

For the five mole percent. solution the equation obtained was

$$E_t = -0.094589 + 0.099982\ (\log A) - 0.00018642\ (\log A)^2 \qquad (5)$$

and thus for the transference numbers

$$t_+ = 0.8452 - 0.003152 \log A \qquad (6)$$

The mean deviation, positive and negative, of the observed values from those calculated by equation (5) was 0.18% of the total electromotive force.

The values of the transference numbers given in Table I were computed from equations (4) and (6). The values of log A there given are, with the exception of those at 0.001, 0.002 and 0.005 M, from the observed results of the activity coefficient determined from the cells without liquid junction. The values of log A at the bracketed concentrations were obtained from the calculated values of the activity coefficient and the corresponding values of the transference numbers were computed by assuming that the validity of equations (4) and (6) may be extended to these concentrations, although the equations were formed from the data between 0.01 and 1 M inclusive.

The distribution of the curves may be seen from Figure 1 where the cation transference number × 1000 is plotted against the square root of the molality. There are plotted also, for comparison, the values found by Harned and Fleysher[1] for the cation transference numbers of hydrochloric acid in 50 mole percent. alcohol and in absolute alcohol. According to the "best values" of Noyes and Falk[2] the cation transference numbers of hydrochloric acid in water at 18° rise from 0.832 at 0.005 normal to 0.844 at 1 normal. At 25° the values are doubtlessly about 1% lower and rise in about the same manner or perhaps with slightly greater rapidity. It will be noted that the transference number of the hydrogen ion increases with increasing acid concentration in the one mole percent. glycerol solution while in the other three solvents it decreases, the decrease being more rapid the smaller the water content. The distribution of the curves indicates a similar behavior at constant acid concentration to that found by Krumreich[3] for the cation transference numbers of 0.01 normal silver nitrate in mixtures of ethyl alcohol and water at 40°. The transference number of the silver ion was found to increase from 0.482 in pure water to 0.488 in 30% alcohol after which it decreased rapidly to 0.410 in 99.8% alcohol. Had the glycerol content been greater in the present study the curve would doubtlessly have decreased much more rapidly than in the five mole percent. solution and given values of the transference numbers considerably lower than those in water. It is conceivable that measurements in alcoholic solutions of higher water content would give values of the cation transference number which would rise with increasing acid concentration and, indeed, would be greater than those in pure water at the same concentration. Such behavior may be attributed to changes in the relative solvation of the ions in the different solvents.


## Summary

Measurements at 25° of cells of the form

Ag | AgCl | HCl (m) | HCl (0.01 M) | AgCl | Ag

in which m is given a number of values up to one molal in solvents of one and five mole percent. glycerol, have been presented.

From these data and the results from corresponding cells without liquid junction, the cation transference numbers of hydrochloric acid have been calculated.


*Philadelphia, Pennsylvania.*

---

[1] Harned and Fleysher: J. Am. Chem. Soc., 47, 92 (1925).
[2] Noyes and Falk: J. Am. Chem. Soc., 33, 1436 (1911).
[3] Krumreich: Z. Elektrochem., 22, 446 (1916).

## NEW BOOKS

**The Chemical Action of Ultraviolet Rays.** *By Carleton Ellis and A. A. Wells. 23 × 16 cm; pp. 362. New York: Chemical Catalog Company, 1925. Price: $5.00.* The chapters of this interesting book are entitled: introduction—nature of ultraviolet radiation; sources of ultraviolet rays; metal vapor lamps—mercury arc lamps; protective glasses and filters; observations on photochemical mechanism; reactions of gases in ultraviolet rays; various photochemical and photolytic reactions—general and inorganic; photochemical and photolytic reactions—organic (2); the effect of ultraviolet rays on halogenation reactions; photosynthesis—the formation of carbohydrates and proteins from atmospheric gases; sterilization by ultraviolet rays; biologic effects and therapeutic applications—experimental studies (2); miscellaneous applications of ultraviolet rays.

"At the present time much interest is displayed in what may be termed the photoequivalence law of Einstein and the radiation hypothesis of Lewis-Perrin. Photochemists are now striving not so much for the accumulation of facts on the synthesis and photolysis of chemical bodies as they are to establish the laws which govern the union and disunion of the elements and their compounds under the action of radiation. The establishment of laws governing such changes would make it possible to predict in a large number of cases the outcome of radiation of a given character. There is no question therefore of the importance of investigations tending to confirm the Einstein and Lewis-Perrin proposals or to replace these by others which may better fit the facts. Aside from the foregoing it should be noted that the principal fields of study and investigation which are now occupying the attention of photochemists are the synthesis of carbohydrate and protein material by the aid of light or ultraviolet radiation, the improvement of monochromatic light sources and the production of cold light. This last-mentioned subject is of great practical interest as our modern methods of producing light for heating bodies to incandescence is decidedly wasteful. The production of light without heat and therefore the elimination of the loss of energy due to radiated heat would of course represent a revolutionary step. Considerable progress has been made by Harvey and others in the field of luminescence and phosphorescence through a study of living creatures capable of emanating cold light, such for example as the firefly or glow-worm. These subjects, however, take us beyond the scope of the present volume. The other topic of investigation mentioned above, namely the improvement of monochromatic light sources, is beginning to receive a considerable measure of attention and many developments in this direction during immediate coming years are predicted. With better means for research, such as is likely to be afforded through refinements in apparatus giving radiation of definite and limited wave-length, the possibilities of photosynthesis and photolysis will be greatly expanded," p. 18.

"A mercury arc lamp is described by Heraeus which has a tungsten anode placed at such a distance from the mercury as to maintain permanency of the arc even at high pressures and with great resistance. In this lamp a ten-fold increase in brightness corresponds to a twenty-fold increase in the ultraviolet radiation in the neighborhood of 366$\mu\mu$ and there is smaller consumption of energy and a more permanent length of arc than with carbon arc lamps," p. 50.

"According to some authorities the production of cataract may be at least partially due to the action of rays of short wave-length which have been proven to give rise to a certain turbidity of the eye lens, when present in large quantities. In particular it has been suggested that the prevalence of cataract among glass workers might be explained in this way. Schanz and Stockhausen have declared that ordinary glasses, and even those constructed of blue glass, fail to stop the ultraviolet rays of the most dangerous nature.

"While developing certain blue glasses Luckiesh noticed that cobalt glass appeared to be more transparent than clear glass to ultraviolet rays in the neighborhood of 300$\mu\mu$. Conclusive evidence was obtained by means of clear and blue glasses (soda-lead) of (1) equal thickness and (2) of the same content except that the blue glass contained in addition a

very small percentage of cobalt. Clear and blue specimens of the same thickness were compared in pairs by photographing the spectrum of the quartz mercury arc through each. These experiments established the fact that the glass containing the slight amount of cobalt was more transparent to the mercury lines near 300$\mu\mu$. Since this observation was first made it has appeared to Luckiesh that certain blue glasses which have been developed chiefly for scientific purposes owed a portion of their usefulness to this augmented transparency in the region of 300$\mu\mu$," p. 74.

"Luther and Goldberg have shown that oxygen acts as an inhibitor in all photochlorinations, and they consider that the effect is due to absorption by oxygen of radiation reemitted by the chlorine, which would promote the reaction if not thus absorbed. Bodenstein extends the inhibiting effect of oxygen to all secondary photochemical reactions, except those in which oxygen itself takes part," p. 98.

"The dissociation of hydrogen in low-voltage arcs was observed by Duffendack and Compton not to take place below a minimum voltage of 13 but above 16 volts the rate was rapid, decreasing to 65 volts. Dissociation from contact with the hot filament was always superimposed on the electrical dissociation. With mercury arcs, the dissociation was several times more rapid, the hydrogen molecules presumably being activated by excited mercury atoms.

"Dickinson notes that hydrogen and oxygen in contact with mercury combine to form water at 45°C. or even at room temperature, when illuminated by rays from a quartz mercury arc lamp cooled by a blast of air. This is said to be due to dissociation of the hydrogen by collisions with mercury atoms excited by absorption of the mercury line 253.7 uu. In the absence of any one of the three substances or of the exciting radiation, no reaction takes place," p. 101.

"The decomposition of ozone by light in presence of chlorine has been studied quantitatively by Weigert, the rays of a quartz mercury lamp being used, and the rate of decomposition being measured by means of the change of pressure of the gas. There is no induction period, and decomposition stops when the gas is cut off. The rate of decomposition is independent of the concentration of the chlorine and it is nearly proportional to the intensity of the light. By placing a vessel containing chlorine between the source of light and the ozone tube, a measurement of the quantity of light absorbed by the chlorine is obtained. In this way Weigert showed that the rate of decomposition of the ozone is proportional to the quantity of light absorbed by the chlorine mixed with it. It is suggested that the light produces some intermediate product which is destroyed rapidly by the action of ozone," p. 107.

Coehn and Becker find that at 160° the conversion of sulphur dioxide into sulphur trioxide is only sixty-five percent and not one hundred percent, there having been a very large displacement of the equilibrium, p. 116.

"Plotnikow has expressed the opinion that every element or compound which has a free valence electron is photochemically unsaturated, that the photoactivity is a periodic function of their atomic numbers, and that every photochemically unsaturated compound is photoactive. Light tends to convert the unsaturated into the saturated, and in the process energy may be either absorbed or evolved. In general the longer light waves influence the reactions in which there is a loss of energy, and the short waves those in which there is a gain. A photochemically inactive system may be made active by the addition of such substances as uranium, iron, and chlorine which are rich in valence electrons and which act as catalyzers. These are classified as contact, transfer, chemical, and optical catalysts depending upon the manner in which they enter into reaction. According to Nazarov photochemical effects are now usually regarded, at least as far as their initial stages are concerned, as photoelectric effects, and since the latter are independent of the temperature, and since, further, the velocity of a photochemical reaction depends on the mass of the activated molecules, and this on the velocity of activation, if follows that the temperature-coefficients of photochemical processes should be less than those of reactions occurring in the dark. It appears probable that the temperature-coefficient of a photochemical reaction

is of a magnitude characteristic of the structure of the photochemical component which absorbs the light. Thus in the absorption of light by the molecules containing, as photochemical components, iodine or bromide, the temperature-coefficients have the same value, 1.40," p. 120.

"Curtis states that solutions of aniline green and magenta are not bleached when exposed to a quartz mercury lamp, neither are they bleached by the addition of three per cent hydrogen peroxide to them until the mixture is rayed. To be sure that the bleaching was due to hydrogen peroxide and not to ozone, solutions of the dyes were submitted to radiation while a stream of oxygen was bubbled in but there was no bleaching in this case, hence it appears that the oxidizing power of hydrogen peroxide with respect to the bleaching of dyes is increased by exposing the mixture to rays of short wave-lengths. On the other hand, Holmes reports that solutions of magenta, malachite green, methyl violet, and crystal violet, which have been decolorized by sulfur dioxide, when exposed to ultraviolet of wave-length between 220$\mu\mu$ and 330$\mu\mu$ develop their original colors. Comparison of the absorption spectra of the original dyes and those which had regained the color showed that the regained color is due to the original dye, since the absorption spectrum is the same in both cases. The reaction with sulfurous acid is reversible and consists of a decolorizing action and a colorizing action, the latter being photochemical. The large quanta of energy supplied by the ultraviolet rays cause the photochemical action to increase and consequently a displacement of the position of equilibrium occurs. The equilibrium position can also be displaced by chemical and thermal means," p. 125.

The change in color of minerals and glasses, "under the influence of radium rays is in many cases the outcome of a reducing action while the ultraviolet rays have an oxidizing action; consequently ultraviolet and radium rays frequently induce opposite changes." The ultraviolet transparency of certain colored media is of interest from the standpoint of absorption. Absalom makes the observation that many gems and minerals which in ultraviolet rays are transparent when colorless, do not lose their transparency in the colored specimens; nor is any effect noted on artificially coloring a specimen by means of cathode rays, although colored metallic salts and aniline dyes are opaque. This is strong evidence that the color of minerals is due to colloidal metals, especially in such cases as hyacinth (zircon) and yellow topaz. Deeply colored solutions of the alkali metals and magnesium in liquid ammonia also are extremely transparent in the ultraviolet, which tends to show that these metallic solutions are colloidal," p. 135.

"In view of the effect of colored light upon plant growth and pigmentation, Gardner suggested a study of the precipitation of lithopone under colored light or ultraviolet radiation. Believing that the coloration of zinc oxide in lithopone might be due to the presence of zinc sulfide, Nishizawa mixed zinc sulfide and glycerol on paper and exposed it to the action of ultraviolet rays. There was no coloration of the zinc compound and it was found by similar experiments that other polyatomic alcohols have the same protecting properties. Certain organic salts such as zinc tartrate and Rochelle salts have a like effect, while some others are without influence. Magnesium and calcium hydrate also serve as protectors to the zinc compounds. It was shown that linseed oil and turpentine have no effect on this protective action, and that only minute quantities are necessary to afford complete protection. Based on the above experiments a new method of manufacture of lithopone was devised, in which the zinc sulfide is treated with glycerol, or the saccharides, and salts and esters of tartaric and polyhydroxystearic acids. The sulfide may be incorporated with the organic compound itself, or with its aqueous solution. The sulfide may be precipitated in the presence of the organic compound, or the organic compound may be formed in the presence of the zinc sulfide. Prepared in this manner the sulfide shows no appreciable change when exposed for several hours to the action of ultraviolet rays or by gradually heating to a temperature of 120°C," p. 138.

"Some relation is to be expected between the absorption spectrum of a substance and its photochemical activity. According to Henri and Wurmser, the latter depends solely on that part of the absorption spectrum coinciding with the atomic groups affected by photo-

chemical action. The rest of the light energy absorbed appears as heat. This gives the possibility that photochemical decomposition may differ with different wave-lengths, depending on the groups responsible for absorption. Thus Bielecki and Henri were able to break up the absorption curves of aldehydes and ketones into simple elementary curves. Aldehydes gave two and ketones three curves. They conclude that rays of different wave-lengths are absorbed by different groups," p. 142.

"The polymerization products [of vinyl esters], which form more or less rapidly in accordance with the intensity of illumination and the temperature, are solid, colorless, and transparent, celluloid-like masses which are odorless and can be turned, cut, planed, and otherwise manipulated to form various articles. These solids, rendered plastic in hot water, can be molded and, upon cooling, the material becomes hard again. Chlorinated esters may be polymerized by heat and light as a two-stage operation in the following manner: 1 kilogram of vinyl chloracetate is mixed with from 0.5 to 1 gram of benzoyl peroxide and carefully heated in a large vessel provided with a reflux condenser. At from 80° to 100° polymerization takes place, while the temperature rises rapidly. At this time care should be taken to cool the reaction vessel. The violence of the reaction may be modified by diluting the reaction liquid with an indifferent solvent; for instance, in the present example, about 300 grams of chlorobenzene can be used. The reaction product is a viscous syrupy mass which can be further treated by exposing to light without a diluent, solid masses being obtained as the remaining, unaltered vinyl ester polymerizes. The syrupy solution or a solution made from the completely polymerized ester may be used as a lacquer or other coating compound. When allowed to dry in thin layers, colorless films of a celluloid-like nature are said to be obtained. Vinyl chloride may be polymerized by ultraviolet rays, but the product derived is not as satisfactory as that obtained from the esters mentioned. According to Kuhl the polymerization of vinyl esters (vinyl acetate or vinyl chloroacetate) by ultraviolet light yields solid masses which may serve as substitutes for celluloid and which are fireproof and odorless. The polymerization is assisted by catalytic agents (organic peroxides) to give thick syrups which on illumination give solid masses having valuable properties," p. 151.

"According to Maynard the direct union of metallic mercury and methyl iodide is not hastened by ultraviolet rays but is accelerated by a specially arranged arc light. The reaction is preceded by the formation of a small amount of mercurous iodide. If mercurous iodide is used with methyl iodide, methyl mercuric iodide is formed rapidly. The action of metallic mercury is confined almost entirely to methyl iodide. The use of mercurous iodide makes possible the extension of the reaction to higher iodides and even to benzyl iodide," p. 151.

"A detailed study of the photolysis of acetaldehyde has been made by Berthelot and Gaudechon who state that ultraviolet rays of long wave-length do not convert the aldehyde into acetic acid in the absence of oxygen. Under the influence of medium and extreme rays oxidation takes place even in the absence of oxygen, a portion of the aldehyde being converted into acetic acid. The amount of acid produced is far greater when the aldehyde is in the form of vapor than when it is liquid. With rays of wave-length 250$\mu\mu$ polymerization is rapid, both para and meta acetaldehyde being formed. No resinification results from the action of long ultraviolet rays, and it is only slowly produced by the medium and extreme rays. The presence of water checks polymerization and resinification, but favors acidification, formic acid produced in this case and in amount almost equal to that of the acetic acid. Of three compounds studied, viz.: acetaldehyde, ethyl alcohol and acetic acid, only acetaldehyde is decomposed by sunlight (wave-length greater than 300$\mu\mu$). Rays from a mercury lamp screened by thin glass which absorbs all rays of wave-lengths less than 300$\mu\mu$ decompose acetaldehyde in accordance with the equation $CH_3 . CHO = CO + CH_4$. Frequently the proportion of methane to carbon monoxide actually found is somewhat less than corresponds to this equation, for the light causes polymerization of some of the aldehyde to paraldehyde which is then photolyzed to carbon monoxide and ethane or more complex substances. These latter reactions are most readily produced by the extreme ultraviolet rays."

"According to Berthelot and Gaudechon simple sugars may be divided into four classes according to their resistance to light; ketoses are attacked by ultraviolet rays $\lambda = 300\mu\mu$, the aldoses by the rays $\lambda = 300$ to $250\mu\mu$, the straight chain polyhydric alcohols by rays $\lambda = 250$ to $200\mu\mu$, the ring polyhydric alcohols only by the ultraviolet of wave-length $200\mu\mu$. With the longer radiations producing the first stage in the action, the liquid remains neutral and does not reduce Fehling's solution in the cold. With decreasing wave-length decomposition increases, the liquid becomes acid, and carbon dioxide can be detected in the gaseous products, the amount of hydrogen evolved increases and the solution begins to reduce Fehling's solution in the cold, finally, methane is liberated. The volumes of carbon monoxide and hydrogen evolved in the first stage always bear a simple ratio to one another," p. 159.

"The influence of light upon various acids and their salts is interpreted by Jaeger and Berger largely by ionic equations, and from the results it is concluded that each photochemical reaction is specific and very dependent upon conditions obtaining at the moment, so that it is scarcely ever possible to predict its course. Among the conditions governing the reaction the presence of certain ions in the solution must be considered a factor of great importance. In the photochemical decomposition of salts the velocity of reaction is greatly influenced by the presence of certain cations in the solution. The addition of certain neutral salts first increases the velocity and on further addition retards it or completely stops it. The greater the electrical charge of the cation of the salt added, the smaller the quantity required to bring the rate of decomposition to a maximum, p. 165.

"The leuco-bases of Brilliant Green, Malachite Green, Crystal Violet, Rhodamine B, 3B and 6G, also leucaniline and "leuco blue," are sensitive to the respective complementary colors of the dyes and may be used for actinometric purposes. Mixed with collodion they are more light-sensitive than the dyed silver bromide and silver chloride films hitherto used in photometry. As it is sensitive to ultraviolet, according to Eder the leuco-base of Brilliant Green is specially suited for use in plant physiology experiments, being sensitive to that part of the spectrum which is active in chlorophyll formation," p. 193.

"From a study of the assimilatory quotient $CO_2/O_2$ Willstätter and Stoll contend that formaldehyde is the only intermediate possible between carbon dioxide and the carbohydrates. This quotient under all conditions was found experimentally to be unity; that is, for each volume of carbon dioxide absorbed one volume of oxygen is liberated. In the formation from carbon dioxide of formaldehyde the quotient is 1.0; for glycollic acid 1.33; for formic acid 2.0; and for oxalic acid 4.0," p. 222.

"As to the actual part which chlorophyll plays in the photosynthesis of carbohydrates in the living plant, Thatcher points out that three possible modes of action are now receiving experimental study. The first of these, which has naturally been longest considered as the probable function of chlorophyll, is that it acts chemically as a catalyst by forming unstable intermediate products with formaldehyde or possibly other simple intermediate compounds of the photosynthetic process. Indeed, several investigators have shown that chlorophyll actually does form a compound with formaldehyde from which complex the formaldehyde may be either given off or absorbed in order to establish a proper equilibrium in the photosynthetic process, and to afford in the plant a mechanism by which the quantity of free formaldehyde is regulated. In this way the amount present in free form at no time reaches that which would be toxic to the cell protoplasm. The second of these conceptions is that, regardless of the color and of the general chemical reactivity of chlorophyll, the mineral constituent (magnesium) which it contains is held in proper colloidal form to exert a definite catalytic effect upon the photosynthetic process. The third, and most recent, explanation of the mechanism of chlorophyll action is that the pigment acts as a photocatalyst, or light screen, to absorb and transmit the energy from light rays of the proper wave-length to accomplish the several steps in the photosynthesis of carbohydrates," p. 231.

"We have already learned that the ultraviolet component of solar radiation at the earth's surface is practically identical with the region which is possessed of stimulative action and which is not endowed with lethal power. In other words, living beings on the face of the earth have, at least partially, adapted themselves to exposure to rays of wave-lengths not

shorter than 300$\mu\mu$. No natural occasion has arisen to evolve a mechanism protective against the shorter waves; these, therefore, preserve their fatal effect on living beings.

"The fact that our protection against the solar ultraviolet is incomplete has led Woodruff to suggest that our remote ancestors evolved in dark, cloudy regions, where such rays could reach the earth in only feeble amounts. The surmise may be correct, but it is at least as easy to suppose that the advantages of the stimulative action outweighed the relatively unimportant ill effects, and that excess of the latter was countered by the development of pigment," p. 272.

"Gebhard has confirmed the theory that the bleaching of dye solutions or of dyed tissues by light is due to the primary formation of a peroxide of the dye. The peroxide is best detected by acidified potassium iodide and starch, by alkaline potassium permanganate, or by diphenylamine and concentrated sulphuric acid. Chromic, molybdic, and titanic acids do not indicate the presence of a peroxide, which fact furnishes one of Gebhard's several arguments against the primary formation of hydrogen peroxide. The rays which are most effective in the production of the peroxide are those complementary to the color of the dye. Blue, violet and ultraviolet rays exert a decomposing action on the peroxide, or occasion a transference of the active oxygen to unattacked molecules of the dye. Gebhard utilizes Mumm's theory of oxidation in the presence of water and shows by an electrolytic experiment that the perhydroxyl-ions are instrumental in bleaching the dye," p. 313.

*Wilder D. Bancroft*

**The Constitution of Matter.** *By Max Born. Translated by E. W. Blair and T. S. Wheeler. 22 × 15 cm; pp. vii+80. New York: E. P. Dutton and Company, 1923. Price: $2.50.* The subject is presented under three general headings: the atom; from mechanical ether to electrical matter; the fusion of chemistry and physics. On the first page the author says: "The modern theory of the atom has its origin in chemistry. Physicists have turned only slowly and reluctantly to the atomic point of view, and while atoms and molecules have long been in daily use by the chemist, it is but a short time since there were physicists who regarded the atomic theory as a sometimes seemingly useful, but in the main avoidable, hypothesis. It is not so to-day. The physicist, helped by the investigations of the last few years, may now presume to instruct the chemist in the nature and the actions of the atom. For physical methods penetrate deeper into the atom than do chemical; while the speculations of chemists on the structure of atoms and the forces at work between them, especially as regards valency, were somewhat arbitrary, being chiefly based on one manifestation of atomic force—chemical combination, the idea of the atom as conceived by present-day physicists is, in many vital respects, free from such arbitrariness. One can be confident that future investigation will amplify, but at the same time leave, the clear outline that we now know."

We encounter adsorption even when determining the value of the quantum, p. 7. Ehrenhaft of Vienna worked with considerably smaller drops than Millikan used and believed that he had detected much smaller charges. "More recent experiments, particularly those of Regener and his collaborators and of Bär suggest, however, that the phenomena observed by Ehrenhaft cannot be explained by a subdivision of the elementary charge, but are due rather to the adsorption of gases on the surfaces of the minute spheres, which then appear to possess abnormally small densities."

"As we have already seen, the lattice of the [rock-salt] crystal is not composed of NaCl molecules, but of individual Na and Cl atoms. This is proved, not only by Laue's X-ray photographs, but also by the thermal behavior of the crystal. The energy of a body consists in the motions of its smallest constituents; in crystals, these vibrate about their centres of gravity. According to a fundamental law of statics, the energy of these vibrations is divided amongst the individual constituents so that in time each and every constituent possesses *the same* amount of energy which can be determined from the kinetic theory of gases. From thermal measurements one can deduce the number of particles, each containing this amount of energy, which must be present in unit mass, so that this may contain the observed heat-content. In this way it was proved that the constituents cannot be NaCl

molecules, for the unit mass would then contain only half as many particles, and consequently only half the observed heat-content, as it would if they were atoms," p. 42.

"If such a NaCl solution is evaporated so that the rock-salt crystallises out, the process consists of the individual Na and Cl atoms uniting to form the above-mentioned lattice. What happens then to the charge of the atoms; do these cancel one another, or do the atoms retain their ionic character in the solid state as well?

"Madelung has answered this question by the interpretation of an optical property of crystals such as NaCl. Imagine a piece of rock-salt placed between two parallel, charged, metal plates; then the lattice is exposed to an electrical field. If we assume that the Na atoms are positively, and the Cl atoms negatively, charged then the former will be attracted in the direction of the field, and the latter in the opposite direction. Owing to the rigidity of the crystal, this attraction will produce only a very small relative displacement of the Na and Cl ions. Now consider the well-known phenomenon of resonance: if a pendulum is allowed to oscillate freely in its natural period, the amplitude can be increased with a minimum of work. In the same way, an oscillating electrical field of suitable period will cause a maximum displacement in the crystal. Light-waves are such oscillating electrical fields; it is to be expected, therefore, that light of a suitable wave-length will appreciably affect the crystal, and *vice versa* be affected by it. Rubens has proved this; he found that infra-red light of a very long and definite wave-length is strongly reflected by the crystal, whilst light having a slightly different frequency is unaffected. By repeated reflections he was able to isolate this selective light, and on this account called it the "residual rays."

"These residual rays proved that the atoms of the crystal were charged. That this charge for crystals of the type NaCl is exactly one electron, has been shown by calculating the known frequency of the light from the charge of the electron, the masses of the ions and the measurable elastic forces of the crystal.

"Recently, however, the ion-charge has been tested directly by Debye and Scherrer, by means of X-ray photographs. The X-rays perturb the electrons of the atom, thus producing secondary rays, which proceed from the atom; these, by reason of their interference produce the phenomena discovered by Laue. The intensity of the interference spots will depend on the number of electrons present in the atoms; conversely, by measuring the intensity of the interference spots, conclusions can be drawn as to the number of electrons the atom contains. In this way it has been shown that, in the crystal of lithium fluoride, the Li atom has one electron less, and the F atom one more, than in the neutral state. Similar conditions undoubtedly exist in all compounds of the alkali metals (Li, Na, K, Rb, Cs) with the halogens (F, Cl, Br, I)," p. 44.

Nernst's third law of thermodynamics is considered by the author as indeed "a great achievement—the determination of chemical processes by purely physical measurements. It is a fusion of chemistry with physics, which apparently leaves nothing to be desired.

"But there yet remains another problem, the solution of which must always be an ideal of the physicist—the proof of the unity of all physical and chemical forces and their reduction to reactions between the elementary components of matter—electrons and atoms, or atom-nuclei. Modern physics already possesses models of the atom, which certainly approximate to the facts, and with these it can explain numerous mechanical, electrical, magnetic, and optical phenomena. It must not stop with these, but must endeavor also to reduce chemical properties to atomic forces, in so far as they are known. In this respect Nernst's theory is a good starting-point, for it reduces the complexity of chemical processes to a series of simple constants. It is now the task of the molecular physicist to calculate from the properties of the atom these constants which the physical-chemist can determine by calorimetric and similar measurements. This opens up an extensive field of thermochemical investigation," p. 51.

"When we contemplate the path by which we have come we realize that we have not penetrated far into the vast territory of chemistry; yet we have travelled far enough to see before us in the distance the passes which must be traversed before physics can impose her laws upon her sister science," p. 78.

*Wilder D. Bancroft*

**Three Centuries of Chemistry.** *By Irvine Masson. 14 × 21 cm; pp. 191. London: Ernest Benn, 1925. Price 10 shillings, 6 pence.* The French savant who described chemistry as a French science, founded by Lavoisier, would certainly have refused to go back to the seventeenth century for the initial development of modern chemistry. Without doubt, however, as Professor Masson shows, the basis of this wonderful structure is to be found in the philosophy of Francis Bacon and the experimental work of Robert Boyle. The present volume on broad philosophic lines and characterized by much literary skill, deals in some detail with that new spirit of investigation which became manifest in England in the first half of the seventeenth century and which somewhat later led to the founding of the Royal Society.

It was Boyle, one of the original Fellows, whose work first showed the value, in the realm of chemical phenomena, of direct experimental evidence in contrast with so-called discoveries, made by reason or argument alone. As the author says: "Boyle dragged chemistry out of a welter of sophisms and charlatanry, endowed it with life and ideals and material, and set it forward upon the true path."

The predominance of the phlogistic hypothesis during the greater part of the eighteenth century was not so much an aberration from this true path, as a continuance of the ways of thought which Boyle and his school had striven to counteract. Professor Masson maintains that in his attitude towards chemical phenomena, although not in time, Lavoisier was the immediate successor of Boyle, whilst Stahl and his disciples were really the heirs of the old spagyrical mentality. "If Boyle's '*Sceptical Chymist*' is for chemistry the Book of Genesis, Lavoisier's '*Traité Elementaire*' is its Book of Exodus, for it shows how he led his people out of a captivity that has endured for nearly a century."

The slow progress made during the eighteenth century towards clarity on such fundamental matters as calcination and combustion is faithfully portrayed, and the contributions of the leading workers—Black, Cavendish, Priestley, Scheele, and Lavoisier—are set forth in detail. The significance of Lavoisier's appeal to the balance is emphasised, as is also the effect of his work in finally disposing of the old 'elements.' "The union [of fuels] with atmospheric air which had been discovered so long ago, and which phlogistians admitted to occur as a merely secondary event ensuing upon an efflux or transfer of phlogiston, was now proved to be the primary event: the union was further narrowed down to one widely distributed simple substance, oxygen, and the relic of the element of Fire was at last recognized as an illusion. With it had vanished the Elements of Water and Air and Earth, so that the ancient stronghold invested by Boyle was finally carried by assault by Lavoisier."

The period of 1800-1925 is handled by the author on quite different lines. No attempt is made to enter into detail and attention is concentrated on 'the search for the structure units' which has characterized so much of the chemists' work during the last century and a quarter. The physical molecule, the chemical molecule, the atom, and the ion are the topics round which the discussion centres and the gradual evolution of definite ideas in regard to these units, their assembly and interplay, is sketched in an extraordinarily able way. Professor Masson's historical studies convince him of the impossibility at the present time of separating the spheres of physics and chemistry: "there is now only one Physical Science, to which physicists and chemists variously contribute: and perhaps the outstanding intellectual achievement of our time is that which enables such a statement to be justified."

*J. C. Philip*

**Factory Practice in the Manufacture of Azo Dyes.** *By W. B. O'Brien. 23 × 16 cm; pp. viii+176. Easton: The Chemical Publishing Company, 1924. Price: $5.00.* "A factory process is merely a routine based upon theoretical and experimental considerations. The soundness of chemistry indispensable in theoretical and research work must be inherent in factory processes, but, apart from chemistry, economy in regard to labor and materials and conformation to the limitations of the short working day becomes of paramount importance. A lay belief somewhat generally accepted attributes an indefinable, mysterious elusiveness to the work of dyestuff production. Such belief, while serious enough in the stubbornness with which it persists, is in no way justified. Similarly to other large industries, success in

dyestuff manufacturing depends upon capital, organization and hard work. The advantage possessed, elsewhere than in America, due to earlier participation in the industry, has been largely compensated by economic and circumstantial factors affecting the industry here," p. 3.

"The time required for the completion of a coupling reaction in the factory depends much upon the efficiency of the contact obtained between the diazo and component. In case both are completely soluble, reaction may be completed immediately after mixing, or at the most within a few hours. In the cases of slightly soluble diazos and components, used in suspension, as much as forty-eight hours' agitation of their mixture may be necessary to completely utilize the one present in lesser amount. Efficient agitation and a fine state of division in the reacting materials promotes the contact and is necessary for completing the coupling reaction. The less soluble diazos are to be had in a finely divided condition as a result of the method of their preparation, but a process should include directions for producing this state for slightly soluble components used in suspension. The volume or concentration of the coupling mixture influences the progress of the reaction differently for individual cases. Some azo dyes on formation precipitate immediately in a thick slimy state of particles which hinder contact between unreacted portions of the diazo and component and completion of such coupling is favored by efficient agitation rather than by concentration, but in cases where the resulting dye is very soluble, or else precipitates in a crystalline form, concentration is advantageous," p. 4.

"In the manufacture of azo dyes the unit quantity of the production is the batch or charge. For practical work the batches prepared should be of a size sufficient to yield from 500 to 1,000 pounds of dye, selling strength, in a single charge. On such a scale the production can be of sufficient volume to carry the manufacturing expense, while the size of the batches is not too great for good control and completion within twenty-four hours," p. 14.

"The most of the azo dyes are marketed in a powder form, hence the wet product of the making building must be dried and pulverized. Drying of any batch of dye consumes more time than does the work of coupling and filtering; a charge may be completely coupled in twenty-four hours and filtered within another twenty-four hours for each set of tubs and filters, but drying for the same charge will require from four to eight days. Adequacy of facilities for drying permits of speed in production," p. 33.

"The general run of azo colors is not considered explosive, more dangerous members of the class having become less used, but some azo dyes are known to ignite and burn with a smoldering flame during drying or milling; the Alizarine Yellows, R and GG, are often mixed with three percent ammonium sulfate before entering into the ovens, to prevent possible ignition," p. 36.

"Common salt is mixed with direct dyes and dyes which are to be applied in a sulfuric acid bath, including the mordant dyes and acid dyes; also with basic azo dyes. Sodium sulfate is mixed with dyes which are to be applied in a bath acidified with acetic acid, such as the "sulfon" colors. A dyestuff may be marketed in several strengths, such as the "ordinary", and the "concentrated," with greater, or less, reduction in the milling. Certain of the "highly concentrated" wares consist of unreduced dye, the manufacture being directed with a view to obtaining as pure a product as possible, with less regard for yield and cost in the production. Reduction of dyes is not considered adulteration or falsification but is an operation necessary for obtaining a consistently standard product, due to the fact that no two batches run to similar strengths as first prepared. Discrepancy in the strengths of dyes marketed for the same brand by different manufacturers comes from a difference in standards adopted, but the products of one factory can be expected to be in accordance with the standards announced by that factory. There is nothing, however, to prevent a purchaser from remilling and further reducing the dye for resale; the appearance of dye does not indicate the general extent to which reduction has been made, and only a laboratory test of each package can show the actual strength of the dye," p. 37.

"In the manufacture of dyes and intermediates the number of professionally trained employees required to carry on the work forms a high percentage of the total help, as a result of the technical and varied character of the work. The circumstance has been dwelt

upon, in the educational advertising campaigns of dye manufacturers, that as a matter of experience rather than point of view a minimum ratio of one professionally trained chemist to ten operators is compatible with successful production. The chemistry of a factory process allows the possibility of varied results, similar to a laboratory experiment. While for the azo dyes the mechanical features of a process, such as the filtration, drying and milling, may be regulated and conducted in the factory by non-professional operators, the chemical nature of the "making" operation resists standardization to the extent that every factory charge is in degree an experiment whose course must be followed by a chemist as for a laboratory experiment," p. 166.

The chapters are entitled: introduction; buildings, major equipment, operation, materials; diazotization of aniline; dyes prepared from diazotized aniline; diazotization of the homologues of alcohol; diazotization of the nitro anilines; diazotization of the sulfonated anilines; diazotization of acetyl paraphenylene diamine and anthranilic acid; mono azo dyes from ortho amino phenol derivatives; mono azo dyes from alpha naphthylamine and naphthionic acid; mono azo dyes from amino naphthol sulfonic acids; tetrazotization of benzidine; relation of the chemist to the industry—experimental work and small scale production.

*Wilder D. Bancroft*

**Les Méthodes physiques appliquées à la Chimie.** *By P. Job. 22 × 14 cm; pp. viii+251. Paris: Gaston Doin et Cie, 1926. Price: 30 francs.* This is the fourth volume of a series of monographs on Physics and Chemistry published under the direction of Professors Langevin, Perrin, and Urbain.

It is a well written, clear and systematic exposé of the circumstances and the manner in which various physical measurements can afford assistance to the chemist. The nature of the chemical problem is first considered and then the physical methods applicable to the case. The general principles of each method are set forth very well with the help of numerous diagrams but without going into details. In practically all instances the methods are illustrated by actual cases culled from the literature and this is one of the best features of the book. With hardly any exceptions, all the physical methods which have been applied to chemical problems are dealt with as well as a few which seem as though they might be helpful although they have not actually been used as yet.

The book does not aim at supplying the minute details necessary for the successful application of the methods described, although a brief description of the methods of making the various measurements is given in an appendix. For fuller details the reader is referred to numerous text-books and to a wide and judicious selection of international literature.

The experienced reader will, perhaps, find little new in the book but, all the same, it is one that he might well read with pleasure and with profit. It would be a useful book for an English-speaking student to read who wished to improve his knowledge of French, and degree students might be encouraged to read it, especially as the price is low.

It is very free from misprints, only one of any consequence having been noticed—on page 197 where the first half of line eight from the bottom has been repeated in the second half of the line. There is a good index.

The general scheme of the book may be gathered from the following summary of the matters dealt with. It is divided into two parts, each of six chapters.

Part one is concerned with Pure Substances and successive chapters deal with: (1) Identification of pure substances and determination of their purity; (2) Qualitative and quantitative analysis; (3) Molecular weight of gases, dissolved substances, liquids, and solids: (4) Atomic weights; (5) Constitution of pure substances; (6) Allotropic forms.

Part two deals with mixtures, solutions, and heterogeneous systems; and the six chapters consider: (1) Determination of the individual substances present; (2) Constitution of solid mixtures; (3) Constitution of liquid mixtures which are in equilibrium; (4) Constitution of gaseous mixtures which are in equilibrium; (5) Reacting chemical systems; (6) Foretelling reactions. These twelve chapters account for 183 pages of the book and in addition there are a brief introduction and conclusion the Appendix of 50 pages, index and table of Contents.

*H. Bassett*

**Organische Chemie.** *By R. Pummerer. Second enlarged and improved edition. 22 × 15 cm; pp. x+210. Dresden and Leipzig: Theodor Steinkopff, 1923. Price: 90 cents.* The subdivisions are organic valence problems; coal and tar dyes; the study of natural products. The chapters are entitled: metallo-organic compounds; radicals; thermo-chemistry, spectro-chemistry, absorption spectra; colored, unsaturated compounds; oxonium salts and betains; readily reacting sulphur compounds; compounds with twin double bonds; keto-enol isomerism; ennobling coal; dyes and intermediates; methods of oxidation and hydrogenation; hydrogenated carbocyclic compounds; sugars; anthocyans; tanning materials; enzymes and hormones; alkaloids; blood pigments, chlorophyll, assimilation.

The possible catalytic action of glass is well illustrated, p. 61, by the fact that keto-acetyl-dibenzoylmethane can not be made to give a melting-point of 107° when tubes of Jena glass are used. The oxidation of ethylene to formaldehyde can only be carried out successfully when the ethylene is stabilized by dilution with fairly large amounts of nitrogen, p. 83. Connstein and Lüdecke have found, p. 132, that the yield of glycerol can be increased from three percent to 10-16% by alkaline fermentation of sugar. Addition of neutral sodium sulphite cuts out the danger of lactic acid fermentation and increases the yield of glycerol to 36% of the sugar taken. During the war the Germans made glycerol commercially by fermentation of a sugar-rich molasses. This process cannot compete at present prices with the usual one for obtaining glycerol from fats.

Pentagalloylglucose probably occurs in Turkish tannin which on hydrolysis yields five mols of gallic acid to one of glucose. The Chinese tannin contains approximately twice as much gallic acid (ten mols) to one of glucose as the Turkish tannin does, p. 157.

Leaves free from chlorophyll do not assimilate; but yellow-leaved varieties, poor in chlorophyll, show unexpectedly strong powers of assimilation and consequently there is no proportionality between the chlorophyll content and the power of assimilation, p. 191. Variations in light and heat affect the yellow leaves quite differently from the green leaves and consequently Willstätter and Stoll conclude that there is another substance besides chlorophyll which is of importance in producing assimilation.

While chlorophyll forms a true solution in alcohol, it goes into colloidal solution in water. From the absorption spectrum and from the reaction with carbon dioxide, it seems certain that the chlorophyll in the green leaf is in colloidal and not in true solution.

*Wilder D. Bancroft*

**Ueber Kolloidchemie.** *By R. Zsigmondy. Second edition. 20 × 13 cm; pp. 53. Leipzig: Johann A. Barth, 1925. Price: 3.60 marks.* This is a new edition of a lecture given in 1906 at Stuttgart with some additional foot-notes. It is really quite surprising how little change is necessary in order to make it a perfectly satisfactory lecture today. This does not mean that there has been no progress in nearly twenty years because that would be absurd. It merely means that a lecture dealing primarily with facts and not with theory does not necessarily ever go out of date. Except that we don't differentiate sharply any more between suspension colloids and emulsion colloids, the presidential address of A. A. Noyes before the American Chemical Society at Philadelphia would be just as interesting today as when it was given. It could be adapted to modern use with only minor changes in the presentation.

The references in the foot-notes giving the changes are chiefly to Zsigmondy's own book which is probably good advertizing.

*Wilder D. Bancroft*

# A RELATIONSHIP BETWEEN ATOMIC NUMBERS AND THE PROPERTIES OF IONS IN THE CRYSTAL LATTICE.

## II. The Characteristic Frequency and the Constraint*

BY ARTHUR F. SCOTT

In order to account for the properties of crystalline solids on the basis of the modern lattice theory it has been found necessary to postulate two distinct forces, one, an attractive force of an electrostatic nature, and the other, an opposing or repellent force that is not of a purely electrostatic nature. It should be mentioned in this connection that the pioneering speculations of Professor T. W. Richards in this field, embodied in his suggestive theory of the compressible atom, led directly to the same conclusion. Professor Richards distinguishes the attractive force as chemical affinity, "a force which binds atoms together", and the other force as "an inherent distending tendency." Further, both conceptions of the solid state agree in a very important particular in that they recognize the fact that these forces are characteristic of the atoms themselves. Or, to restate this idea in the language of the lattice theory, ions in a crystal lattice cannot be treated as point charges; in short, it must be recognized that ions have definite, characteristic structures which control the action of their external forces, attractive and repellent alike. Although it is known that the structures of atoms depend upon their atomic numbers and that therefore the forces under consideration must likewise be related to the atomic numbers, very little progress has been made toward solving the problem in terms of the ultimate factors. It is the object of this paper to present preliminary considerations which may afford some insight into this rather involved problem.

For this purpose we shall make use of the characteristic frequencies of solids; which term, as we shall use it, signifies the definite, upper limit of the infrared spectrum as defined by Debye[1]. Ordinarily this physical constant of solids must be determined directly from measurements of heat capacity, although in the case of salts, it can also be determined from measurements of residual rays. But because the experimental data, thermal and optical, which are essential for the evaluation of the characteristic frequency are so scant, recourse must be had to the various indirect methods that have been suggested. Inasmuch as we shall have to employ computed values of the characteristic frequency subsequently, it will be profitable to digress at this point in order to examine the source of our material.

Of the various indirect methods which have been suggested, the formula proposed by Lindemann[2] is generally considered to be the most satisfactory, especially in respect to the metallic elements, and is expressed by the equation:

$$\nu = 2.80 \times 10^{12}\sqrt{T/MV^{2/3}} \qquad (1)$$

* Contribution from the Department of Chemistry of Reed College.

[1] Debye: Ann. Physik, (4) 39, 789 (1912).

[2] Lindemann: Physik. Z., 11, 609 (1910).

where $\nu$ is the frequency; T is the melting-point temperature; M and V are the atomic weight and volume of the substance. This formula was originally deduced from the assumption that at the melting point the amplitude of vibration of the atoms about their position of equilibrium is equal to the distance between them. In spite of the improbability of the above mechanism, we may still accept the formula for our present purpose because the identical expression has been developed from dimensional considerations[1].

From the viewpoint of our present knowledge concerning the structure of crystalline solids, there is, however, a rather obvious alteration to be made in the statement of the above formula. It is no longer necessary to employ the $V^{1/3}$ term as a measure of the distance between ions in a solid; rather it would seem advisable and more accurate to make use of the "nearest approach" of ions in a crystal lattice as determined by crystal structure analysis. With this change equation (1) assumes the form:

$$\nu = \text{const.}/d_o\sqrt{T/M} \qquad (2)$$

where $d_o$ is the "nearest approach" and the constant is chosen arbitrarily. In this paper the constant will always be taken as equal to $3.83 \times 10^4$.

Table I is presented to show the effect of such an alteration. Column (1) contains the values for the frequency calculated according to equation (2) for which the essential data are given in Table II. The values obtained from equation (1) are given in column (2) and are taken from Mellor[2]. In column (3) we have the experimental values as determined from thermal data. These values are taken from a compilation by Eucken[3]. The figures for zinc, sulfur, and iodine are taken from a table of Nernst and Lindemann[4] and are the frequencies used in their formula. Although not exactly comparable to the other values, they are approximate enough to give some idea of the magnitude of $\nu$. Furthermore, as Debye has shown, the characteristic temperature of solids may be determined from the elastic constants of the substance. Making use of these values of the characteristic temperature, Allen[5] has calculated $\nu$ for the elements given in column (4).

A scrutiny of the contents of Table I shows that the results of equation (2) are notably in better accord with the experimental values than those obtained by equation (1). This statement is particularly true for those elements possessing a structural arrangement other than a "face" or "body-centered" cubic lattice, for example, the diamond. When one takes into account the arbitrary temperature at which $d_o$ is measured and the fact that the melting point temperature employed does not always correspond to the melting point of the modification existing at ordinary temperature, it is somewhat surprising that

[1] Einstein: Ann. Physik, (4), 35, 689 (1911); Grüneisen: (4) 39, 257 (1912); Verh. deutch. Ges., 13, 836 (1911).

[2] Mellor: "Treatise on Inorganic and Theoretical Chemistry", 1, 829.

[3] Eucken: "Gründriss physik. Chemie", 83, 102.

[4] Nernst and Lindemann: Z. Electrochem., 17, 822 (1911).

[5] Allen: Proc. Roy. Soc., 94A, 100 (1917).

TABLE I

A Comparison of the Characteristic Frequencies obtained from Various Sources

| Element | 1 Calc. Eq. 2. | 2 Calc. Eq. 1. | 3 Thermal Debye | 4 Elastic Consts. |
|---|---|---|---|---|
| Diamond | $43.1 \times 10^{12}$ | $31.7 \times 10^{12}$ | $39.00 \times 10^{12}$ | |
| Aluminium | 7.85 | 7.70 | 8.30 | $8.26 \times 10^{12}$ |
| Phosphorus | 9.71 | 6.12 | | |
| Sulfur | 6.47 | 3.92 | 7.3 | |
| Argon | 1.49 | | 1.74 | |
| Iron | 8.81 | 8.30 | 9.45 | 9.67 |
| Nickel | 8.39 | 8.07 | | 9.01 |
| Copper | 6.74 | 5.88 | 6.60 | 6.81 |
| Zinc | 4.67 | 4.35 | 4.8 | |
| Silver | 4.49 | 4.36 | 4.50 | 4.39 |
| Cadmium | 2.98 | 2.74 | 3.50 | 3.48 |
| Iodine | 2.38 | 1.66 | 2.0 | |
| Platinum | 4.68 | 4.36 | | 4.68 |
| Gold | 3.47 | 3.36 | | 3.44 |
| Lead | 1.88 | 1.66 | 1.83 | 1.49 |
| Bismuth | 1.99 | 1.64 | | 2.30 |

the agreement is so close. Because of its greater accuracy as well as its dimensional correctness, equation (2) will be used hereafter in preference to equation (1).

In anticipation of the needs of the subsequent discussion, $\nu$ has been calculated for all the elements for which relaible data are available; and the results are given in Table II. In order to condense the tabulation as much as possible, the values for the atomic weights are not included but these constants are the accepted ones, having been taken from the recent report of the Atomic Weight Committee[1]. Also no definite references are given for the melting point temperatures selected, but in practically every case they have been taken from Landolt-Börnstein's Tabellen. A review of the literature has prompted a few deviations from the figures given in the Tabellen. A further word in explanation of the data seems desirable. In order to supplement the meagre data from X-ray analysis a number of values for $d_o$ were computed in the usual manner from the atomic volumes of the elements. In all of these cases the value for the density employed in the calculation is taken from Landolt-Börnstein's Tabellen; and the type of lattice assumed was in each particular instance determined by the types of lattices known for the neighboring elements in the periodic table. The figure for vanadium was also computed in this manner because the X-ray data could not be considered reliable enough. The data attributed to Bragg come from his computation of the radii of combination and have been used when all other sources failed. The basic assumption is of

[1] J. Am. Chem. Soc., 47, 597 (1925).

## TABLE II

### The Characteristic Frequencies of Elements

e = maximum number of valence electrons.
Z = atomic number.
M.P. = melting point in degrees absolute.
$d_o$ = "nearest approach" of atoms in crystal lattice, in Angstroms.
$\nu$ = characteristic frequency $\times 10^{-12}$.
m = atomic weight.
k = constraint.

| Element | e | ln(Z+e) | M.P. | $d_o$ | Type of Lattice Known or Assumed. | $\nu$ | $k\nu \simeq m\nu$. |
|---|---|---|---|---|---|---|---|
| H | 1 | 0.693 | 15 | | dens. = 0.0763 | 4.51 | 4.51 |
| He | 2 | 1.386 | Ca. 2 | 2.93 | F.C.C.[1] | 2.94 | 5.88 |
| Li | 1 | 1.386 | 167.85 | 3.03 | B.C.C.[2] | 10.28 | 27.1 |
| Be | 2 | 1.792 | 1551 | 2.28 | Hexagonal[3] | 21.83 | 65.6 |
| B | 3 | 2.079 | 2800 | 1.86 | Hypothetical[4] | 33.13 | 109.0 |
| C | 4 | 2.303 | Ca.3600 | 1.54 | Hexagonal[5] | 43.1 | 149.0 |
| F | 7 | 2.773 | 50 | 1.35 | Hypothetical[6] | 4.60 | 20.1 |
| Ne | 8 | 2.890 | | | | (2.0)[7] | 8.9 |
| Na | 1 | 2.485 | 370.9 | 4.00 | B.C.C.[3] | 3.845 | 18.4 |
| Mg | 2 | 2.639 | 923 | 3.22 | Hexagonal[2] | 7.33 | 36.1 |
| Al | 3 | 2.773 | 931.7 | 2.860 | F.C.C.[8] | 7.85 | 40.8 |
| Si | 4 | 2.890 | 1686 | 2.35 | Tetrahedral cubic[2] | 12.63 | 66.9 |
| P | 5 | 2.996 | 863 | 2.08 | Hypothetical[6] | 9.71 | 54.1 |
| S | 6 | 3.091 | 384 | 2.05 | Hypothetical[6] | 6.47 | 36.6 |
| Cl | 7 | 3.178 | 172.1 | 2.10 | Hypothetical[6] | 4.02 | 23.9 |
| A | 8 | 3.258 | 84 | 3.73 | F.C.C.[1] | 1.49 | 9.4 |
| K | 1 | 2.996 | 336.5 | 4.48 | B.C.C.[3] | 2.51 | 15.7 |
| Ca | 2 | 3.091 | 1082 | 3.93 | F.C.C.[9] | 5.05 | 32.0 |
| Sc | 3 | 3.178 | | | | (7.0)[7] | 46.6 |
| Ti | 4 | 3.258 | 2061 | 2.90 | Hexagonal[10] | 8.65 | 60.0 |
| V | 5 | 3.332 | 1983 | 2.89 | B.C.C.[11] | 8.26 | 59.0 |
| Cr | 6 | 3.401 | 1793 | 2.508 | B.C.C.[12] | 8.97 | 64.7 |
| Mn | 7 | 3.466 | 1533 | 2.55 | B.C.C.[1] | 7.93 | 58.7 |
| Fe | 8 | 3.526 | 1806 | 2.472 | B.C.C.[8] | 8.81 | 65.8 |
| Co | 8 | 3.555 | 1751 | 2.514 | F.C.C.[12] | 8.30 | 63.7 |
| Ni | 8 | 3.584 | 1725 | 2.474 | F.C.C.[8] | 8.39 | 64.3 |
| Cu | 1 | 3.401 | 1355.8 | 2.543 | F.C.C.[8] | 6.74 | 53.8 |
| Zn | 2 | 3.466 | 692.3 | 2.670 | H.C.P.[12] | 4.67 | 37.7 |
| Ga | 3 | 3.526 | 302.8 | 3.03 | F.C.C.[1] | 2.63 | 22.0 |
| Ge | 4 | 3.584 | 1231 | 2.43 | Tetrahedral cubic[13] | 6.49 | 55.3 |
| Se | 6 | 3.689 | 473.2 | | dens. = 4.82 | 3.39 | 30.2 |
| Kr | 8 | 3.784 | 104 | 3.97 | F.C.C.[1] | 1.08 | 9.6 |
| Rb | 1 | 3.638 | 312 | 4.93 | B.C.C.[1] | 1.49 | 13.7 |
| Sr | 2 | 3.689 | 1102 | 4.33 | F.C.C.[1] | 3.14 | 29.4 |
| Y | 3 | 3.738 | 1523 | 3.80 | B.C.C.[1] | 4.17 | 39.3 |
| Zr | 4 | 3.784 | 1803 | 3.18 | Hexagonal[10] | 5.36 | 51.1 |

TABLE II (continued)

| Element | e | ln(Z+e) | M.P. | $d_o$ | Type of Lattice Known or Assumed. | $\nu$ | $kt \simeq m\nu$. |
|---|---|---|---|---|---|---|---|
| Cb | 5 | 3.829 | 2223 | 2.95 | B.C.C.[1] | 6.35 | 61.3 |
| Mo | 6 | 3.871 | 2840 | 2.720 | B.C.C.[8] | 7.66 | 75.0 |
| Ru | 8 | 3.932 | 2223 | 2.640 | Hexagonal[12] | 6.78 | 68.4 |
| Rh | 8 | 3.970 | 2243 | 2.700 | F.C.C.[12] | 6.62 | 67.2 |
| Pd | 8 | 3.989 | 1822.2 | 2.729 | F.C.C.[8] | 5.80 | 59.9 |
| Ag | 1 | 3.871 | 1233.5 | 2.884 | F.C.C.[8] | 4.49 | 41.6 |
| Cd | 2 | 3.912 | 593.9 | 2.96 | H.C.P.[12] | 2.98 | 31.5 |
| In | 3 | 3.951 | 427 | 3.24 | Tetragonal F.C.[12] | 2.28 | 24.4 |
| Sb | 5 | 4.025 | 903 | 2.87 | Rhombohedral[14] | 2.89 | 31.9 |
| Te | 6 | 4.060 | 725.5 | | dens. = 6.25 | 2.45 | 27.6 |
| I | 7 | 4.094 | 386.5 | | dens. = 4.933 | 1.66 | 18.7 |
| Xe | 8 | 4.127 | 133 | 4.14 | F.C.C.[1] | 0.94 | 7.6 |
| Cs | 1 | 4.025 | 301.45 | 5.34 | B.C.C.[1] | 1.01 | 11.6 |
| Ba | 2 | 4.060 | 1123 | 4.52 | F.C.C.[1] | 2.42 | 28.4 |
| La | 3 | 4.094 | 1083 | 3.75 | F.C.C.[1] | 2.85 | 33.6 |
| Ce | 3 | 4.111 | 908 | 3.64 | F.C.C.[10] | 2.68 | 31.7 |
| Pr | 3 | 4.127 | 1213 | 3.71 | F.C.C.[1] | 3.02 | 35.9 |
| Nd | 3 | 4.143 | 1113 | 3.65 | F.C.C.[1] | 2.92 | 35.0 |
| Ta | 5 | 4.357 | 3071 | 2.833 | B.C.C.[12] | 5.56 | 74.9 |
| W | 6 | 4.382 | 3660 | 2.732 | B.C.C.[8] | 6.25 | 84.8 |
| Os | 8 | 4.431 | 2773 | 2.66 | Hexagonal[10] | 5.49 | 75.8 |
| Ir | 8 | 4.443 | 2628 | 2.690 | F.C.C.[12] | 5.25 | 73.0 |
| Pt | 8 | 4.454 | 2037 | 2.766 | F.C.C.[8] | 4.68 | 62.5 |
| Au | 1 | 4.382 | 1336 | 2.874 | F.C.C.[8] | 3.47 | 48.7 |
| Hg | 2 | 4.407 | 234 | | dens. = 14.383 | 1.26 | 19.2 |
| Tl | 3 | 4.431 | 576 | 3.38 | F.C.C.[15] | 1.90 | 27.2 |
| Pb | 4 | 4.454 | 600.4 | 3.479 | F.C.C.[8] | 1.88 | 27.0 |
| Bi | 5 | 4.477 | 544 | 3.11 | Rhombohedral[14] | 1.99 | 28.8 |
| Rn | 8 | 4.543 | 202 | 4.01 | F.C.C.[1] | 0.91 | 13.6 |
| Th | 4 | 4.543 | 1973 | 3.54 | F.C.C.[10] | 3.15 | 48.1 |
| U | 6 | 4.585 | 1623 | 2.99 | B.C.C.[1] | 3.40 | 52.4 |

The types of arrangements have been abbreviated as follows: face-centered cubic (F.C.C.), body-centered cubic (B.C.C.), hexagonal close-packed (H.C.P.).

[1] Calculated.
[2] Hull: Phys. Rev., **10**, 661 (1917).
[3] McKeehan: Proc. Nat. Acad. Sci., **8**, 270 (1922).
[4] From graph by author: J. Phys. Chem., **29**, 304 (1925).
[5] Debye: Physik. Z., **18**, 291 (1917).
[6] Bragg: Phil. Mag., (6) **40**, 169 (1920).
[7] From Figure 1.
[8] Davey: Phys. Rev., **25**, 753 (1925).
[9] Hull: Phys. Rev., **17**, 12 (1921).
[10] Hull: Phys. Rev., **18**, 88 (1921).
[11] Hull: J. Franklin Inst., **193**, 189 (1922).
[12] Hull: Phys. Rev., **17**, 571 (1921).
[13] Kolkmeyer: Proc. Roy. Acad. Sci., Amsterdam, **21**, 405 (1919).
[14] Ogg: Phil. Mag., **42**, 163 (1921).
[15] Becker and Ebert: Z. Physik, **16**, 165 (1923).

course that in the pure element two ions can never come closer together than twice the radius of combination. That the points fit so well on the following graph indicates the approximate correctness of Bragg's premises. To obtain the atomic volumes of the inert gases, the densities employed were those calculated by Herz[1] according to the method of Lorentz[2] and are the hypothetical values at absolute zero. According to Simon and von Simson[3], solidified argon forms face-centered cubic crystals; consequently the values for $d_o$ for all of the inert gases have been calculated from the atomic volumes at absolute zero, assuming that this structure is correct. Finally the values of $\nu$ for a few elements have been computed by equation (1) because this seemed to be the only way available. These data are also included in Table II.

In addition to the characteristic frequencies of the elements, we shall subsequently have need also of the same constants for a group of comparable salts. The simplicity of structure and especially the completeness of the requisite data of the alkali halides make these salts singularly suitable for our purpose. However, when it comes to the question of selecting some indirect method by means of which we can calculate the frequency, the obvious intrinsic differences in the nature of salts and metals offers adequate warning that we cannot hope for the same formula to apply with equal validity to the two types of substances. That there is a substantial basis for this statement will, it is hoped, be implicitly demonstrated in the course of this paper. As a matter of fact, Lindemann's formula, equation (1), although it does give results of the proper magnitude, is by no means as accurate as the dimensional formula proposed by Madelung and Einstein[4]. The latter may be written:

$$\lambda = C\chi^{\frac{1}{2}}M^{\frac{1}{2}}\rho \qquad (3)$$

Here $\lambda$ is the wave-length; $\chi$, the compressibility; and $\rho$, the density. C is a constant which, when calculated from the residual-ray wave-length of sodium chloride, has the value, $1.162 \times 10^5$ sec.$^{-1}$; and M is computed from the atomic weights, $M_1$ and $M_2$, of the two ions according to the formula:

$$M = \frac{(M_1M_2)}{(M_1 + M_2)} \qquad (3a)$$

The frequency is obtained, of course, by dividing the velocity of light by the wave-length. The following Table III will serve to illustrate the relative validity of the two formulae.

---

[1] Herz: Z. anorg. Chem., 105, 171 (1919).

[2] Lorentz: Z. anorg. Chem., 94, 240 (1916).

[3] Simon and von Simson: Naturwissenschaften, 11, 1015 (1923).

[4] Madelung: Physik. Z., 11, 898 (1910); Einstein: Ann. Physik, 34, 170, 590 (1911); 35, 679 (1911).

## TABLE III

### A Comparison of the Characteristic Frequencies obtained from Various Sources.

| Salt | 1 Residual-Ray. | 2 Thermal. | 3 Calc. Eq. 1. | 4 Calc. Eq. 3. |
|---|---|---|---|---|
| NaCl | $5.77 \times 10^{12}$ | $5.87 \times 10^{12}$ | $6.37 \times 10^{12}$ | $(5.77) \times 10^{12}$ |
| KCl | 4.73 | 4.80 | 5.10 | 4.80 |
| KBr | 3.63 | | 3.76 | 3.73 |
| KI | 3.19 | | 2.93 | 3.08 |

Column (1) contains the results of Rubens[1] and his students from optical measurements. The values for the frequency obtained from thermal data are given in column (2) and are taken from the compilation by Eucken which was already been mentioned. In column (3) we have the recent calculations of Herz[2] made by means of equation (1); it should be noted, however, that for these calculations he employed the density of the salts at the melting point temperature on the assumption that in the Lindemann equation $\nu$ is a function of the melting point. Even though this device improves the results considerably, for example, giving the value of $\nu$ for sodium chloride, $6.37 \times 10^{12}$, instead of the previous value, $7.2 \times 10^{12}$, it can be seen at once that the results do not agree so well as in the case of the elements. The results from the Madelung-Einstein formula as calculated by the author are presented in column (4) and are taken from Table IV. A comparison of the figures in the above Table shows, as Born[3] has pointed out, that equation (3) is doubtless the correct dimensional formula for salts.

Hence, the frequency, $\nu$, has been calculated for the alkali halides which have the same structure as rock-salt. The essential data and results are given in Table IV.

The data given in Table IV are taken from various sources. The density values of the chlorides, bromides, and iodides of sodium, potassium, and rubidium for 0°C. are taken from a paper by Baxter and Wallace[4]. The same constants for the corresponding lithium salts at 25°C. are from measurements by Baxter[5]. Spangenberg[6] has published the values for the fluorides with the exception of rubidium fluoride. This last figure, as well as the compressibility data for sodium, potassium, and rubidium fluorides has been taken from a computation made by the aurthor[7] according to the method proposed by Fajans and Grimm[8]. The compressibility figures for lithium and potassium

[1] Rubens: Sitzungsber. königl. preuss. Akad., 1917, 47.
[2] Herz: Z. anorg. Chem., 128, 135 (1924).
[3] Born: "Atomtheorie des festen Zustandes", 625.
[4] Baxter and Wallace: J. Am. Chem. Soc., 38, 259 (1916).
[5] Baxter: J. Am. Chem. Soc., 31, 558 (1904).
[6] Spangenberg: Z. Kryst., 57, 494 (1923).
[7] Scott: J. Phys. Chem., 29, 304 (1925).
[8] Fajans and Grimm: Z. Physik, 2, 299 (1920).

TABLE IV

The Characteristic Frequencies of the Alkali Halides

$(Z_c - Z_a)$ = the absolute value of the difference of the atomic numbers of the cation and anion.

$\chi$ = the compressibility in bars $\times 10^{12}$

$\rho$ = the density at 0°C.

k = constraint.

$$m = \frac{4\, m_1 m_2}{m_1 + m_2}$$

$\nu$ = characteristic frequency $\times 10^{12}$.

| Salt | $\ln(Z_c - Z_a)$ | $\rho$ | $\chi$ | $\nu$ | $k\nu \simeq m\nu$ |
|---|---|---|---|---|---|
| LiF | 1.792 | 2.640 | 1.53 | 13.7 | 61.8 |
| LiCl | 2.639 | 2.068 | 3.7 | 9.21 | 44.4 |
| LiBr | 3.446 | 3.464 | 5.0 | 7.81 | 39.5 |
| LiI | 3.912 | 4.061 | 7.2 | 6.71 | 34.4 |
| NaF | 0.693 | 2.808 | 2.6 | 7.88 | 50.8 |
| NaCl | 1.792 | 2.168 | 4.3 | (5.77) | 43.1 |
| NaBr | 3.178 | 3.213 | 5.3 | 4.73 | 41.7 |
| NaI | 3.738 | 3.677 | 7.1 | 4.07 | 38.0 |
| KF | 2.303 | 2.491 | 3.31 | 5.33 | 38.1 |
| KCl | 0.693 | 1.992 | 5.2 | 4.80 | 40.8 |
| KBr | 2.773 | 2.756 | 6.4 | 3.73 | 36.9 |
| KI | 3.527 | 3.133 | 8.8 | 3.08 | 34.9 |
| RbF | 3.332 | 3.722 | 6.1 | 4.62 | 36.3 |
| RbCl | 2.996 | 2.806 | 7.3 | 3.57 | 35.7 |
| RbBr | 0.693 | 3.358 | 8.2 | 2.69 | 34.6 |
| RbI | 2.773 | 3.560 | 9.3 | 2.34 | 32.7 |

fluoride are taken from determinations by Slater[1]. The remaining compressibility data are those recently published by Richards and Saerens[2]. Obviously, as the foregoing description of the data indicates, too much confidence should not be placed in the computed values of the characteristic frequency.

Returning to our main thesis we find that, apart from its application to the phenomenon of specific heat, the characteristic frequency has received but little consideration, notwithstanding the fact that there are several reasons for believing it to be closely related to the non-mechanical properties of the elements. For instance, we have Haber's "square-root" rule[3] which, although based upon a too great simplification of the probable conditions, is exceedingly exact; and it can be interpreted only on the assumption that the forces which

[1] Slater: Phys. Rev., (2) 23, 488 (1924).
[2] Richards and Saerens: J. Am. Chem. Soc., 46, 934 (1924).
[3] Haber: Verh. deutsch. physik. Gesell., 13, 1117 (1911).

hold the ions together in a lattice are identical with the forces which control the peripheral, or valence, electrons. Moreover, that the characteristic frequency, like most of the other physical properties of the elements, is intimately related to the atomic number is demonstrated by the Lothar Meyer type curve obtained by Biltz[1] and the interesting, although unexplained relationship of Allen[2]. The relationship to the atomic numbers is not so surprising when one takes into consideration the fact that the melting point temperatures and atomic volumes, of which according to equation (1) the frequency is a function, are properties exhibiting a periodic variation with the atomic number. At this point, in order to avoid any subsequent misunderstanding, it should perhaps be pointed out that the above periodicity is clearly associated with the valences of the elements. Consequently we may expect that, along with the atomic numbers, the valence electrons are also responsible for the nature of atomic properties. All of this suggestive evidence, moreover, may be taken as sufficient grounds for believing that a definite connection exists between the characteristic frequency and the other properties of the elements, particularly those forces to which we ordinarily attribute chemical behavior. If this is true of the elements, it may likewise be true of salts, even though we have no direct evidence on the subject.

The first requirement towards an understanding of these facts would necessarily be the restatement of the above qualitative relationship in a quantitative form. At the outset our inquiry is met with the difficulty that there is no information available on this point. Indirect evidence, however, concerning the relationship between the characteristic frequency and the atomic numbers may be adduced in the following fashion. Imagine a case where the frequencies of the inert gases (as solids of course) are expressed by some function of Z (atomic number) and e (valence electron), which we will write as usual,

$$\nu = f\,(Z,e) \qquad (4)$$

Passing to the adjacent group of elements in the periodic table, the alkali metals, we may picture their crystal lattices as consisting of positive ions, without attempting to place the valence electron in any definite position. If these positive ions have electronic structures identical to those of the corresponding inert gases, then the sole noteworthy difference between the members of these two groups lies in the fact that Z for each alkali metal is greater by one than each of the corresponding inert gases. In order to discover the effect of this uniform increase in the atomic number on the obscurely related frequency, let us next imagine the simplest possible condition, namely, that this increase in the atomic number affects the indefinite function (4) as a whole. If this is so, we may express this uniform variation of the function by a constant factor or parameter, $\alpha$, as follows:

$$\nu = \alpha\, f(Z,e) \qquad (4a)$$

---

[1] Biltz: Z. Elektrochem., 17, 676 (1911).
[2] Allen: Proc. Roy. Soc., 94A, 100 (1917).

The ions of the elements of the second, third, and possibly fourth group are likewise assumed to have an electronic structure similar to the corresponding inert gases. Hence, by the same reasoning, we can conceive of other factors, $\beta$, $\gamma$, and $\delta$ in place of $\alpha$, expressing the effect of an increase of two, three, or four in the atomic numbers corresponding respectively to the second, third, and fourth groups of elements in the periodic table. Without attempting to define more precisely the form of our function, we can nevertheless readily test our assumption, for it is easy to see that the frequencies of the alkali metals should be expressible as a linear function of the frequencies of the inert gases, where the slope of the line is equal to $\alpha$. The lines of the other three groups plotted in a similar manner should likewise be linear functions with their respective parameters as tangents.

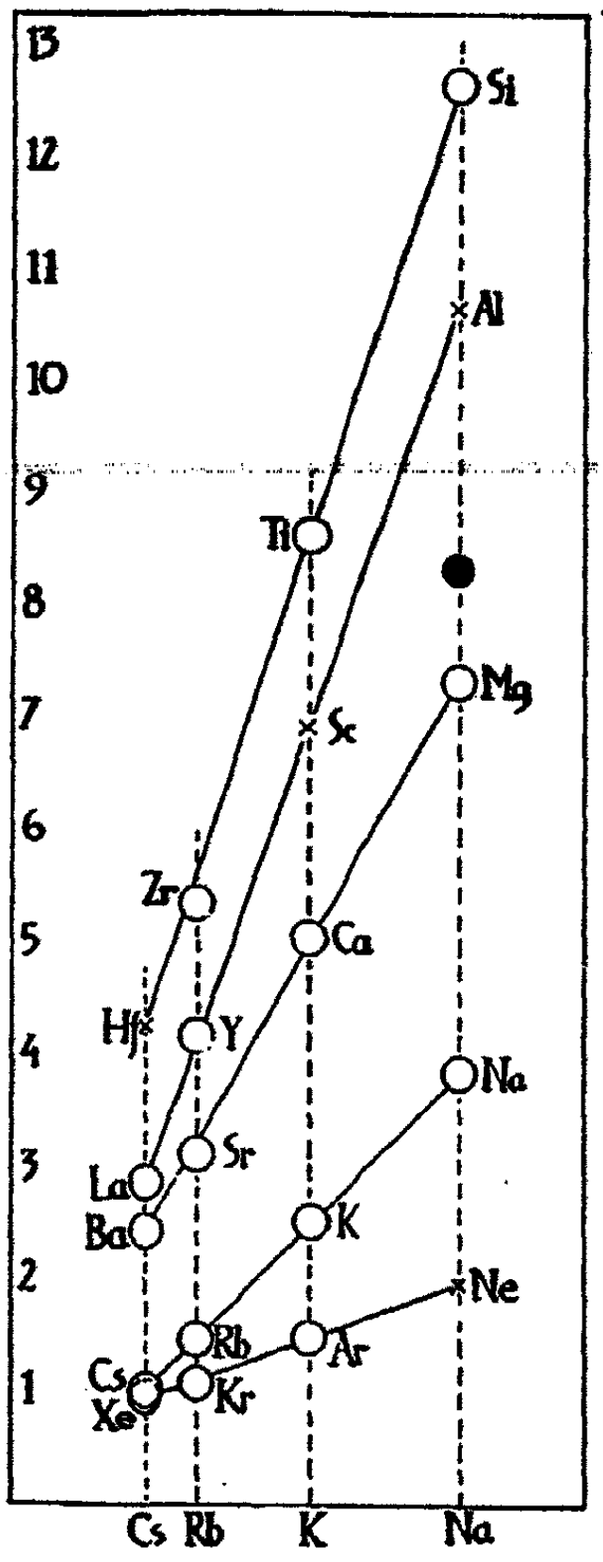



FIG. 1

Frequencies of Elements plotted against Frequencies of Alkali Metals.

That such a condition is realizable can be seen from Fig. 1 where this device has been employed. In this particular example, however, it was considered expedient to take the frequencies of the alkali metals as determinant points on the abscissa, but this fact obviously has no effect on the interpretation of the diagram. The data for this graph can be found in Table II. With the exception of the point for aluminium, the thermal value of which is indicated by a black dot, this mode of portrayal is accurate well within the limits of experimental error. Concerning the gross discrepancy of the aluminium value, it can only be remarked that the same discrepancy recurs in all subsequent considerations; and the hypothetical value, 10.66, (indicated by a cross), appears always to be satisfactory as the normal one.

In order to furnish an indication of the accuracy of the above mode of representation, it was found necessary to draw Fig. 1 on such a large scale that the points for the elements of the first period could not be included. Consequently the points for these elements have been calculated and the values are subjoined. For the sake of comparison the "observed" values of Table I are also given.

| | Li | Be | B | C |
|---|---|---|---|---|
| calculated. | (10.28) | 18.32 | 28.39 | 30.64 |
| observed. | 10.28 | 21.83 | 33.13 | 43.1 |

The agreement is not very close. If the basic premise is accepted, there are two explanations which may be offered as to the cause of this disagreement. Either the above considerations do not extend to ions with the electronic struc-

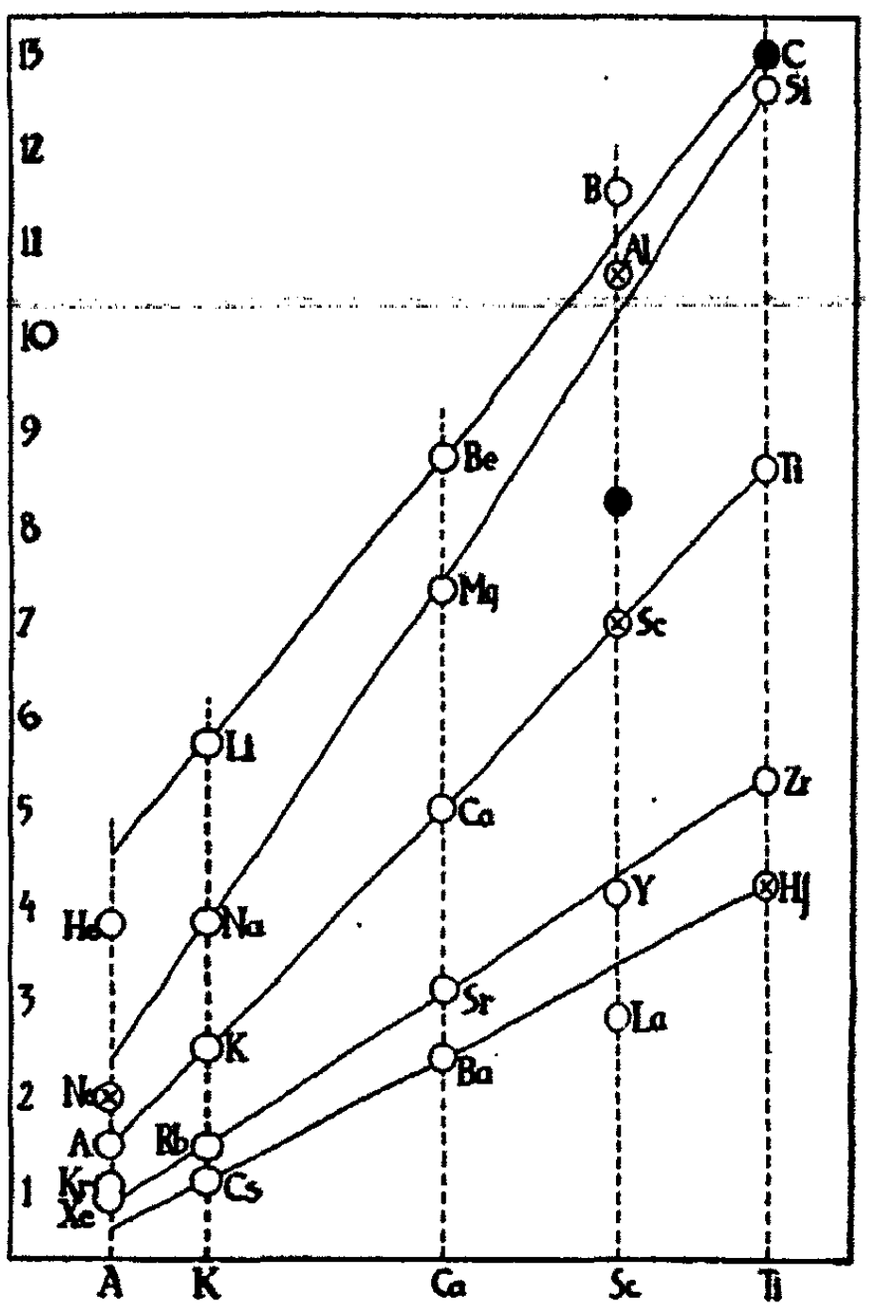



FIG. 2

Frequencies of Elements plotted against Frequencies of Elements of the Third Period.

ture of helium, or else the determinant point for lithium is at fault. An examination of the latter possibility shows clearly that it has no foundation.

But before coming to any definite conclusion regarding the behavior of the elements with an ionic structure similar to that of helium, it will be instructive at least to reverse the above procedure as has been done in Fig. 2. Here it has been found convenient to use the values of the frequencies for the elements of the third period as the determinant points for the abscissa. The value used for scandium is the hypothetical one determined from Fig. 1. In order to ac-

commodate the elements of the first period to the graph, their frequency values have been divided by four and then increased by approximately three.

Before analyzing the information afforded by this diagram, the irregular behavior of the elements of the third group should be accounted for. The difficulty hinges on the value of scandium used as the determinant point. If a value slightly greater than the hypothetical one should be used, the points for boron, aluminium, and scandium would all fall on one line; if, on the other hand, a slightly smaller value should be used, the heavier elements and scandium would be on a straight line. The fact that the scandium point should be so irregular is not particularly disturbing because it is more or less expected on the basis of the Bohr theory. Since this matter will be treated more in detail later, the discussion of its application may be postponed for the present. With this situation understood, we may summarize the information offered by the two diagrams as follows: The characteristic frequency of the elements is a function of the atomic number and of the number of valence electrons, which last factor distinguishes different groups. This function varies with each group and period by some characteristic, constant parameter. This statement is possibly subject to three limitations: first, the elements of the first period deviate from this rule in their relation to the elements of the same group; second, the inert gases in their relation to the adjacent metallic elements are doubtless also exceptions; and third, in the case of the third group elements a marked discontinuity makes its appearance with scandium.

When the elements with an ionic structure other than that of an inert gas are treated in the same manner as those already discussed, we obtain unambiguous idication of regularities identical with those shown in the first two figures. But no similar representation is offered for these elements because their data are less certain and also less suited to the purpose of a graph.

If our guiding idea is correct, that the characteristic frequencies of solids are determined by the so-called chemical forces, it is only natural to expect the other class of polar compounds, the salts, to follow a somewhat similar rule. For there is essentially no great difference in the structures of these two classes of substances. We may, for instance, believe that potassium chloride is similar to metallic potassium with the chlorine ion substituted for the valence electron. Under these conditions the results should be the same if one compares a series of alkali chlorides with the other corresponding series of alkali halides because then we should be comparing the influence of the different anions. And the influence of a specific anion should be the same in every case and should depend on the atomic numbers of the constituent ions. In short, a series of salts such as the alkali halides should be capable of the same sort of treatment as the elements in Figs. 1 and 2. To test this conclusion we may make use of the data for the alkali halides, which are presented in Table IV. In Fig. 3 we have such a graph, where the values for the chlorides of the alkali metals have been used as the determinant points for the abscissa. The agreement, as can be seen, is all that the experimental data warrants. We may therefore assume that the same rule which was shown to hold for the metals is

likewise valid for salts. It should be mentioned, however, in passing, that the above relationship is analogous to one for the molecular volumes which was first pointed out by Fajans and Grimm[1]. Moreover, these are not isolated cases, for the author[2] has already listed eight separate properties of the alkali halide salts which all exhibit the same regularity. No doubt the elucidation of one of these relationships will help in the understanding of the others.

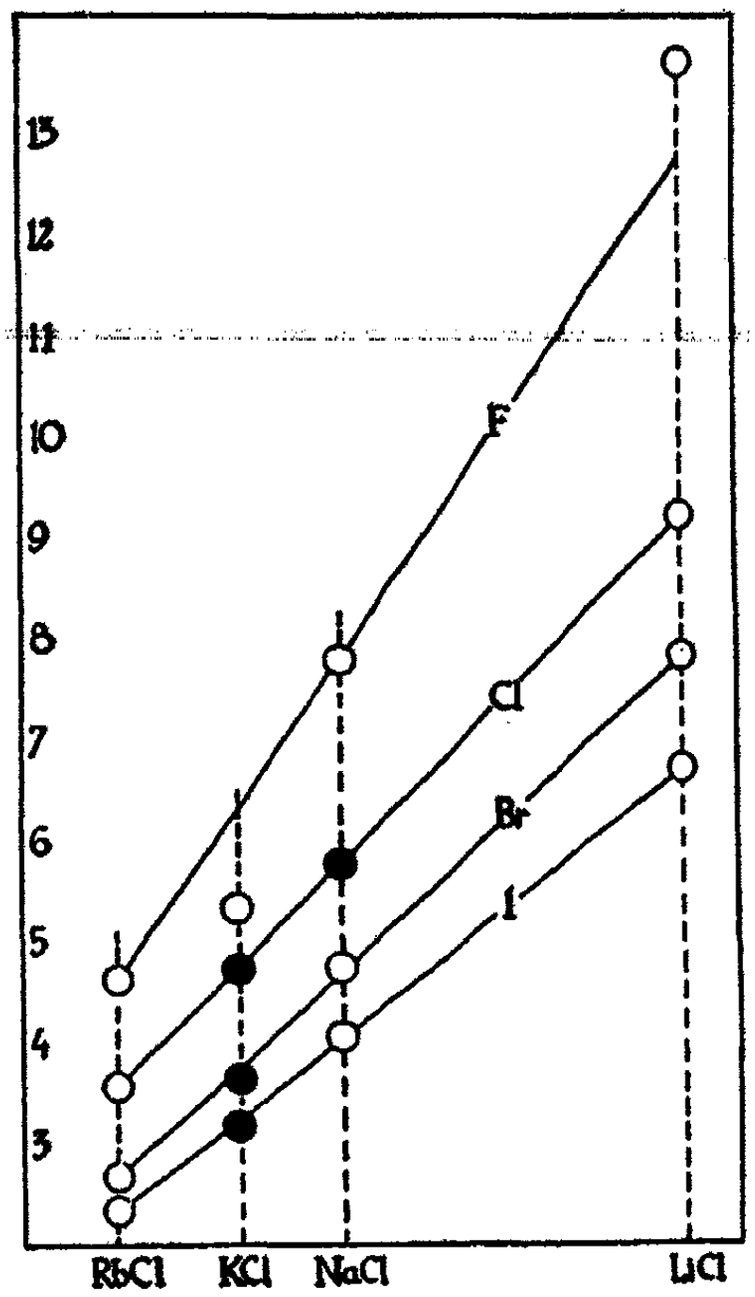



FIG. 3

Frequencies of the Alkali Halides plotted against Frequencies of the Alkali Chlorides.

We may now proceed a step further in our inquiry concerning the nature of the forces which control the behavior of ions in the crystal lattice. We have the expression

$$\nu = 1/2\pi\sqrt{k/m} \qquad (5)$$

where $k$ is the constraint on the ion and $m$ its mass. It is the constraint factor that is of chief importance to this discussion. By definition the constraint is a restoring force per unit displacement and thus provides a measure of the re-

[1] Fajans and Grimm: Z. Physik., 2, 299 (1920).
[2] Scott: J. Phys. Chem., 29, 304 (1925).

sistance to the displacement of an ion. Obviously it is characteristic of a solid and we may postulate at the outset that the constraint is the resultant of two forces, the attractive and the repellent. Let us analyze this term qualitatively from the standpoint of modern atomic theory. We find that it is one of the canons of this theory that the internal structure of atoms up to the periphery is regulated exclusively by the positive nuclear charge, the atomic number. Positive ions, therefore, formed by the loss of peripheral electrons, may be considered to have dimensions dependent on the atomic number. It is not meant that ions have a definite volume; rather, this term is intended to suggest a limit to the domain of the ion. In a word, it is the realm where the repellent forces, the non-electrostatic forces, come into play; and therefore this repellent force may be considered to be related to the atomic number. On the same grounds we may believe the residual or external field, that is, the attractive force of ions, to be similarly related to the atomic number. But with an ion, the external action is also dependent on the number of electrons lost by the original, neutral atom; and consequently, since periodicity is a function of the number of electrons in the outer shell, we should expect the external field to exhibit distinct periodic changes, and at the same time to vary regularly with the atomic number. Hence, if our general premise is correct, that the constraint is to some extent at any rate a measure of the resultant of the two forces, attractive and repellent, we may then expect the controlling factors of this property to be the atomic numbers of the ions in the lattice.

Thus, qualitatively at least, we find that atomic theory confirms the fact already mentioned, namely, that the frequency is related to the atomic numbers and valence electrons of the ions in the lattice. There is another aspect of the question which may be of assistance. The nearest distance to which point centers of two ions in a salt, say, can approach will be determined by the two forces under consideration. In short, on the basis of our postulate we may further assume that the distance between the point centers is in some way related to the constraint factor. To anticipate our results we may state that the distance between ions varies in some manner as the square-root of the constraint. Now, in a previous communication the author has presented an empirical rule which expresses the relationship between the lattice distance (nearest approach of ions) and the atomic numbers to an apparently quantitative degree. It is:

$$d_o = a \ln(Z_c - Z_a) + b. \qquad (6)$$

where $d_o$ is the shortest distance between the point centers of ions in a crystal lattice; $(Z_c - Z_a)$ represents the absolute value of the difference of the atomic numbers of cation and anion; and $a$ and $b$ are constants. In the case of elements it was shown that equation (6) may be written in the form:

$$d_o = a \ln(Z + e) + b. \qquad (6a)$$

where all the symbols have the same significance except e, which equals the maximum number of valence electrons.

Consequently, if the foregoing analysis is correct, we should be able to express the constraint by a similar function, wherein the constants will probably

differ because we have no means of knowing the relationship between $d_o$ and the constraint. Furthermore, it will be helpful to make an explanation regarding the constants, a and b. From all that has been said previously one would expect the constants to be characteristic of each group or period. However, recent studies by Bohr indicate that in the case of elements which follow argon the additional electrons fill up the vacant places in the inner orbit instead of going into the outermost orbit. Such a change in the normal sequence must naturally produce a discontinuity or break in the regular variation of properties dependent on the atomic number and valence electrons; and con-

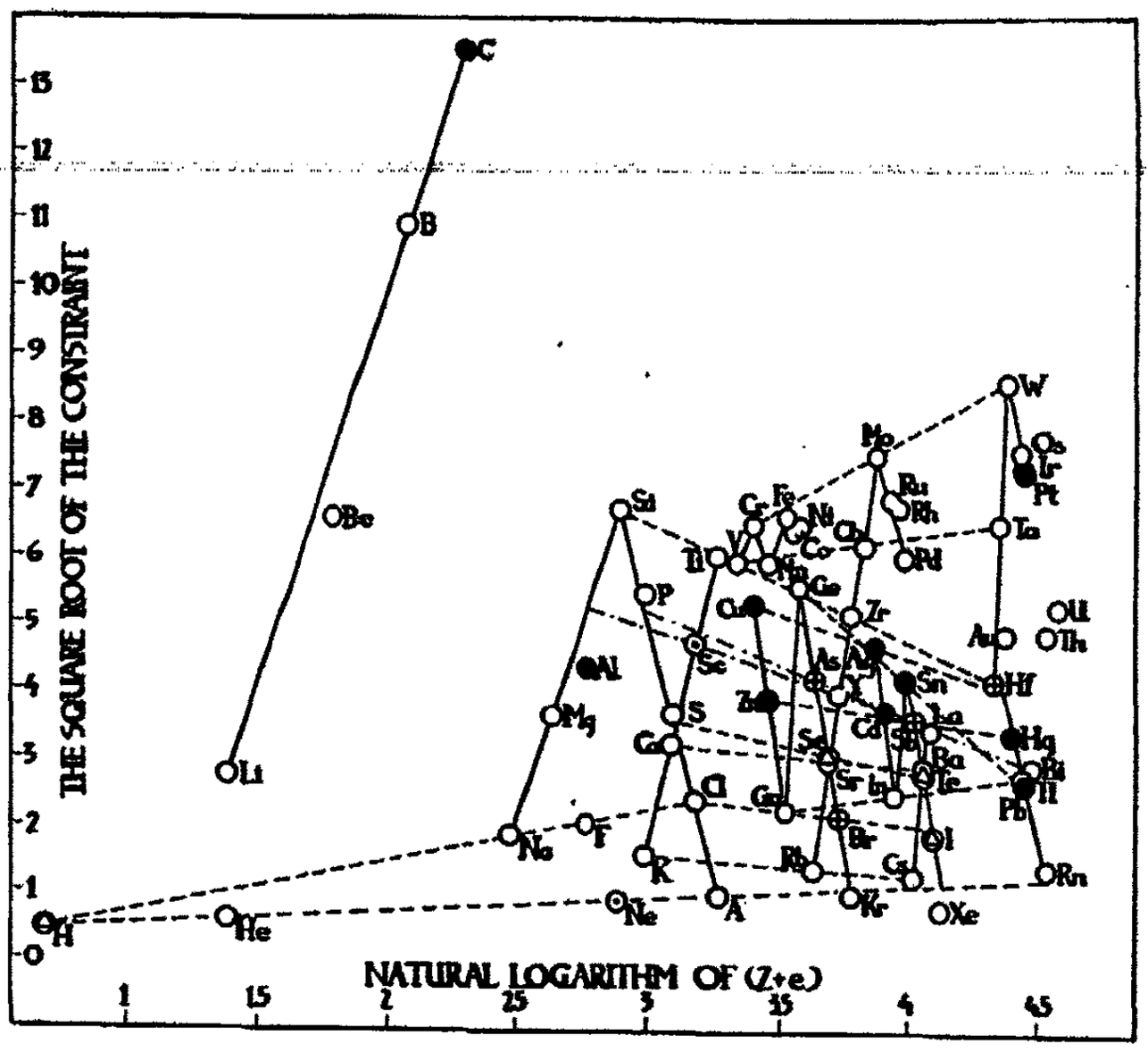



FIG. 4

Periodic Variation of the Square Root of the Constraint of the Elements.

sequently, we must expect this divergence from the normal rule on the part of the electrons to appear in a presentation of equations (6) and (6a) in the periods following argon. Incidentally, it was this abnormal performance of electrons which was alluded to in the discussion of the irregular behavior of the scandium point in Fig. 2. We shall meet with this feature again.

The above discussion may now be summarized by means of an equation:

$$k^{\frac{1}{2}} = 2\pi m^{\frac{1}{2}} \nu = a \ln(Z_o - Z_n) + b. \qquad (7)$$

In the accompanying diagram, Fig. 4, we have the square root of the con-

straint, $k^{\frac{1}{4}}$, plotted against the function of the atomic numbers, thus depicting the above relationship. All the data essential to the construction of this figure are given in Table II. In a few cases the thermal values for $\nu$ have been used and these points are indicated as formerly by black dots. In plotting the graph it was found desirable to divide the values of the constraint by ten. An inspection will show, however, that the values thus plotted are of approximately the same magnitude as the frequencies themselves; that, in fact, the diagram is really a representation, in relative terms to be sure, of the frequencies; and that, finally, the above procedure makes the errors in the "constraint" data of about the same magnitude as in the frequency data, being slightly diminished for the lighter elements and somewhat increased for the heavier elements.

Fig. 4 offers a new means of portraying the variation of the atomic forces, and hence also of the frequency, with the atomic number. We find here a confirmation of the conclusions which were drawn from an examination of Figs. 1 and 2, that the elements of the first period exhibit a normal variation with each other but show a distinct divergence from a normal behavior in relation to the elements of their respective groups. With the remainder of the elements we have a definite variation within each group and period. The representation of the elements of the eighth group is not very significant, first because of the uncertainty regarding the data, and second because of the arbitrary choice of eight for the number of valence electrons. Apart from these elements, the only outstanding defect is that of aluminium, which has already been mentioned in connection with Figs. 1 and 2. Lines for the third group and the fifth sub-group have been drawn arbitrarily, the circles with crosses indicating where the various points might be expected to come according to the abscissa function.

The general agreement of the data is excellent and may be taken as evidence of the fact that we have here a quantitative expression relating the atomic forces and the atomic numbers. Nothing can be stated at this time regarding the constants involved. Nor is it advisable to discuss the many interrelations or the interpretation of the data from a chemical viewpoint. These speculations the author hopes to make up in a subsequent communication.

It remains now to treat the salts in the same way, to see whether they follow the same principle as the elements. This has been done for the alkali halides and is shown in Fig. 5, where we have the square root of the constraint of the different salts plotted against the atomic number function. All of the necessary data are to be found in Table IV. Superficially this diagram appears to be extremely unsatisfactory, a situation which results from the patent uncertainties in the data. Yet, it has been included because, when studied in the light of the information afforded by Fig. 3, there are rather obvious regularities some of which have been indicated by the scheme of the drawing. Instead of going into this matter in detail, a procedure which would be scarcely justified by the flimsy nature of the evidence, we may summarize the probable character of the regularities briefly by stating that they are similar in every respect to

those which the author has already enumerated and discussed for the case of the lattice distance.

In conclusion therefore, we may assume that the same principle applies to all polar compounds alike; that the forces which bind ions together in a lattice are controlled by the atomic numbers, the proper function of which is possibly the one that has been discussed in this paper. If this is so, we then have a means of understanding the many relationships that have been pointed out from time to time between the physical properties of metals and salts, for many of these properties are directly connected to the forces existing between ions in a lattice. Moreover, it should be possible to derive quantitative expressions

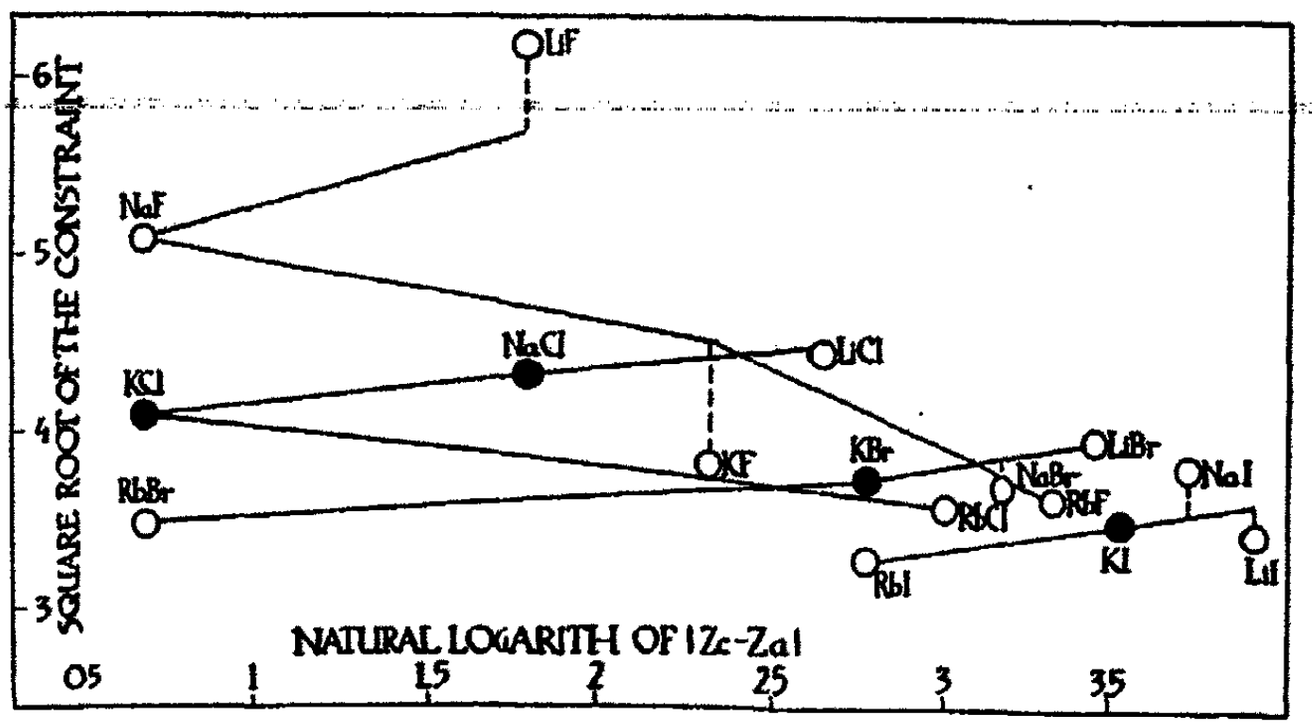



FIG. 5

Variation of the Square Root of the Constraint for a Series of Halide Salts of the Alkali Metals with the Function ln|Zc-Za|.

for the relationships between these same properties and the atomic numbers. Finally, if we may believe that the forces which bind ions together are the same forces which hold the valence electrons in an atom, we have a new and definite way of studying the chemical properties of elements and salts.

## Summary

The present paper is to be regarded as a continuation of a previous attempt to establish a quantitative relationship between atomic numbers and the properties of ions. Attention is directed chiefly to a study of the forces existing between ions in a crystal lattice. The constraint is taken as a measure of these forces. It is shown how the square root of the constraint of both pure elements and salts may be expressed with certain qualifications by a linear equation involving the natural logarithm of the absolute difference of the atomic numbers of the ions in a crystal. Some relationships between the con-

straint and the physical properties of solids are suggested, a condition which should make it possible to express these same properties in terms of the above function. Furthermore, it is indicated how this empirical relationship may be applied to the chemical properties of ions in metals and salts.

In order to supply the needs of the present study it was necessary to calculate the characteristic frequencies of the elements and salts. These data based so far as possible on recent crystallographic information are presented for about seventy elements and also the alkali halides.

19-63

# A LABORATORY STUDY OF NITROGEN FIXATION IN THE HIGH TENSION ARC*

BY HERMAN V. TARTAR AND MELVILLE F. PERKINS[1]

Because of the interest in the utilization of cheap hydroelectric power in the Northwest for the fixation of atmospheric nitrogen by the arc process, some experimental work has been carried on in this laboratory. A portion of the results are presented herein and deal mainly with (1) the effect of pressure on the yield of fixed nitrogen, (2) the equilibria obtained with various mixtures of nitrogen and oxygen and (3) the effect of moisture on the yield when air is used.

An extensive review of the literature on the fixation of nitrogen need not be given here. Investigations on the effect of pressure on the oxidation of nitrogen by means of the alternating current arc are not numerous.[2] Practically no quantitative data have been reported on the effect of reduced pressure of this type of arc operating with *good energy efficiency* (shown by yield of fixed nitrogen) at atmospheric pressure. For long the question has been in the minds of investigators as to whether the reaction between nitrogen and oxygen as obtained from the electric arc may be represented as typical reversible reactions conforming to the law of mass action[3]. Published data are not available giving the results of properly determined equilibria using different mixtures of nitrogen and oxygen with arcs operating under conditions necessary for a good yield of fixed nitrogen. Lastly, the literature dealing with the effect of moisture on the oxidation of nitrogen in air by means of the electrical discharge, is both meagre and conflicting[4]. In fact, no extensive quantitative data are available.

## Description of Apparatus

### (a) *Electrical Equipment*

The power available was a 110 volt, 60 cycle, alternating current. An air-cooled, closed-core transformer of three and one-half kilowatts capacity, was used to give the high tension current. The transformer was calibrated for both resistance and core losses. An adjustable reactance was used to stabilize the arc and control the electrical conditions.

---

* Contribution from the Chemistry Department of the University of Washington.

[1] Du Pont Fellow in Chemistry at the University of Washington, 1921-1923.

[2] Haber et al: Z. Elektrochem., 13, 725 (1907); 14, 689 (1908); 16, 789, 796 (1910); Briner and Naville: Helv. chim. acta, 2, 348 (1919); J. Chim. phys., 17, 329 (1919); Final Report Nitrogen Products Committee (British), p. 241 (1920).

[3] See Knox: "Fixation of Atmospheric Nitrogen", pp. 7-36 (1921) for review of literature prior to 1920; Steinmetz: Chem. & Met. Eng., 22, 299, 353, 411 (1920); Daniels, Keene and Manning: Trans. Am. Electrochem. Soc., 44, 247 (1923).

[4] Warburg and Leithäuser: Ann. Physik, (4) 20, 743 (1906); Sapozlinikov, Guidima and Kotovi: J. Russ. Phys. Chim. Soc. 45, 1076 (1913); Briner and Naville: J. Chim. phys. 17, 329 (1919); Final Report Nitrogen Products Committee (British), p. 241 (1920); Gros: Compt. rend. 170, 811 (1920); Report on the Fixation and Utilization of Nitrogen, p. 137, Bulletin 2041, U. S. War Dept. (1922).

A voltmeter, ammeter, and wattmeter connected in the primary circuit gave the power input and also the power factor. In the secondary circuit the potential across the arc was indicated with a Kelvin electrostatic voltmeter and the current with a milliammeter.

There was some inaccuracy in the smaller readings on the scale of the electrostatic voltmeter and consequently the voltage (used in evaluating

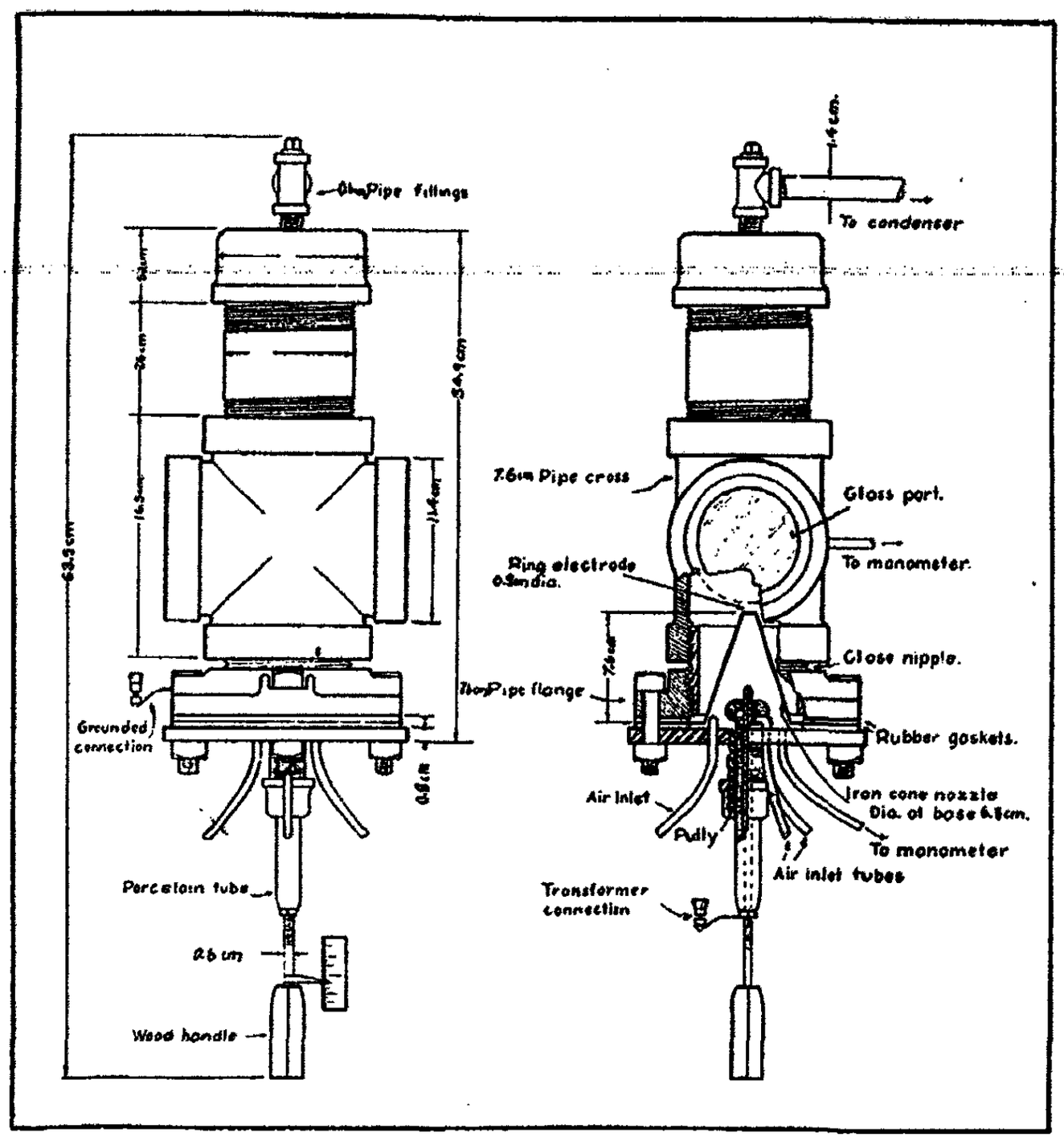



FIG. 1
Arc Furnace

yields) across the arc was calculated from the milliammeter readings, the power factor and the net wattage obtained by deducting the transformer loss from the total wattage indicated by the wattmeter in the primary circuit.

(b) *The Arc Furnace*

The arc furnace shown diagrammatically in Fig. 1 was selected because it gave a good yield of fixed nitrogen. The essential parts were an upper elec-

trode (which was grounded) shaped like a hollow frustrum of a cone, a lower centrally located rod electrode and gas inlet pipes. The gas entered through these pipes at a point slightly above the base and was forced with a whirling motion through the upper electrode. This motion of the gases spread the arc flame and also brought the cold air in very close contact with it; in fact, the arc, thus produced, might be regarded as somewhat similar to that of the Schönherr furnace. The central rod electrode was provided with a screw thread to permit the adjustment of the distance between the electrodes. The furnace enclosure was made largely from 7.6 cm. (3 inch) standard iron pipe fittings and could easily be taken apart. The upper electrode was fastened on a collar and this bolted between the flanges, see Fig. 1. The lower rod elec-

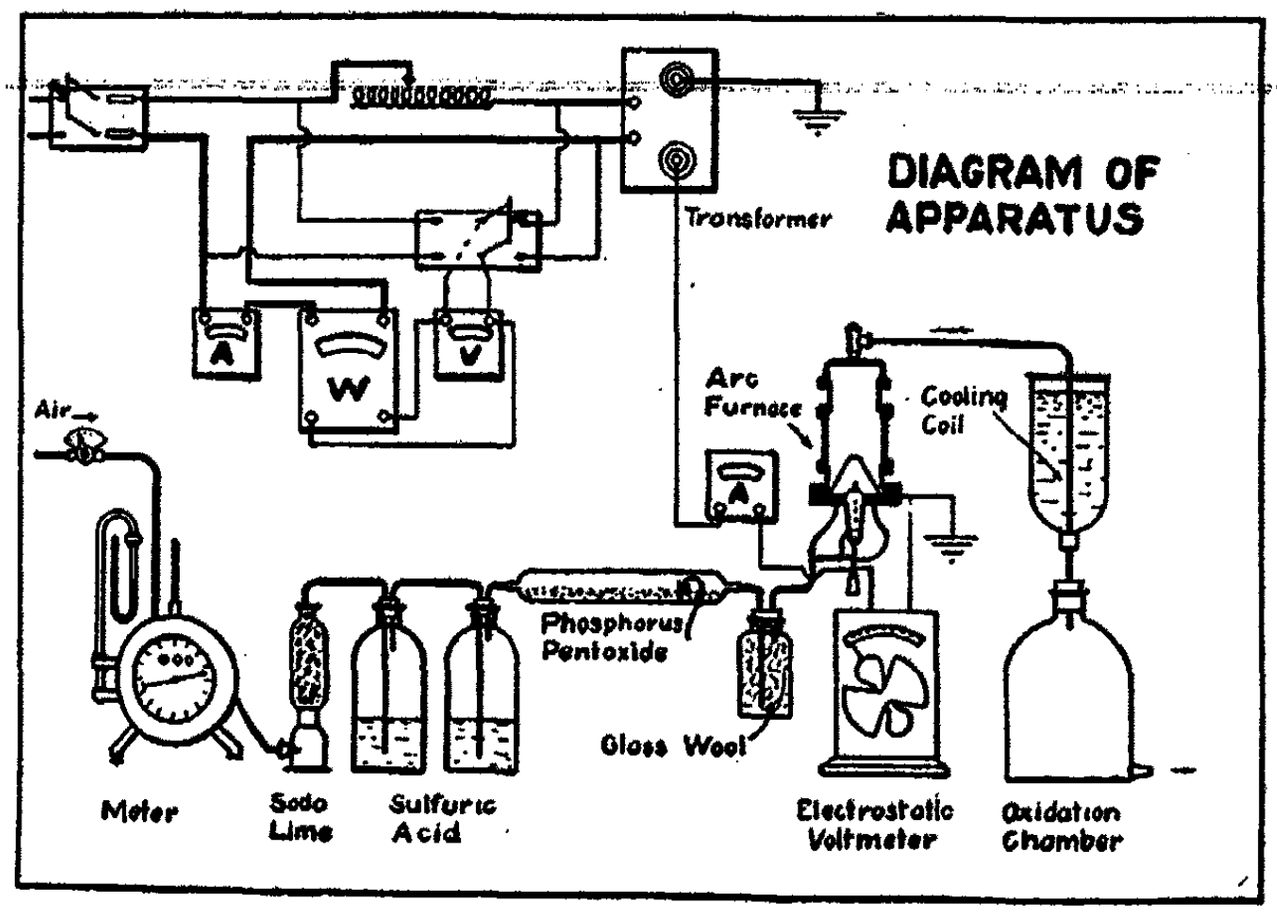



FIG. 2

trode was insulated from the remainder of the furnace by means of a porcelain tube set in stiff putty in a pipe bushing which was screwed into the base plate. The gas inlet pipes were 0.63 cm. (1/4 inch) copper tubes fitted tightly into the base plate. They were spaced 120° apart and were equally distant from the central electrode. The gas was given a rapid whirling motion by the nozzle-shaped ends of the inlet tubes which directed the flow tangentially against the frustrum-shaped electrode. A glass window in the side of the furnace permitted observation of the upper part of the arc at all times. Two other openings in the furnace allowed the necessary connections with pressure manometers to give the gas pressure below and above the upper electrode.

This laboratory arc furnace gives under proper conditions, an efficiency of 58 grams of fixed nitrogen (as $HNO_3$) per kilowatt hour, an efficiency near that obtained in commercial practice.

(c) *The Gas Apparatus*

The gas apparatus served two functions: first, to condition and measure the gas before it reached the arc; and second, to absorb the products formed by the action of the arc. Most of the gases were supplied from tanks under considerable pressure, needle valves being used to regulate the flow. The mixtures of nitrogen and oxygen were measured by passing them through the usual wet type of gas meter. The corrosive gases were passed through an all-glass flow meter to determine the volume. When necessary, moisture was removed from the gas by passing it first through concentrated sulfuric acid and then over phosphorus pentoxide.

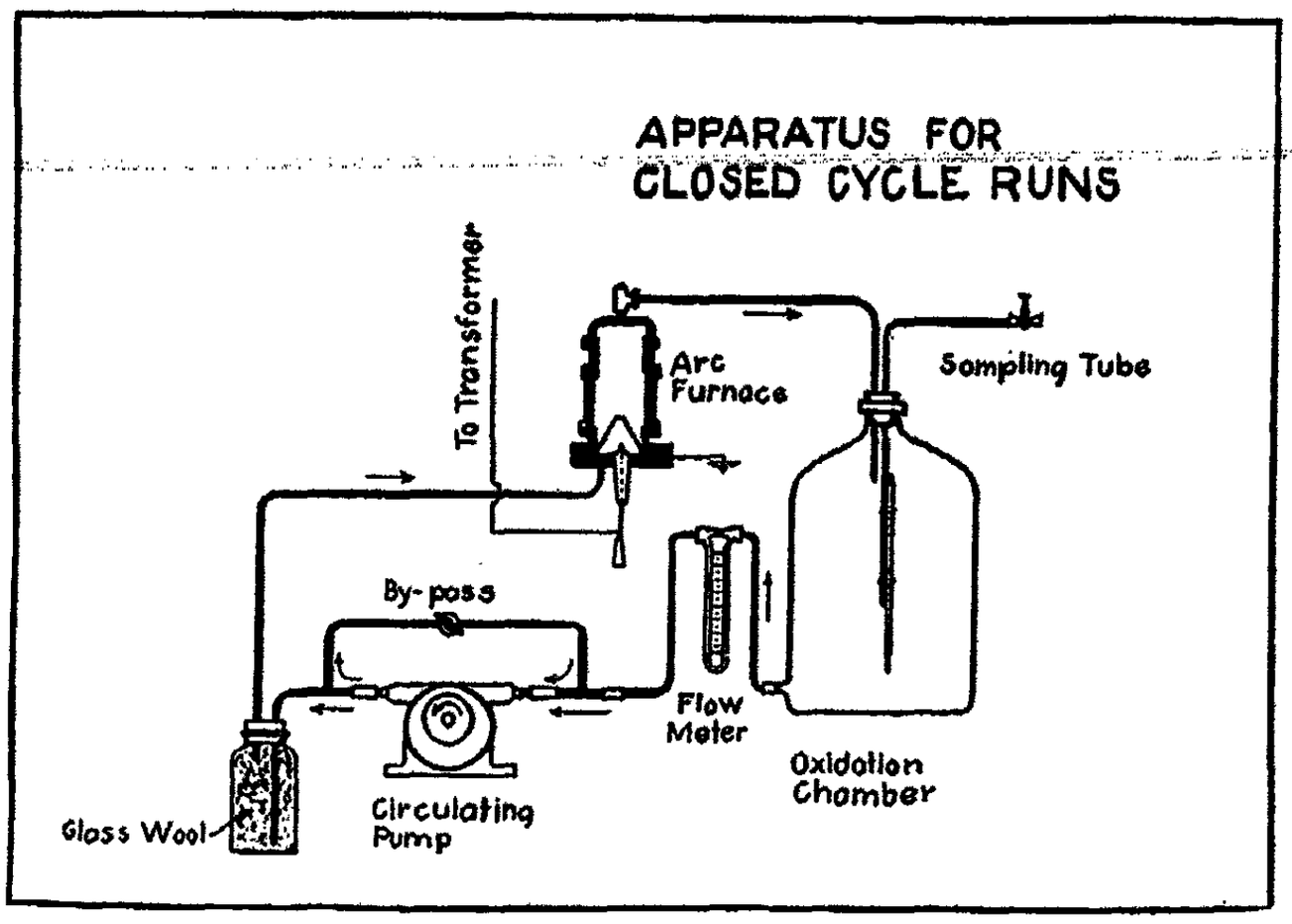



FIG. 3

After leaving the arc, the gas was conducted through a water-cooled glass condenser and then into a five-liter aspirator bottle (hereafter designated as the *oxidation* chamber) in which a considerable portion of the cooled nitric oxide was oxidized to nitrogen peroxide.

The general arrangement of the electrical equipment, furnace, and gas apparatus is shown in Fig. 2.

The apparatus just described was used when the gas was passed but once through the arc, a procedure which is here designated as a *direct run.* In other experiments, the gas was confined in a closed system and circulated repeatedly through the arc, here designated as a *closed cycle run.* A 15-liter bottle served as a gas reservoir and was connected in a closed circuit with the arc furnace, the flow meter and a small "Cenco" positive-acting rotary pump. The pump was equipped with a by-pass or shunt. See Fig. 3. By varying the

rate of flow of the gas through the by-pass the desired velocity of the gas through the closed cycle was easily controlled.

(d) *Methods of Analysis.*

The gas leaving the oxidation chamber was sampled in one or more different ways, namely: by vacuum flasks or by an absorption train. The vacuum flasks were round-bottom pyrex flasks, some 500 cc. and some 2000 cc. capacity, with narrow necks fitted with carefully ground stop-cocks. The oxides of nitrogen in the sample were absorbed in an excess of tenth-normal, carbonate-free sodium hydroxide. The excess of alkali was titrated to neutrality with standard acid using para-nitrophenol as an indicator. This procedure was checked against that used by the U. S. Government[1] at Nitrate Plant No. 1, and by the Devarda reduction method.

The absorption train consisted of 6 hydrometer jars 5 cm. wide and 50 cm. long each fitted with inlet and outlet tubes and connected in series with the oxidation chamber. The jars contained a known amount of standard alkali mixed with hydrogen peroxide solution (3%). Glass wool was placed in the jars to break the gas into small bubbles and thus bring about complete absorption of the oxides of nitrogen. At the end of a run the excess of alkali was titrated with standard sulfuric acid using methyl red as the indicator.

When the absorption train was used to evaluate the fixation of reduced pressure runs, a "Cenco" rotary pump was placed in the gas line as a "booster pump" just ahead of the absorption towers so that absorption could take place under atmospheric pressure.

The results obtained using the vacuum flasks and the absorption train were concordant.

## Effect of Velocity of Gas through the Arc upon the Yield

In starting experimental work on the formation of nitric oxide with an arc furnace, a determination must be made of the influence of the velocity of air through the arc upon the per cent by volume of nitric oxide and the yield per kilowatt hour. In this investigation, the work was extended to include the mixtures of nitrogen and oxygen varying from the ratio found in air to that of "invert air" (4 vols. oxygen to 1 vol. nitrogen). The composition of gas for each experiment was checked by the analysis of a composite sample extending over the entire run.

The relation between the velocity of air and the electrical values and yield is shown by the data in Table I, also by Fig. 4. The almost constant amperage is due to the reactance in the circuit.

An inspection of Table I and Fig. 4 shows that with constant current and distance between the electrodes, the concentration of nitric oxide for any given mixture decreased with the velocity; and within the limits tried, 200 to 600 liters per hour, the concentration of nitric oxide was a linear function of the velocity.

[1] J. Ind. Eng. Chem., 11, 745 (1919).

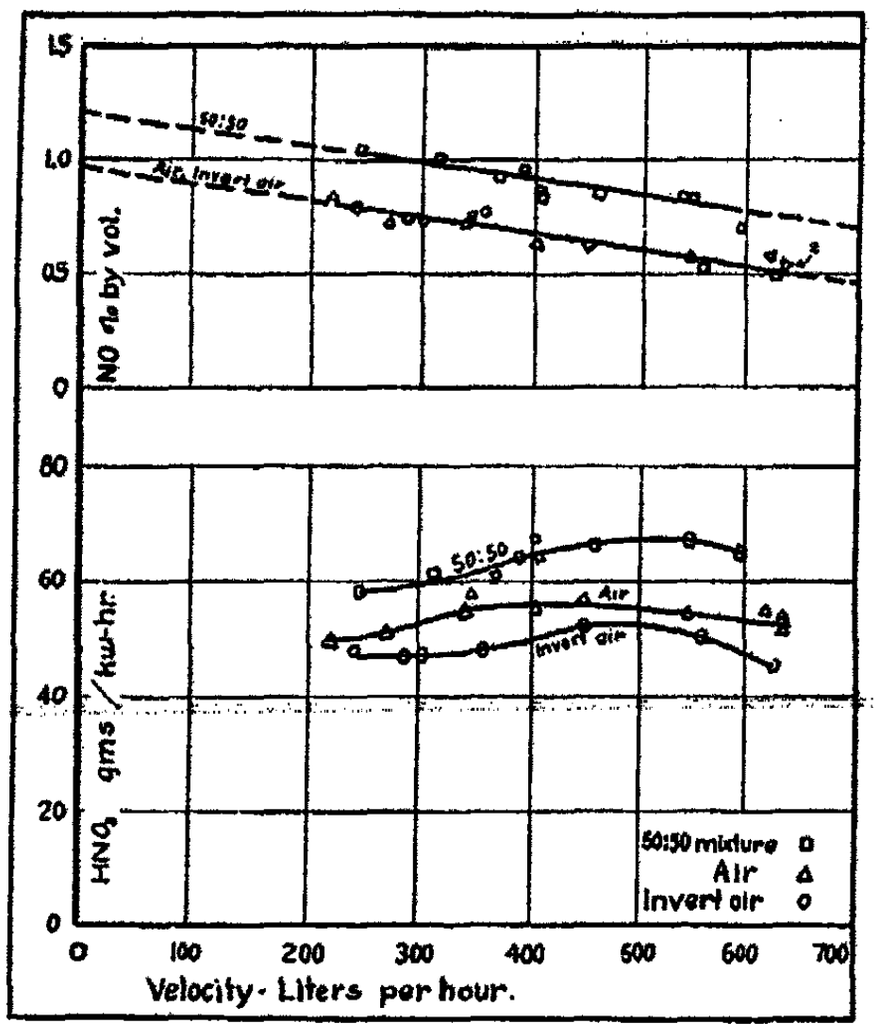



FIG. 4 (upper part)

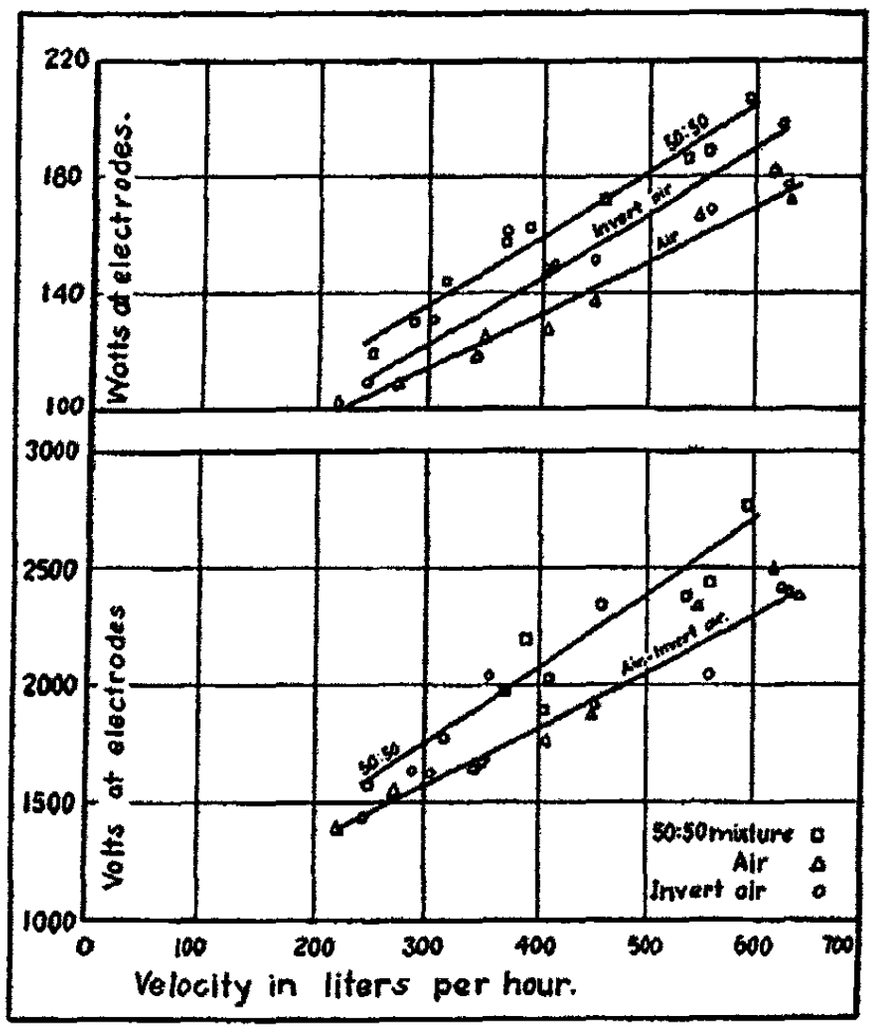



FIG. 4 (lower part)

FIG. 4. (2 parts—upper and lower). Direct Runs on Mixtures of Oxygen and Nitrogen; Arc at Atmospheric Pressure; Velocity of Gas thru Arc, 200 to 600 Liters per Hour.

The yield of fixed nitrogen reached a maximum value at an intermediate velocity which depends somewhat on the composition of the gas and its rate of flow. The maximum yields occurred at velocities varying from 350 to 500 liters per hour; or 2000 to 3000 liters per kilowatt hour. These yields at these velocities could be secured only with a current of 90 milliamperes. Doubling the current gave an increase in the concentration of nitric oxide but a decrease in the yield per kilowatt hour. Several runs were made using a current of 30 milliamperes with various gas mixtures at a velocity of approximately 340 liters per hour. The results are recorded in Table II.

TABLE I

Direct Runs on Mixtures of Oxygen and Nitrogen; Arc at Atmospheric Pressure; Velocity of Gas, 200 to 600 Liters per Hour

| Expt. No. | At electrodes: Current milli-amperes | At electrodes: Approx-imate voltage | At electrodes: Watts, corrected for trans-former losses | Velocity of gas thru arc. Liters per hr. Stand. cond. | Nitric oxide. per cent by volume | Oxygen, per cent by volume | Nitrogen, per cent by volume | Nitric acid ($HNO_3$) gms. per kw.-hr. | Watt-hours required as heat of formation of nitric oxide |
|---|---|---|---|---|---|---|---|---|---|
| *Air* | | | | | | | | | |
| 64f | 95 | 1410 | 104 | 220 | 0.84 | air | air | 50.0 | 2.06 |
| 64g | 92 | 1550 | 109 | 273 | 0.73 | " | " | 51.5 | 2.23 |
| 64h | 92 | 1660 | 119 | 339 | 0.72 | " | " | 56.0 | 2.65 |
| 64e | 94 | 1680 | 125 | 342 | 0.76 | " | " | 58.6 | 2.91 |
| 75 | 95 | 1710 | 128 | 352 | 0.72 | " | " | 56.0 | 2.84 |
| 64i | 93 | 1780 | 127 | 404 | 0.63 | " | " | 56.0 | 2.82 |
| 64j | 93 | 1880 | 137 | 448 | 0.62 | " | " | 57.3 | 3.12 |
| 64k | 90 | 2340 | 167 | 546 | 0.59 | " | " | 54.4 | 3.61 |
| 64n | 90 | 2500 | 182 | 622 | 0.57 | " | " | 55.5 | 4.01 |
| 64l | 89 | 2400 | 172 | 632 | 0.52 | " | " | 54.4 | 3.71 |
| 64m | 89 | 2400 | 177 | 634 | 0.52 | " | " | 52.1 | 3.67 |
| *Approx. 50% $N_2$. 50% $O_2$* | | | | | | | | | |
| 66 | 92 | 1590 | 120 | 241 | 1.05 | 43.48 | 55.47 | 59.0 | 2.81 |
| 64 | 95 | 1790 | 144 | 314 | 1.00 | 49.50 | 49.50 | 61.8 | 3.54 |
| 63 | 94 | 1980 | 158 | 371 | 0.93 | 44.03 | 55.04 | 61.4 | 3.85 |
| 64b′ | 90 | 2200 | 163 | 390 | 0.96 | 48.72 | 50.32 | 64.7 | 4.18 |
| 64c | 93 | 1900 | 148 | 404 | 0.87 | 45.76 | 53.37 | 67.0 | 3.93 |
| 64b | 90 | 2020 | 150 | 407 | 0.84 | 48.18 | 50.98 | 64.0 | 3.81 |
| 64c′ | 89 | 2340 | 172 | 461 | 0.87 | 48.07 | 51.06 | 65.8 | 4.48 |
| 65 | 93 | 2380 | 187 | 535 | 0.84 | 39.58 | 59.58 | 67.5 | 5.02 |
| 67 | 91 | 2450 | 189 | 546 | 0.83 | 49.59 | 49.58 | 67.2 | 5.05 |
| 68 | 89 | 2780 | 208 | 593 | 0.70 | 49.65 | 49.65 | 65.6 | 5.42 |
| *Invert Air* | | | | | | | | | |
| 69 | 93 | 1430 | 110 | 240 | 0.80 | 78.60 | 20.60 | 48.7 | 2.13 |
| 70 | 93 | 1640 | 130 | 289 | 0.75 | 79.23 | 20.02 | 47.2 | 2.44 |
| 73 | 94 | 1630 | 132 | 302 | 0.74 | 73.63 | 25.63 | 47.4 | 2.48 |
| 73b | 91 | 2040 | 162 | 357 | 0.78 | 78.61 | 20.61 | 48.5 | 3.10 |
| 71 | 94 | 1910 | 151 | 450 | 0.63 | 76.68 | 22.69 | 53.2 | 3.19 |
| 72 | 96 | 2050 | 169 | 561 | 0.54 | 78.73 | 20.73 | 50.6 | 3.40 |
| 74 | 92 | 2420 | 199 | 628 | 0.52 | 78.74 | 20.52 | 45.8 | 3.63 |

TABLE II

Direct Runs on Mixtures of Oxygen and Nitrogen: Arc at Atmospheric Pressure: Current 30 Milliamperes: Gas Velocity 340 Liters per Hour

| Expt. No. | At electrodes: Current milli-amperes | At electrodes: Approx-imate voltage | Watts corrected for transformer $I^2R$ loss only | Velocity of gas thru arc. Liters per hour. Stand. cond. | Nitric oxide per cent by volume | Oxygen per cent by volume | Nitrogen per cent by volume | Gms. Nitric Acid ($HNO_3$) per kw.-hr. (Approximate) |
|---|---|---|---|---|---|---|---|---|
| *Air* | | | | | | | | |
| 121 | 30 | 2400+ | 80 | 351 | 0.28 | Air | Air | 35 |
| 126 | 30 | | 80 | 344 | 0.28 | " | " | 34 |
| 126′ | 30 | | 80 | 344 | 0.32 | " | " | 39 |
| *Approx. 50% $O_2$, 50% $N_2$* | | | | | | | | |
| 122 | 30 | 2400+ | 80 | 328 | 0.33 | 49.0 | 50.7 | 38 |
| *Invert Air* | | | | | | | | |
| 123 | 30 | 2400+ | 80 | 302 | 0.13 | 79.6 | 20.3 | 14 |
| 124 | 30 | | 80 | 322 | 0.09 | 81.5 | 18.4 | 10 |
| 125 | 30 | | 80 | 336 | 0.14 | 77.5 | 22.4 | 16 |
| 127 | 30 | | 80 | 344 | 0.11 | 77.0 | 22.9 | 13 |
| 127′ | 30 | | 80 | 344 | 0.15 | 77.0 | 22.8 | 18 |

The data of Table I (and Fig. 4) also show that air and invert air gave the same concentration of nitric oxide at the corresponding velocities. Furthermore, under similar conditions, the 50-50 mixture gave the greatest concentration of nitric oxide. The *relative increase* in the nitric oxide content due to oxygen enrichment depended upon the velocity of the gas at which the comparison was made. At 230 liters per hour there was a gain of 25 per cent; at 550 liters the gain was 40 per cent. This effect of velocity suggests an explanation for the discordant results reported by various investigators for the increase in nitric oxide content resulting from oxygen enrichment of the gas supplied to an arc. An idea of the wide divergence of these results may be obtained from the following quotation from Norton[1]: "McDougal and Howles, in 1900, when using a small experimental plant, nearly doubled the actual yield of NO by changing from air to the mixture of equal volumes, and obtained a concentration of 8.5 per cent NO in the cool gases. The fact of a very pronounced increase in the yield is confirmed by Lepel, by Kowalski and Moscicki (who secured an increase of 50 per cent), by Briner and Durand (37 per cent), by Le Blanc and Muranen (29 per cent), and by Guye (16 to 60 per cent)."

The data (Table I) on the yields per kilowatt hour for air and the 50:50 mixture, show that the enrichment with oxygen, gave an increase varying from 14 to 25%, the latter figure being for a velocity of 600 liters per hour. A comparison of the yields with the 50:50 mixture and with invert air shows a gain varying from 21 to 32%. The maximum increases in yield from the use of the 50:50 gas are in general accord with the mass action law. Fig. 4

[1] Norton: Bulletin No. 52, Special Agent Series, U. S. Dept. of Commerce and Labor, p. 84.

brings out the fact that the wattage of the arc was not kept uniform for the different mixtures at any one velocity and consequently close comparisons with respect to the mass law are hardly permissible.

The appearance of the arc changed gradually as the rate of gas flow was increased. At 225 liters per hour (current of 0.1 to 0.2 amperes), a yellow luminous arc was obtained while at 600 liters per hour the steady, luminous zone almost completely disappeared, a blue sparking arc taking its place.

### Direct Runs at Reduced Pressure

In the runs at reduced pressures the arc was operated in practically the same manner as in the direct runs at atmospheric pressure. Two stop-cocks

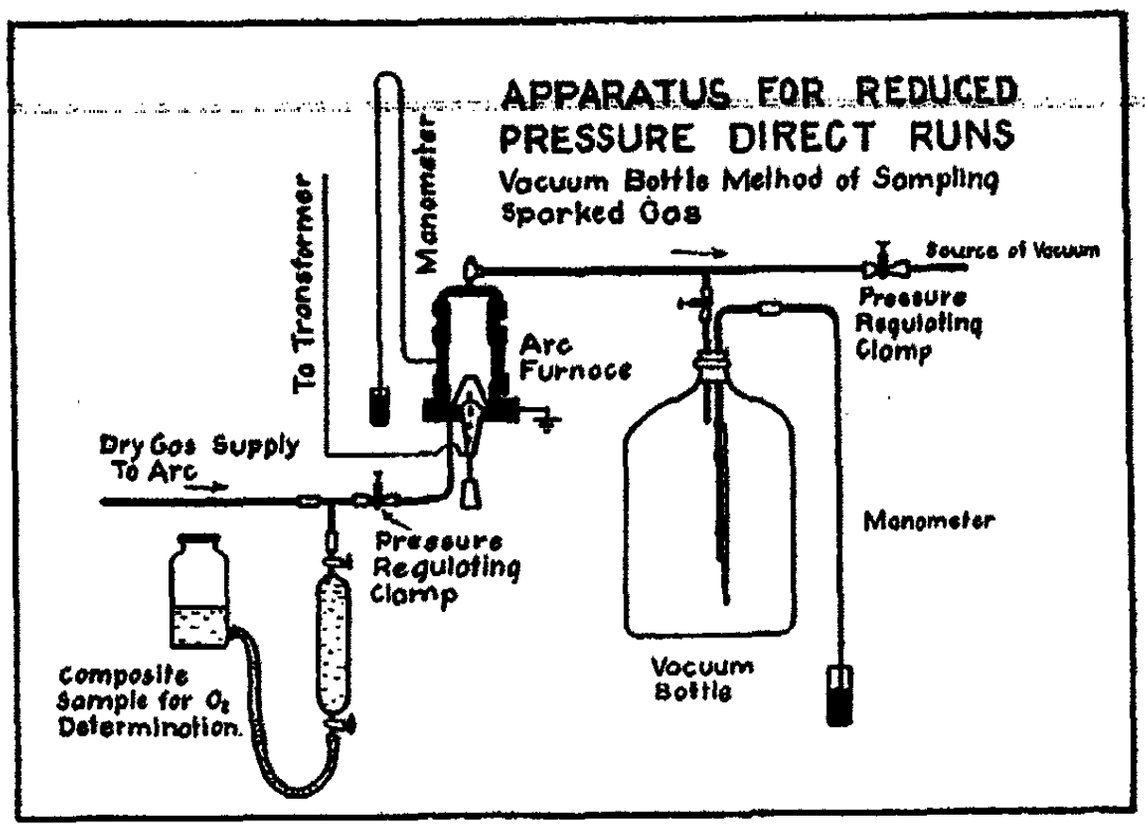



FIG. 5

were inserted in the gas line; one immediately before the arc furnace and the second after the exit from the furnace. The tube from the latter stop-cock was connected to a large capacity vacuum pump. The arrangement of the apparatus is shown in Fig. 5.

The voltage across the arc decreased with the reduction of pressure. The most noticeable change, however, was in the appearance of the arc itself. Under normal pressure and an air velocity of 340 liters per hour, the arc appeared to be made up of two intermixed parts, one was a bright luminous zone which extended from the rod electrode to about one-half inch above the upper electrode; the other consisted of spark-like streamers that played with a rotary motion between the electrodes. As the pressure was reduced, the luminous zone rapidly disappeared and the spark-like streamers became more numerous, slightly distorted and of a more blue color. The luminous zone disappeared entirely with further reduction in pressure and the arc had the appearance of a spark or brush discharge.

Samples of the gas were taken at the exit of the furnace by the vacuum flask method. Large bottles, 20 liters capacity provided with tightly fitting stoppers with stop-cocks, were substituted for the vacuum flasks previously mentioned.

The experimental data for the reduced pressure runs are reported in Table III and graphically represented in Fig. 6.

TABLE III

Direct Runs on Mixtures of Oxygen and Nitrogen: Arc at Reduced Pressures

| Expt. No. | Pressure in arc chamber mm. of Hg. | At Electrode: Current milli-amperes | At Electrode: Approx-imate voltage | Watts corrected for transformer losses | Velocity of gas thru arc. Liters per hr. stand. cond. | Nitric oxide per cent by volume | Oxygen per cent by volume | Nitrogen per cent by volume | $HNO_3$, gms. per kw.-hr. |
|---|---|---|---|---|---|---|---|---|---|
| *Air* | | | | | | | | | |
| 92 | 130 | 98 | 800 | 66 | 206 | 0.24 | Air | Air | 21.6 |
| 93 | 149 | 96 | 950 | 65 | 219 | 0.20 | " | " | 19.0 |
| 100 | 298 | 96 | 1120 | 80 | 236 | 0.36 | " | " | 30.0 |
| 86 | 455 | 95 | 1200 | 85 | 196 | 0.62 | " | " | 39.9 |
| 88 | 451 | 97 | 1180 | 84 | 201 | 0.58 | " | " | 39.0 |
| 105 | 594 | 93 | 1170 | 86 | 204 | 0.46 | " | " | 42.6 |
| 64f | 768 | 95 | 1410 | 104 | 221 | 0.84 | " | " | 50.0 |
| *Approx. 50% $O_2$, 50% $N_2$* | | | | | | | | | |
| 96 | 140 | 99 | 900 | 64 | 200 | 0.17 | 44.92 | 54.91 | 15.5 |
| 97 | 147 | 97 | 925 | 62 | 235 | 0.20 | 46.90 | 52.90 | 21.8 |
| 98 | 130 | 96 | — | 61 | 203 | 0.22 | 48.39 | 51.39 | 20.8 |
| 99 | 294 | 97 | 1050 | 76 | 227 | 0.38 | 46.81 | 52.81 | 31.5 |
| 89 | 452 | 94 | 1150 | 80 | 223 | 0.67 | 56.67 | 42.66 | 53.0 |
| 101 | 460 | 94 | 1130 | 81 | 245 | 0.54 | 48.73 | 50.73 | 45.4 |
| 104 | 599 | 93 | 1270 | 101 | 208 | 0.41 | 48.80 | 50.79 | 49.7 |
| 66 | 760 | 92 | 1590 | 120 | 241 | 1.05 | 43.48 | 55.47 | 59.0 |
| *Invert Air* | | | | | | | | | |
| 95 | 145 | 97 | 940 | 59 | 239 | 0.13 | 76.94 | 22.94 | 14.9 |
| 91 | 453 | 96 | 1100 | 85 | 212 | 0.60 | 77.70 | 21.70 | 42.2 |
| 90 | 460 | 96 | 1125 | 86 | 219 | 0.61 | 74.69 | 24.70 | 43.8 |
| 69 | 772 | 93 | 1430 | 110 | 250 | 0.80 | 78.60 | 20.60 | 48.7 |

The results showed that there was a gradual decrease both in the concentration of the nitric oxide and the yield per kilowatt hour as the pressure was reduced. At corresponding pressures, the 50:50 mixture gave a greater yield than the other mixtures.

An important difference between the direct runs made at atmospheric pressure and those at reduced pressure was the length of time required for the passage of the gas particles through the furnace. For a given gas flow (in these experiments, 200-250 liters per hour), the velocity of the particles through the arc chamber increased with the reduction in pressure. At a pres-

sure of 150 mm., the particles were swept through the furnace at a velocity nearly 5 times greater than when the same quantity of gas was passed through at 760 mm.[1]

The results reported here are of interest in connection with the work of Haber and Köenig[2] with alternating current arcs at pressure around 100 mm.

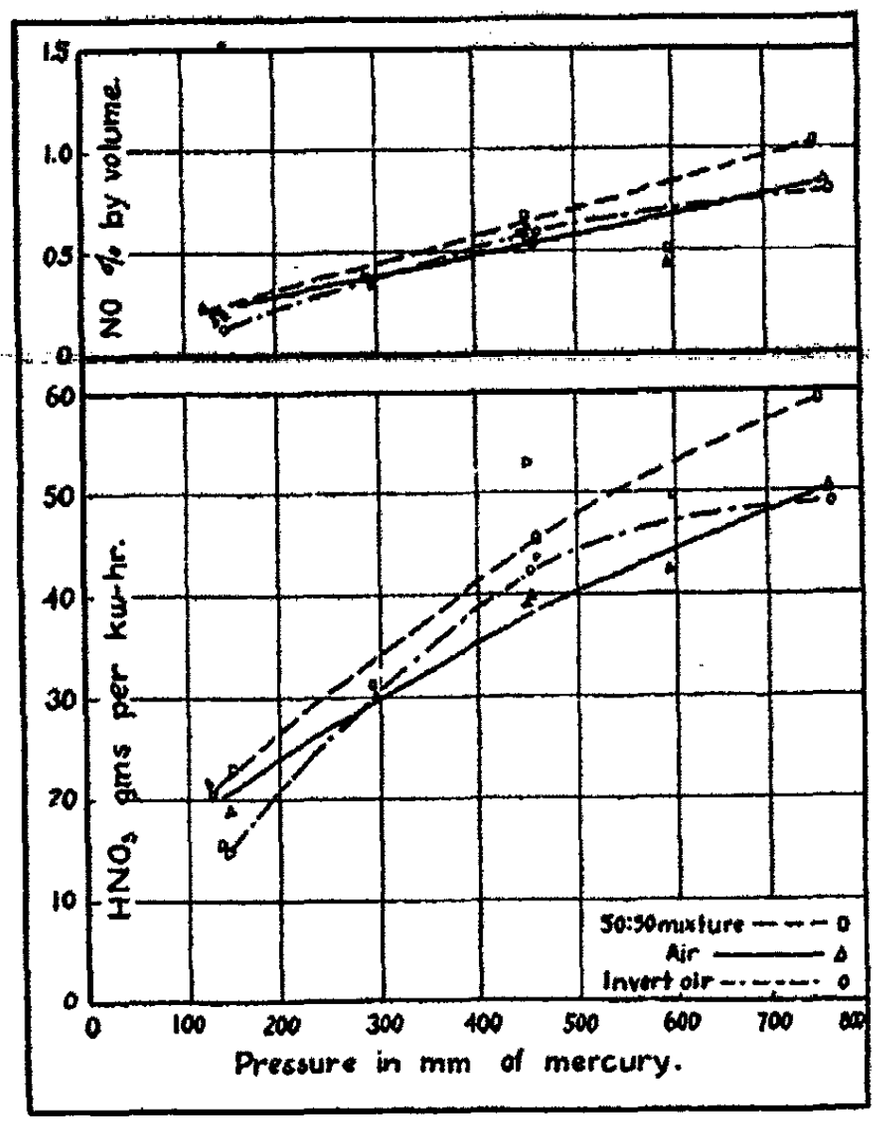



FIG. 6

Direct Runs at Reduced Pressures, (100 to 760 mm.) upon Mixtures of Oxygen and Nitrogen; Gas Velocity 200 liters per hour; Arc Current, 95 milliamperes.

The concentration of nitric oxide obtained depended upon composition of the mixture of nitrogen and oxygen used; 9.8% from air, 14.5% from the 50:50 mixture and 12.5% from "invert air". These high values were obtained, however, with a gas flow of only a few liters per hour. The writers have not obtained any results *indicating that a decrease in pressure may be utilized in securing a greater efficiency in yield by the arc process.*

---

[1] Additional experiments have been made by Mr. P. G. Cohen in this laboratory, reducing the rate of flow of gas through the arc as the pressure was diminished in order to keep the velocity of the particles of gas through the arc constant. The data show that the yield decreased in a manner closely analogous to the results reported above. These additional results will be offered for publication at an early date.

[2] Haber and Köenig: Z. Elektrochem., 13, 725 (1907).

## Closed Cycle Experiments

### (a) *The Experimental Part*

The closed cycle runs were made at atmospheric pressure with a power input ranging from 65 to 200 watts. In most cases, the rate of flow of gas was that required to give the maximum yield of fixed nitrogen with air at atmospheric pressure. Closed cycle experiments were conducted on a series of mixtures of nitrogen and oxygen, the content of the latter substance being varied from 20% to 85% by volume. The purpose of these experiments was to determine the equilibrium concentration of nitric oxide obtained by passing the gas repeatedly through the arc. The combined nitrogen existed in the cooler parts of the apparatus largely as nitrogen dioxide. This substance is completely dissociated above 600° into oxygen and nitric oxide. Furthermore, the rate of dissociation is extremely rapid at higher temperatures and consequently the combined nitrogen was assumed to exist as nitric oxide within and in the immediate vicinity of the arc.

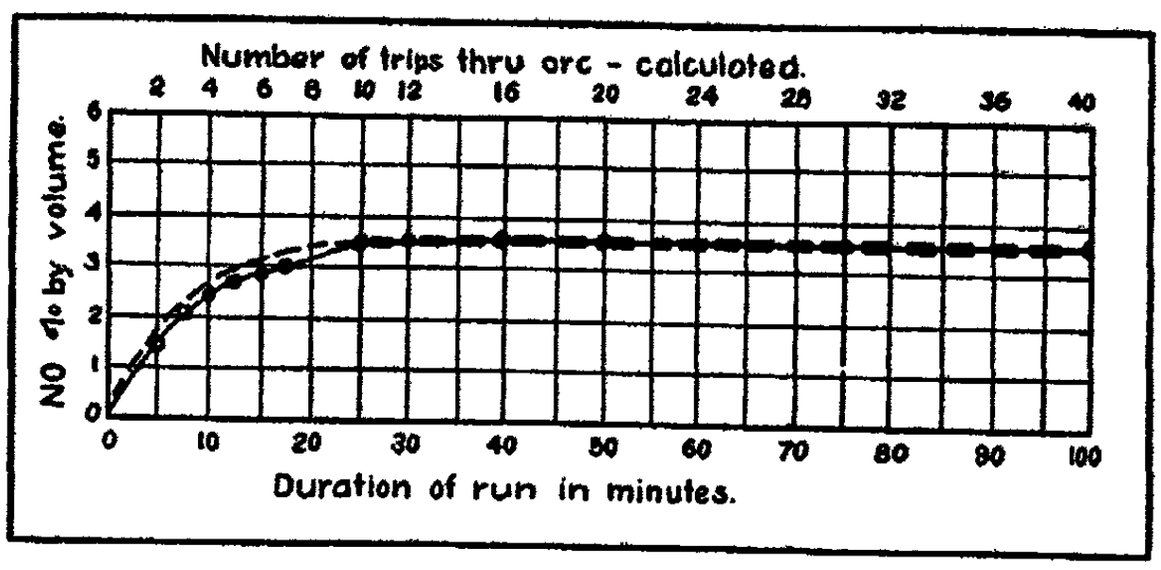



FIG. 7

Closed Cycle Runs at Atmospheric Pressure. Increase of Nitric Oxide with Successive Passages of Mixture thru the Arc at Velocity of 336 Liters per hour; Initial Mixture = Air.

Equilibrium was approached from either direction by obtaining the same final concentration of nitric oxide from mixtures initially containing, on one hand, no nitric oxide and on the other hand, an excess of this substance. The first closed cycle experiments were made to determine the rate of increase or decrease in the concentration of nitric oxide and the time required to reach equilibrium. The change in the nitric oxide content with successive passages through the arc was followed by taking samples at time intervals corresponding to those estimated for the successive cycles. In experiments 61d and 61e, dry air was introduced to replace the gas removed for analysis. This small periodic dilution prolonged somewhat the time required to reach equilibrium. The dilution was reduced to a minimum by admitting the air into the gas line immediately preceding the arc furnace, thus subjecting the newly introduced gas to the action of the arc prior to diffusion. A correction for the dilution was obtained by making a second run under identical conditions without

sampling until the arc had been operated for 25 minutes. The results of these experiments are given in Table IV and graphed in Fig. 7, the values corrected for dilution being indicated by the dotted line. In the later runs, dilution attending sampling was avoided by allowing gas of approximately the same concentration to replace that withdrawn. The arc was continued in operation until there was no further change in the concentration of nitric oxide. The extremely slow rate of oxide formation with reduced current strength (30 milliamperes) is shown by the data of experiment 61g also included in Table IV.

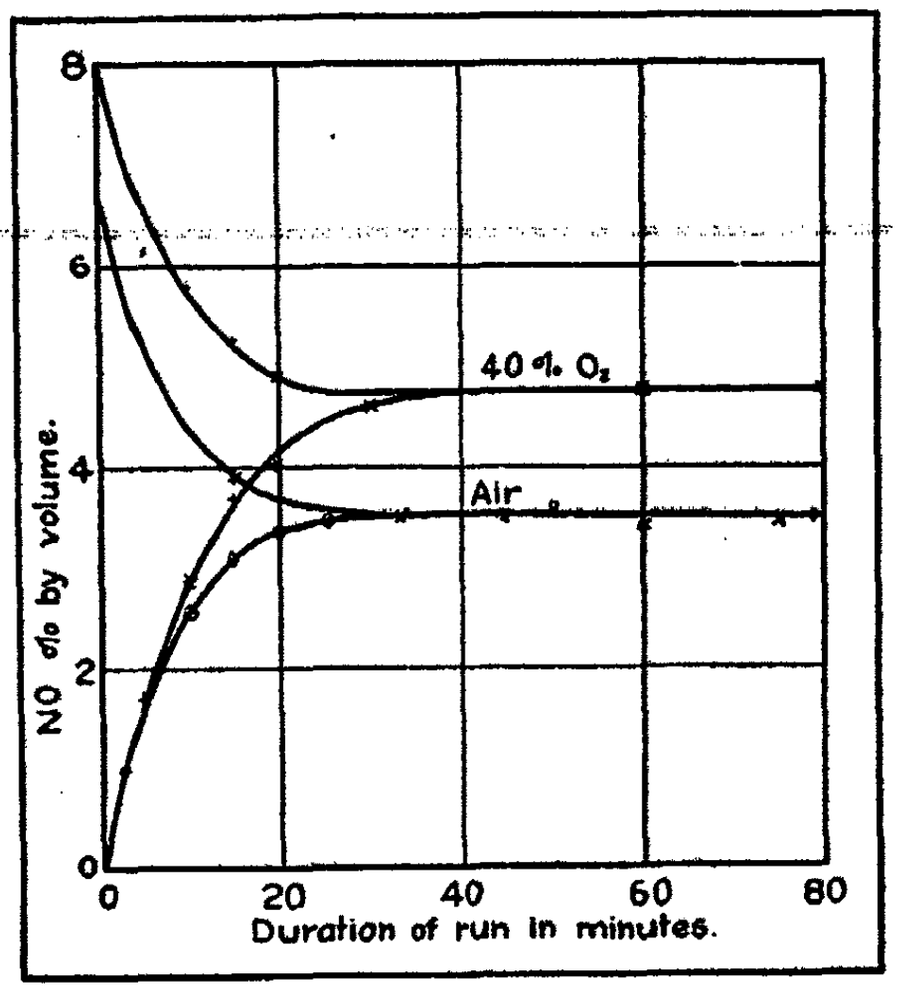



FIG. 8

Closed Cycle Runs at Atmospheric Pressure, approaching Equilibrium from both Directions. Velocity of Gas thru Arc, 330 Liters per Hour. Arc Current, 185 milliamperes.

Equilibrium was also approached from both directions using mixtures which had nearer the same total nitrogen and oxygen content; in one case no combined oxide was present, while in the other, the initial nitric oxide concentration was twice the final equilibrium value. Results obtained with mixtures containing different nitrogen-oxygen ratios are given in Table V and represented graphically in Fig. 8. The curves show that the same final concentration of nitric oxide was reached using gases initially free from, or containing an excess of this substance; also, that at a given time, the rate of decomposition was similar to the rate of formation of nitric oxide. Under these conditions, approximately 10 cycles through the arc were required to approach closely the equilibrium value, 80% of the final concentration of nitric oxide being obtained with about 5 cycles.

The next group of experiments were made expressly for the study of the application of the law of mass action to the formation of nitric oxide in the high tension arc. Here the careful determination of the final equilibrium concentrations was the essential factor, the rate of oxide formation being of secondary importance. The equilibrium constant for the reaction, $N_2 + O_2 = 2NO$, was calculated in accordance with the mass action law as follows (concentrations expressed as per cent by volume):

$$K = \frac{(NO)^2}{(N_2) \times (O_2)}$$

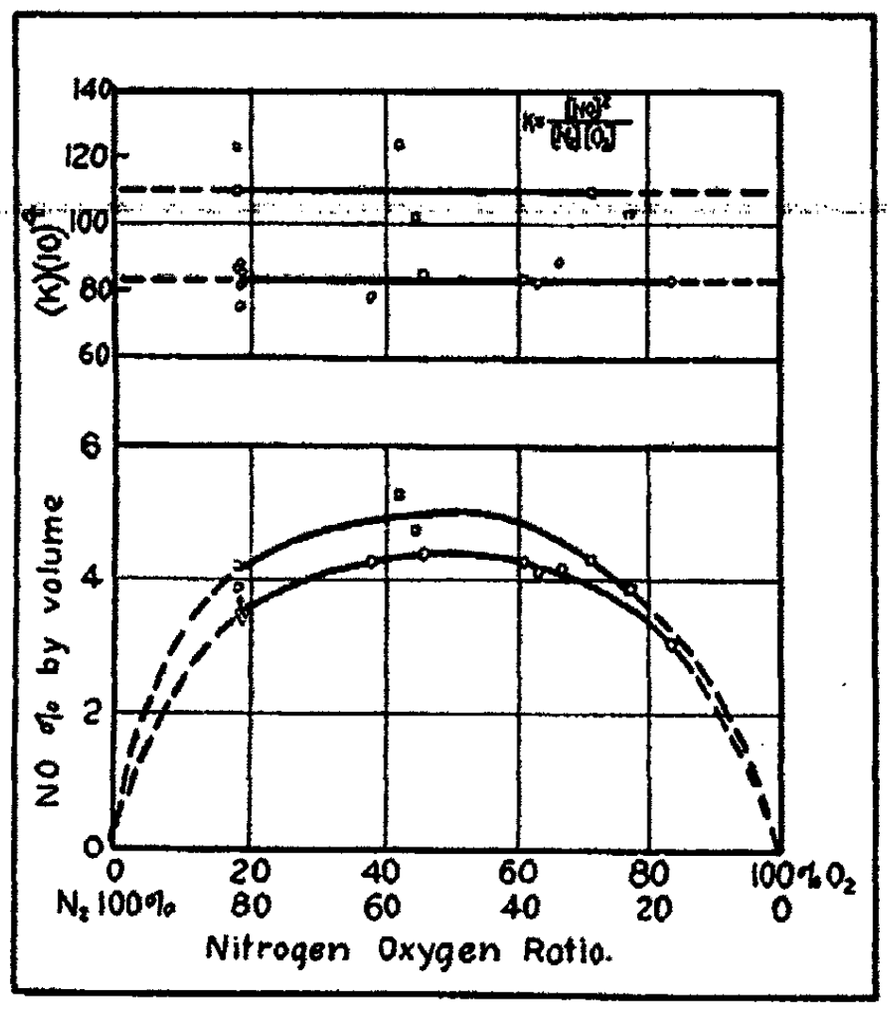



FIG. 9

Equilibria from Closed Cycle Runs.
o = values for arc currents of 100 to 160 milliamperes.
□ = values for arc currents of 30 milliamperes.

These equilibrium runs were made with currents ranging from 30 to 190 milliamperes; the gas mixtures were varied in composition from air to "invert air". The results of these tests are given in Table VI and are shown graphically in Fig. 9. The values obtained for the equilibrium constant $K$ were of the order of (80 to 200) ($10^{-4}$) and, for convenience, have been multiplied by the factor, $10^4$. The values for experiments 51a, 51b, 52a, and 52b were omitted from the graph because a greater gas velocity was used than that necessary for the maximum yield in a direct run. A Thorardson transformer was used to supply the current of 30 milliamperes. The core loss of this transformer was not determined, and consequently the reported wattages are somewhat high. The slow rate of nitric oxide formation with this low current arc greatly prolonged the time required to reach equilibrium.

## TABLE IV

### Closed Cycle Runs at Atmospheric Pressure. Increase of Nitric Oxide with Successive Passages of Mixture through the Arc

| Expt. No. | Minutes duration at time of sampling | At electrodes: Current milli-amperes | At electrodes: Approx-imate voltage | At electrodes: Watts corrected for transformer losses | Velocity of gas thru arc. (stand. cond.) Liters per hour | Nitric oxide, per cent by volume | Oxygen, per cent by volume | Nitrogen, (K) ($10^4$) per cent by volume | |
|---|---|---|---|---|---|---|---|---|---|
| 61d | 0 | 190 | 1240 | 177 | 336 | 0.00 | | | |
| | 2.5 | 191 | 1250 | 185 | 336 | 0.97 | | | |
| | 5.0 | 190 | 1250 | 182 | 336 | 1.55 | | | |
| | 7.5 | 191 | 1260 | 187 | 336 | 2.08 | | | |
| | 10.0 | 191 | 1280 | 188 | 336 | 2.44 | | | |
| | 12.5 | 191 | 1300 | 190 | 336 | 2.71 | | | |
| | 15.0 | 190 | 1300 | 190 | 336 | 2.87 | | | |
| | 17.5 | 190 | 1300 | 192 | 336 | 2.96 | | | |
| | 25.0 | 190 | 1320 | 192 | 336 | 3.54 | 19.03 | 77.43 | 85.1 |
| 61e | 0 | 189 | 1230 | 178 | 336 | 0.00 | | | |
| | 10 | 189 | 1260 | 183 | 336 | | Not sampled | | |
| | 20 | 189 | 1300 | 189 | 336 | | | | |
| | 25 | 188 | 1310 | 189 | 336 | 3.54 | | | |
| | 30 | 188 | 1310 | 194 | 336 | 3.54 | | | |
| | 40 | 188 | 1320 | 194 | 336 | 3.67 | | | |
| | 50 | 188 | 1350 | 200 | 336 | 3.63 | | | |
| | 100 | 188 | 1350 | 200 | 336 | 3.58 | 19.01 | 77.41 | 87.3 |
| 61g | 0 | 30 | 2250 | 60+ | 325 | | | | |
| | 10 | 30 | | | 325 | 0.73 | | | |
| | 20 | 30 | | | 325 | 1.43 | | | |
| | 30 | 30 | | | 325 | 1.81 | | | |
| | 40 | 30 | | | 325 | 2.33 | | | |
| | 50 | 30 | | | 325 | 2.58 | | | |
| | 70 | 30 | | | 325 | 3.28 | | | |
| | 90 | 30 | | | 325 | 3.77 | | | |
| | 130 | 30 | 2640 | 65+ | 325 | 4.21 | 18.70 | 77.10 | 123.0 |

+Approximate Values.

TABLE V

Closed Cycle Runs at Atmospheric Pressure, approaching Equilibrium from both Directions

| Expt. No. | Minutes duration at time of sampling | At electrodes: Current milli-amperes | At electrodes: Approx-imate voltage | Watts corrected for transformer losses | Velocity of gas thru arc. (stand. cond.) | Nitric oxide, per cent by volume | Oxygen per cent by volume | Nitrogen per cent by volume | K ($10^4$) |
|---|---|---|---|---|---|---|---|---|---|
| 61e See Table VII. | | | | | | | | | |
| 114 | 0 | 190 | 1350 | 202 | 335 | 6.67 | | | |
| | 15 | 190 | 1350 | 202 | 335 | 3.92 | | | |
| | 33 | 188 | 1340 | 197 | 335 | 3.52 | | | |
| | 45 | 186 | 1330 | 188 | 335 | 3.52 | | | |
| | 60 | 185 | 1350 | 193 | 335 | 3.44 | | | |
| | 75 | 188 | 1320 | 197 | 335 | 3.49 | | | |
| | 90 | 185 | 1340 | 193 | 335 | 3.52 | 17.24 | 79.24 | 90.6 |
| 115 | 0 | 185 | 1370 | 192 | 330 | 0.00 | | | |
| | 5 | 184 | 1400 | 197 | 330 | 1.72 | | | |
| | 10 | 182 | 1380 | 182 | 330 | 2.90 | | | |
| | 15 | 185 | 1400 | 199 | 330 | 3.72 | | | |
| | 20 | 185 | 1440 | 207 | 330 | 4.05 | | | |
| | 30 | 184 | 1450 | 204 | 330 | 4.60 | | | |
| | 60 | 183 | 1410 | 197 | 330 | 4.78 | | | |
| | 90 | 183 | 1410 | 197 | 330 | 4.78 | | | |
| | 100 | 183 | 1410 | 197 | 330 | 4.78 | 35.61 | 59.61 | 107.0 |
| 116 | 0 | 185 | 1410 | 199 | 330 | 8.02 | | | |
| | 5 | 185 | 1410 | 199 | 330 | 6.13 | | | |
| | 10 | 188 | 1400 | 204 | 330 | 5.81 | | | |
| | 15 | 188 | 1430 | 209 | 330 | 5.21 | | | |
| | 20 | 188 | 1430 | 209 | 330 | 4.90 | | | |
| | 30 | 188 | 1470 | 214 | 330 | 4.78 | | | |
| | 60 | 188 | 1480 | 219 | 330 | 4.78 | | | |
| | 90 | 188 | 1480 | 219 | 330 | 4.78 | 40.61 | 54.61 | 103.5 |

TABLE VI

Closed Cycle Runs at Atmospheric Pressure: Evaluation of Equilibrium Constants

| Expt. No. | Minutes duration at time of sampling | At electrodes: Current milli-amperes | At electrodes: Approximate voltage | Watts corrected for transformer losses | Velocity of gas thru arc. (stand. cond.) Liters per hour | Nitric oxide, per cent by volume | Oxygen, per cent by volume | Nitrogen per cent by volume | K (10⁶) |
|---|---|---|---|---|---|---|---|---|---|
| **100 to 200 Milliamperes.** | | | | | | | | | |
| 49a | 35 | 100 | 1500 | 109 | 328 | 3.60 | 19.00 | 77.40 | 88 |
| 49b | 50 | 193 | 1300 | 145 | 328 | 3.48 | 19.06 | 77.46 | 82 |
| 51a | 30 | 95 | 1850 | 143 | 634 | 3.39 | 19.10 | 77.50 | 78 |
| 51b | 70 | 193 | 1500 | 202 | 634 | 3.64 | 18.98 | 77.38 | 90 |
| 52a | 30 | 95 | 1600 | 114 | 478 | 3.54 | 19.03 | 77.43 | 85 |
| 52b | 50 | 188 | 1200 | 152 | 478 | 3.48 | 19.06 | 77.46 | 82 |
| 54 | 30 | 183 | 1300 | 197 | 340 | 4.10 | 63.30 | 32.60 | 82 |
| 55 | 20 | 183 | 1400 | 224 | 331 | 4.20 | 61.10 | 34.70 | 83 |
| 57 | 30 | 186 | 1500 | 221 | 334 | 3.06 | 83.97 | 12.97 | 82 |
| 58 | 30 | 182 | 1400 | 221 | 334 | 4.15 | 66.92 | 28.93 | 89 |
| 59 | 40 | 184 | 1200 | 205 | 331 | 4.38 | 46.31 | 49.30 | 84 |
| 60 | 25 | 187 | 1450 | 221 | 331 | 4.21 | 38.00 | 57.80 | 78 |
| 61a | 25 | 187 | 1350 | 187 | 328 | 3.34 | 19.13 | 77.53 | 75 |
| 61d | 25 | 190 | 1320 | 192 | 336 | 3.54 | 19.03 | 77.43 | 85 |
| 61e | 50 | 188 | 1350 | 190 | 336 | 3.63 | 18.99 | 77.38 | 88 |
| **30 Milliamperes.** | | | | | | | | | |
| 61g | 130 | 30 | 2640 | 65+ | 325 | 4.21 | 18.70 | 77.10 | 123 |
| 119 | 90 | 30 | 3000 | 70+ | 322 | 3.86 | 18.87 | 77.27 | 110 |
| 117 | 120 | 30 | 2800 | 75+ | 326 | 5.26 | 42.20 | 52.60 | 124 |
| 120 | 90 | 30 | 3000 | 80+ | 324 | 4.78 | 44.50 | 50.70 | 101 |
| 118 | 120 | 30 | 2800 | 75+ | 322 | 4.32 | 72.05 | 23.63 | 109 |
| 128 | 90 | 30 | 2800 | 80+ | 322 | 3.82 | 78.03 | 18.13 | 103 |

+Approximate Values.

(b) *Discussion of Closed Cycle Runs*

The rate of oxide formation experiments (Table IV and Fig. 7) afford interesting information concerning the fixation of nitrogen in the high tension arc. The data make possible the numerical calculation of the relative volumes occupied by the spark-like filaments or streamers in which the nitric oxide is formed and by the cooler gas (in the region between the electrodes) surrounding these filaments. The calculation of these relative volumes is based upon the relation of the concentration of the nitric oxide secured by a single passage of the gas through the arc to the concentration of the oxide at equilibrium. The method of calculation is brought out in the following example. In experiment 61d the nitric oxide concentration for the initial passage of air through the arc was 0.97 per cent; the equilibrium concentration, 3.55 per cent. The latter value is the NO concentration of the cooler gas which was in equilibrium with the gas coming from the filament at the particular tem-

perature at which the equilibrium was "frozen". By extrapolation from their experimental data, Nernst, Finckh and Jellinek[1] estimate the temperature corresponding to this concentration to be 3000° Abs.

In the initial passage through the furnace, the gas from the filament (3.55 per cent NO) was diluted with the air from the cooler zones which reduced the concentration of nitric oxide to 0.97 per cent. This means that out of every 100 cc. of gas which passed through the arc, 27.3 cc. passed through the filaments and 72.7 cc. through the adjacent cooler zones. In the second passage each 27.3 cc. of gas from the filaments (3.55 per cent NO) was cooled by mixing with 72.7 cc. of gas containing 0.97 per cent NO producing a concentration of 1.67 per cent NO. In the third exposure to the arc, each 27.7 cc. of 3.55 per cent gas from the filaments was diluted with 72.7 cc. of 1.67 per cent gas producing a concentration of 2.19 per cent NO. The content of nitric oxide for the succeeding passages may be calculated in a similar manner. The calculated and experimental values for the first 11 cycles are given in Table VII.

TABLE VII

Comparison of Observed and Calculated Nitric Oxide Concentrations for Successive Exposures to Arc

| Cycle | Per cent NO (calc.) | Per cent NO (observed) | Per cent NO (observed, corrected for dilution attending sampling.) |
|---|---|---|---|
| 1 | —— | 0.97 | 0.97 |
| 2 | 1.67 | 1.55 | 1.70 |
| 3 | 2.19 | 2.08 | 2.20 |
| 4 | 2.56 | 2.44 | 2.60 |
| 5 | 2.83 | 2.71 | 2.90 |
| 6 | 3.02 | 2.87 | 3.10 |
| 7 | 3.17 | 2.98 | 3.30 |
| 8 | 3.27 | —— | 3.40 (From curve.) |
| 9 | 3.35 | —— | 3.50 (From curve.) |
| 10 | 3.40 | —— | 3.50 (From curve.) |
| 11 | 3.44 | 3.54 | 3.54 |

The calculated nitric oxide content at the successive cycles corresponds with the observed values indicating that the assumptions made are close to the truth.

Upon the basis of the preceding assumptions and calculations an estimate of the energy efficiency for the most effective operation of an arc can be made. The energy required is that necessary to heat the air in arc filament (only) from room temperature to 3000° Abs. plus the heat of formation in the nitric oxide produced. According to Lewis and Randall,[2] the molal specific heat for air, oxygen, nitrogen and nitric oxide, is best represented by the equation:

$$C_p = (6.5 + 0.001T)$$

[1] Nernst, Finckh and Jellinek: Z. anorg. Chem., 45, 116, 126, (1905); 49, 213, 229 (1906).
[2] Lewis and Randall: J. Am. Chem. Soc., 34, 1128 (1912).

in which $C_p$ is the molal specific heat in calories at constant pressure and T is the absolute temperature. This equation is based upon experimental data reaching to 2000° Abs.; consequently, its application to higher temperature involves an extrapolation. However, this is the best data available so far as the writers are aware. The calculation of the heat required to heat one mol of air from 293° to 3000° Abs. is made by the integration of the equation $Q = C_p dT$ between the limits corresponding to these temperatures.

$$Q = \int_{293}^{3000} (6.50 + 0.001T)\ dT$$
$$= 6.5\,(3000 - 293) + 0.001/2\,(3000^2 - 293^2)$$
$$= 22052 \text{ calories.}$$

In addition to heating the air, 0.0355 mol of nitric oxide is formed. The molal heat of formation of nitric oxide is −21600 cal.; to form 0.0355 mol requires 767 calories. The total heat required is therefore, 22052 + 767 = 22819 calories.

The best efficiency (yield per kw-hr.) secured with the arc used in this investigation was obtained in experiment 64e, previously reported in Table I. The data are as follows: air velocity, 342 liters per hour; arc current 94 milliamperes; power at the electrodes, 125 watts; and the concentration of nitric oxide produced 0.76 per cent. The equilibrium concentration of nitric oxide for these conditions is 3.55 per cent. Using these concentrations as a basis, the calculated air passing through the arc filament is 22.5 per cent of the total air going through the furnace, or 76.95 liters (3.44 mols) per hour. The heat required for the heating of this quantity of air from 293° Abs. to 3000° Abs. is, 3.44 × 22819 = 78497 cal. The actual experimental energy was 125 watt hours, which is equivalent to 107500 calories. Hence, (78497 ÷ 107500) (100) or 73 per cent is the thermal efficiency obtained in this experiment in which the yield was 58 grams of nitric acid per kilowatt hour.

The value of the equilibrium concentration also permits the calculation of the maximum concentration of nitric oxide to be secured by a single passage of the gas through the arc. The velocity of decomposition of nitric oxide has been investigated by Jellinek[1] for the temperature range 689°C. to 1750°C. From this reaction constant and the equilibrium constant for the reaction, the reaction constant for the formation of nitric oxide can be determined. From these data the rates of formation and of decomposition of nitric oxide in any given mixture can be calculated[2]. The calculated time required for the decomposition at 1900° Abs. of 40 per cent of the nitric oxide present in an air mixture at 1 atmosphere containing initially twice the amount of this substance that will be present when equilibrium is established, is 2-1/2 minutes. At 1773° Abs. the time required for this amount of decomposition is 21

[1] Jellinek: Z. anorg. Chem., 49, 263 (1906).

[2] For details concerning the formulations and method of calculation, the reader is referred to pp. 134, Bulletin 2041, U. S. War Dept.; Report on the Fixation and Utilization of Nitrogen.

minutes. The gas from the arc zone should surely be cooled quickly to at least 1900° Abs. to "freeze" the equilibrium. Below this temperature the rate of decomposition will be sufficiently slow that the gas may be cooled less rapidly without appreciable loss of combined nitrogen. In suddenly chilling the gas from the arc filament from 3000° Abs. to 1900° Abs. the cold air will be heated to 1900° Abs. The amount of heat absorbed in heating one mol of air from 293° Abs. to 1900° Abs. may be estimated as follows:

$$Q = \int_{293}^{1900} (6.5 + 0.001T)\, dT$$
$$= 6.5\,(1900 - 293) + 0.001/2\,(1900^2 - 293^2)$$
$$= 12{,}207 \text{ cal.}$$

Previous calculations show that 22052 cal. are required to heat 1 mol of air from 293° Abs. to 3000° Abs. Then

$$22052 - 12207 = 9845 \text{ cal.}$$

the heat to be removed in cooling 1 mol of the gas from the arc filament to 1900° Abs. And 9845 ÷ 12207 = 0.806, the number of mols of cold air required to cool 1 mol of the gas from the filament. If the gas from the filament contains 3.55 per cent of nitric oxide (the equilibrium value) and is cooled without further decomposition by adding 0.806 mol of cold air, the cooled gas will contain 1.91 per cent of nitric oxide. This is the calculated maximum concentration of this substance that can be secured from an arc with cooling as effective as that accomplished in this investigation. This value closely approximates the maximum concentration of nitric oxide which has been secured in commercial practice with good energy efficiency, viz. 1.8 per cent by the Schönherr-Hesselberger furnace.

The equilibrium concentrations (closed cycle runs) for the different amperage arcs indicated that the "freezing" of the equilibrium by mixing with cold air in the furnace was very effective. From Jellinek's data the estimated time for the decomposition at 3000° Abs. of 40 per cent of the nitric oxide in an air mixture containing 200 per cent of the equilibrium concentration of this substance, is $1.2 \times 10^{-5}$ seconds. The writers realize that this reaction velocity was obtained by extrapolation from experimental data secured at lower temperatures. Nevertheless, the rapidity with which the equilibrium was "frozen" with this type of whirling arc is almost incredible.

Many cycles were required to secure equilibrium with currents of 30 milliamperes. This indicates that the volume of the gas passing through the filament was small compared to the volume passing through the surrounding cooler zones, being of the order of a fraction of a per cent. The meagre data so far secured hardly justify the calculation of the actual volume of the filament. However, the results show that a reduction in the arc current strength decreases the effective volume of filament. Furthermore, there is no indication that decrease of current is necessarily attended by a change of the average kinetic energy of the particles in the filament.

The closed cycle experiments furnish trustworthy data (see Tables V and VI) concerning the application of the law of mass action to the fixation of

atmospheric nitrogen in the high tension arc having good energy efficiency. The curves in Fig. 9 show in each case that the concentration of nitric oxide at equilibrium increases in a regular manner to a maximum value as the volumes of nitrogen and oxygen forming the mixture become equal. Furthermore, the consistent values for the equilibrium constant for a series of experiments at a given current strength are in close accord with the mass action law. The difference in the values of the equilibrium constants for arcs of different current strengths is due to the "freezing" of the equilibrium at different temperatures. The writers have not obtained thus far any evidence with the experiments carried out, of any deviation from the mass action law due to any special "electrical effects".

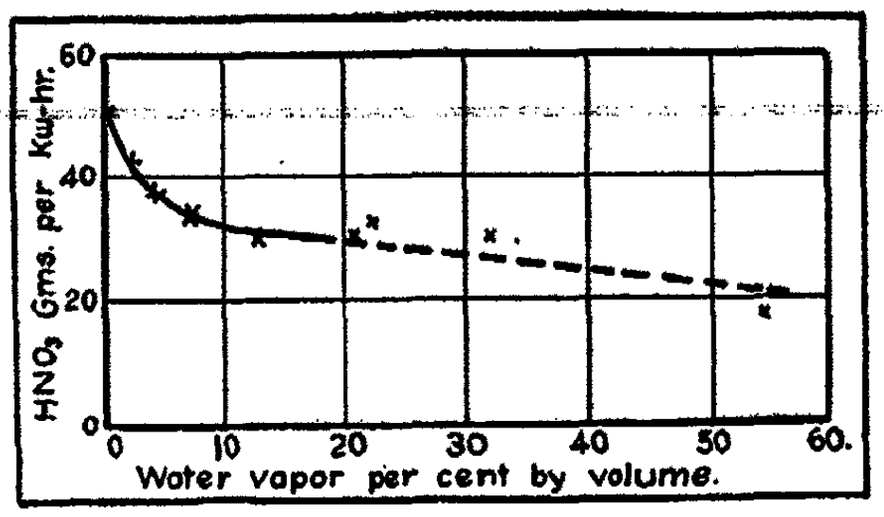



FIG. 10
The Effect of Water Vapor. Direct Runs at Atmospheric Pressure.

## The Effect of Water Vapor

In the arc fixation of nitrogen in commercial quantities the oxygen-nitrogen mixture is simply air. Since the atmosphere contains moisture, information regarding its effect on fixation was determined for mixtures of air and water vapor in which the moisture content ranged from 2 to 50% by volume. The results are given in Table VIII and Fig. 10. In this series of experiments the arc furnace was inverted to prevent short-circuiting the high tension electrode due to condensation after passing through the arc of water from mixtures high in moisture.

The values for experiments with a moisture content as high as fifteen per cent are accurate, but the precision is somewhat less in the runs containihg a greater amount of water vapor because of a tendency toward premature condensation of the moisture. Ample precautions were taken in the analyses to prevent any loss of fixed nitrogen due to a film of moisture on the walls of the apparatus. In order to carry out the experiments with the greatest precision, the entire furnace should be inclosed in a thermostat at a temperature somewhat above the dew point of the air-water mixture used. The authors have not yet had the opportunity to arrange an apparatus of this sort. Consequently, the experiments made thus far with higher percentages of water vapor may be somewhat in error.

These findings show that even with 2.6% moisture, which corresponds to 100 per cent humidity at 22°C., the yield was reduced to 42.1 grams of nitric acid per kilowatt hour which is a 25% decrease in production. Evidently a small amount of moisture may cause a very appreciable decrease in yield.

TABLE VIII

The Effect of Water Vapor

Direct Runs at Atmospheric Pressure on Moist Air

| Expt. No. | Current Milli-amperes | Approx. voltage | Watts corrected for transformer losses | Velocity of gas thru arc. Liters per hour. (Stand. cond.) | Water vapor per cent by volume | Nitric oxide per cent by volume | Gms. $HNO_3$ per kw.-hr. |
|---|---|---|---|---|---|---|---|
| 33 | 96 | 1740 | 136 | 2.6 | 2.6 | 0.56 | 42.1 |
| 34 | 97 | 1700 | 136 | 4.4 | 4.4 | 0.49 | 37.5 |
| 35 | 97 | 1810 | 151 | 7.5 | 7.5 | 0.47 | 33.8 |
| 36 | 96 | 1810 | 151 | 13.7 | 13.7 | 0.39 | 30.7 |
| 30 | 94 | 1720 | 129 | 20.8 | 20.8 | 0.34 | 30.2 |
| 29 | 94 | 1710 | 128 | 21.9 | 21.9 | 0.35 | 32.7 |
| 38 | 96 | 1680 | 141 | 32.0 | 32.0 | —— | 30.2 |
| 39 | 92 | —— | 153 | 54.3 | 54.3 | 0.136 | 18.0 |

## Acknowledgment

Grateful acknowledgment is made to the E. I. du Pont de Nemours and Company for the grant of a fellowship which made possible this investigation.

## Summary

1. A satisfactory laboratory arc furnace with good energy efficiency has been constructed.

2. A high gas velocity favored a high yield of fixed nitrogen per kilowatt hour but gave a lower per cent by volume of nitric oxide. Excessively high air velocities gave a low output in respect to both yield and concentration of fixed nitrogen.

3. The use of reduced pressure (with a gas velocity suitable for a good yield of fixed nitrogen at atmospheric pressure) gave a decrease both in the concentration of nitric oxide and in yield of fixed nitrogen per kilowatt hour.

4. A study has been made of the equilibria obtained with various mixtures of nitrogen and oxygen using a high tension arc with different amperages. The results show that the mass action law applies to the equilibria obtained. The temperatures at which the equilibria were "frozen" show that the cooling from the whirling arc is very efficient.

5. A method has been given which permits the calculation of the concentration of nitric oxide resulting from repeated exposures of a nitrogen-oxygen mixture to a high tension arc.

6. A value, based upon experimental data, has been given for the theoretical maximum concentration of nitric oxide that may be obtained with an arc, at an energy efficiency equivalent to 60 grams of nitric acid per kilowatt hour, for air supplied at room temperature and atmospheric pressure.

7. The presence of water vapor in the air supplied to the arc reduced both the yield and the concentration of the nitric oxide.

# ORGANOGELS OF SILICIC ACID—THE REPLACEMENT OF WATER IN THE HYDROGEL BY ALCOHOL

BY J. B. FIRTH AND W. L. PURSE

Graham[1] showed that various organic liquids were capable of displacing the water of the hydrogel of silicic acid. Thus in the case of alcohol he says of hydrated silicic acid, "the combined water leaves the acid to diffuse into the alcohol and if the alcohol is repeatedly changed the *entire* water is thus removed, alcohol at the same time taking the place of water in combination with the silicic acid. The process is reversed if an alcogel be placed in a considerable volume of water. Such changes illustrate the predominating influence of mass."

Graham's results show that an alcogel prepared and analysed by him contained 383 parts of alcohol to one part of water.

Bachmann[2] showed that the weight of different liquids taken up by silica gel is proportional to their density. Measurements with water, benzene, chloroform, ethyliodide and acetylene tetrabromide gave concordant results.

Neuhausen and Patrick[3] came to the conclusion that it is impossible to remove all the water from the hydrogel of silicic acid by repeated immersions in anhydrous alcohol, acetone or benzene. They state that their results indicate that Graham was in error when he stated that it is possible to replace all the water from a silica hydrogel by other liquids. They are of the opinion that the residual small percentage of water in silica gel is held with a force that exceeds that exhibited between atoms of many stable compounds.

The authors being desirous of preparing, if possible, an alcogel of silicic acid free from water carried out experiments with this object in view, and the results are described in the present communication.

## Experimental

*Preparation of Gels.* The sodium silicate used was specially prepared and was free from iron and gave no indication of carbon dioxide with hydrochloric acid. The composition corresponded to $1Na_2O:2SiO_2$. A solution of density 1.118 was prepared and added to an equal volume of 3N hydrochloric acid.

A series of gels were prepared as follows:—

(a) The acid and silicate solutions were heated to 45° and after mixing, the product maintained at 45° until the gel had set. The resulting gel was then washed with hot distilled water until free from sodium chloride, then dried in a steam oven, heated in an air oven at 320°, again washed with distilled water and finally allowed to dry at room temperature. The resulting gel contained 33 per cent of water.

[1] Graham: J. Chem. Soc., 17, 318 (1864); Pogg. Ann. 123, 529 (1864).
[2] Z. anorg. Chem., 79, 202-208 (1913).
[3] J. Am. Chem. Soc., 43, 1844-6 (1921).

(b) Solutions mixed at 50° and allowed to set at this temperature. The resulting gel was free from sodium chloride and dried at 120°. The resulting gel contained 10.83 per cent of water.

(c) Solutions mixed and gel allowed to set at room temperature. The gel was then washed free from sodium chloride and dried at 100°. The product contained 7.53 per cent of water.

(d) The gel was prepared as in (c) but was dried at 100° without washing out the sodium chloride. A greater portion of the sodium chloride was expressed from the gel during drying.[1]

The resulting product was then washed free from sodium chloride and finally dried at 110°, after which the water content was 14.7 per cent.

### Treatment of the Gels with Alcohol

The alcohol used was dried first over pure lime and finally over metallic calcium. The alcogels were prepared by two methods:—

(a) The gel was immersed in the dry alcohol (1 gram of gel to 150 cc of alcohol) at room temperature and allowed to stand for two days, after which the treatment was repeated three times.

(b) A current of dry air was saturated with alcohol vapour and passed over the gel. The gel was contained in a tube of 5 m.m. bore and fitted with two taps. The tube containing the gel was weighed at intervals, the experiment being continued until no change of weight could be detected over a period of three hours, a condition which it usually required three days to attain.

### Results

The alcogels obtained by both the above methods were analysed by the usual combustion methods of organic chemistry.

Towards the end of the combustion the boat containing the gel was raised to a bright red heat (above 900°) in order to drive off the last traces of water out of the gel.

From the amounts of carbon dioxide and water formed, the percentage of alcohol and water in the gel were calculated. Typical results obtained are given in Table I.

TABLE I

| Method of preparation of gel. | Original% of water. | Dynamic Method. %Alcohol. | %Water | Static Method. %Alcohol. | %Water |
|---|---|---|---|---|---|
| a | 33.0 | 32.18 | 0.73 | 22.73 | 9.81 |
| b | 10.83 | 30.92 | 0.64 | 25.38 | 5.12 |
| c | 7.53 | 30.30 | 0.57 | 24.25 | 5.82 |
| d | 14.7 | 29.09 | 1.11 | 24.23 | 7.06 |

### Discussion

From the above results it would appear that the extent of the replacement of water by alcohol in a silicic acid gel is very markedly affected by the method adopted.

[1] Cf. Fells and Firth: J. Phys. Chem., 29, 241-248 (1925).

Within the limits of the experiments described the replacement of the water is much greater by the dynamic method than by the static method.

Although in our experiments we have not been able to reduce the water content to a value as low as that obtained by Graham, we do not regard Graham's result as impossible. The *complete* replacement of the water by alcohol would no doubt, be very difficult to attain and it seems very probable that the removal of the last traces of water would be a very slow process at ordinary temperatures, particularly by the static method.

Certain of our results by the static method are in fair agreement with those of Neuhausen and Patrick (loc. cit.), yet by the dynamic method much more complete replacement has been obtained. Hence we are of the opinion that the limited results of Neuhausen and Patrick do not justify their conclusion that Graham's results are erroneous. Hoffert[1] and others have shown that the sorptive capacity of a silicic acid gel may vary over quite a wide range; the method of preparation, water content, age of the gel and packing density being some of the factors concerned. Again it has been shown by Hoffert (loc. cit.) that the retentivity of the gels, for example in the case of benzene, also varies.

From our results, under the conditions described, it would appear that the retentivity of water varies with the different gels employed. That some of the water is more tenaciously held does not preclude its *ultimate* replacement under the most suitable conditions.


## Summary

1. The replacement of water by alcohol of four silicic acid gels prepared under different conditions and of different initial water content have been examined.

2. Within the limits of the experiments, the replacement is more complete by the dynamic method than by the static method.

3. The most complete replacement gave a final water content of 0.57 per cent associated with 30.3 per cent of alcohol; the initial water content being 7.53 per cent.


We desire to thank the Department of Scientific and Industrial Research for a grant which enabled one of us (W. L. P.) to take part in this work.

*University College,*
*Nottingham,*
*England.*
*Feb. 2 (1926).*

[1] J. Soc. Chem. Ind., 44, 360T (1925).

# THE REACTIVE NATURE OF ALDEHYDES FROM THE STANDPOINT OF THE APPARENT ELECTROMOTIVE FORCE

BY SAUL B. ARENSON, PLEASANT ERNEST ROLLER AND D. J. BROWN

Haber and Russ[1] were the first to show that for the reversible oxidation and reduction of organic compounds the same factors are involved as for the same type of inorganic reactions. Later work[2] confirms their conclusions for this class of organic compounds. For organic substances that are oxidized or reduced irreversibly, except to show that some of them develop an apparent electromotive force, very little appears in the literature. Baur[3] showed that the alkaline solutions of aldehydes show a large variation in the apparent electromotive force on standing. Stieglitz[4] demonstrated that alkaline solutions of formaldehyde may be used as the negative electrode of a cell to deposit silver from solution at the other electrode apparently reacting the same as a reversible reducing agent. Other alkaline solutions of aldehydes react the same. St. Bugarszky[5] found that the velocity of reduction by aldehydes is inversely proportional to the concentration of the hydrogen ions. While no quantitative measurements are available, apparently the other reactions of aldehydes are affected similarly by the relative concentration of the hydrogen ions.

The following observations were made to secure further information on the relation of the apparent electromotive force to the alkalinity of the solutions and the reactions of aldehydes.

## Experimental

Since preliminary experiments indicated that the apparent electrode potentials of the aldehydes were approximately of the same value as the oxygen electrode, all operations from the preparation of the solutions to the final measurement of the electromotive force were made in an atmosphere of nitrogen. This nitrogen was prepared by passing air or commercial nitrogen thru a chain of bottles filled with copper foil in contact with a solution of ammonium chloride and quite concentrated ammonia, then with the ammonia vapor thru a silica tube containing a tightly wound copper gauze heated to 500-600°C. The excess ammonia was removed by passing the nitrogen thru solutions of sulfuric acid.

"Conductivity water" was used to prepare all solutions. The acid solutions were prepared by recrystallizing $H_2SO_4.H_2O$ twice from conductivity water and then diluting. The sodium hydroxide solutions were prepared by dropping metallic sodium into a two-phase mixture of ether and water, the ether was evaporated in vacuo, and the concentrated solution diluted.

---

[1] Haber and Russ: Z. physik. Chem., 47, 257 (1904).
[2] Clark: Chemical Reviews, 2, 127 (1925).
[3] Baur: Ber., 34, 377 (1901).
[4] Stieglitz: Science, 27, 775 (1907).
[5] St. Bugarszky: Z. physik. Chem., 48, 63 (1904).

The acetaldehyde was prepared from paraldehyde by the method of McLeod[1]. The temperature of the condenser was maintained at 22° ± 2C. It was collected in an oxygen-free container, which in turn was emptied by pressure into a two-liter flask and diluted with conductivity water at 0°C. The strength of the acetaldehyde solution was determined by the method of Seyewetz and Bardwin[2], in which the aldehyde is titrated in the presence of sodium sulfite with a standard acid.

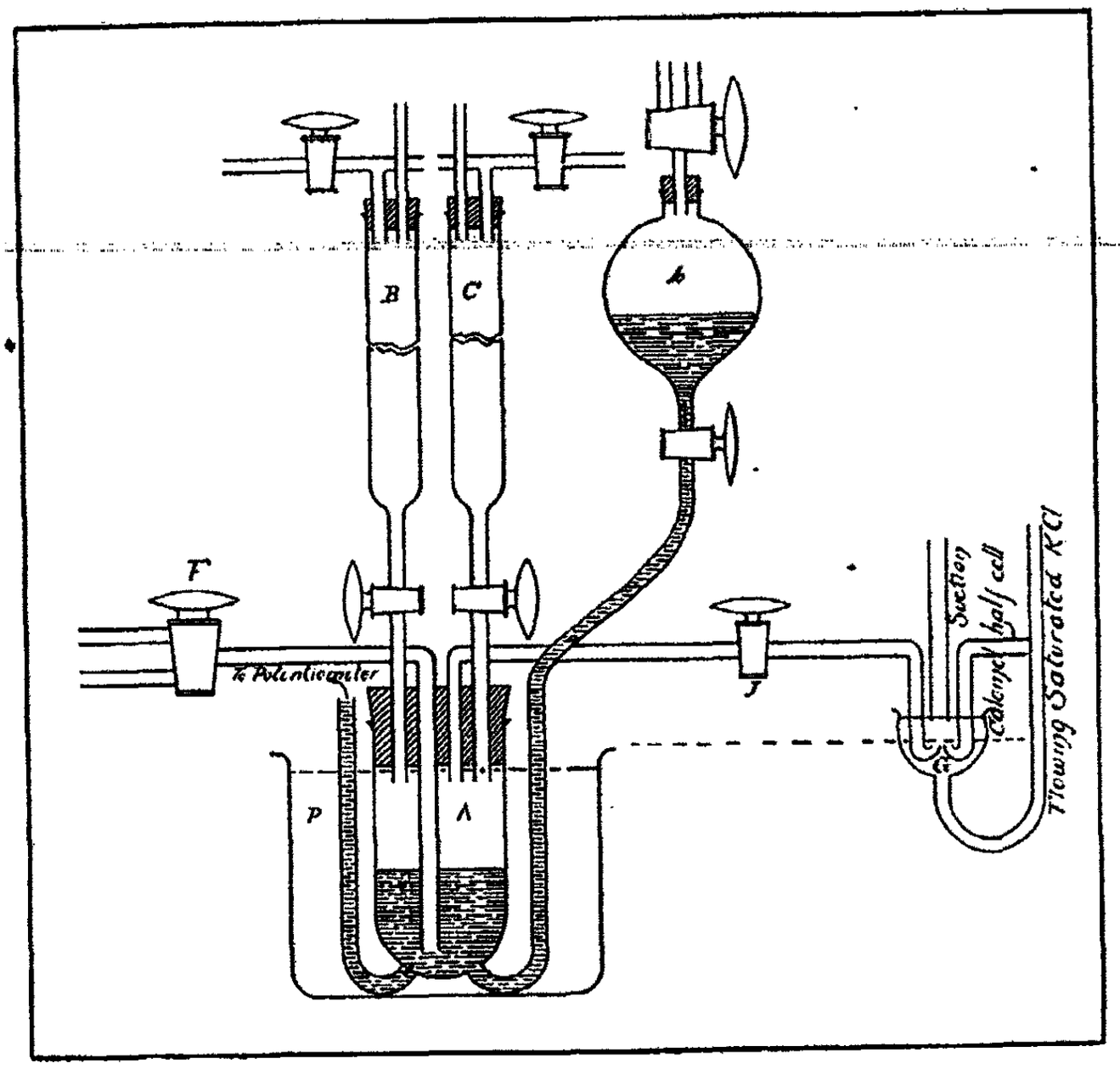



FIG. 1
Aldehyde Half-cell.

Chloral hydrate best grade was recrystallized from carbon bisulfide which had been shaken with lead carbonate and then distilled.

The potentials of the aldehyde half-cell were measured in terms of the calomel electrode by means of a Weston cell, a Leeds and Northrup Type K potentiometer, and Type R galvanometer. Both electrodes were kept in beakers of distilled water which were in a thermostat at 25° ± .05 C. All work except the titrations was done in a room lighted by ruby lights.

[1] McLeod: Am. Chem. J., 37, 20 (1907).
[2] Seyewetz and Bardwin: Bull., 33, 1000 (1905).

The results were obtained by the use of the container for the aldehyde solutions shown in Fig. 1. Tube P was filled with mercury and sealed at the bottom with a platinum insert to complete the circuit from the mercury within the container to the potentiometer. When an observation was being made, the contents of the electrode chamber was caused to flow slowly into the flowing saturated potassium chloride bridge, G. The procedure was as follows:

Mercury from M was forced into A, the contents of A flowed thru J into G. "Oxygen-free" water was then admitted thru F to A while the surface of the mercury was lowered, J being kept closed. F was closed and the container emptied as stated in the first sentence. After A was completely washed, the balance of the water was removed by admitting nitrogen thru F. By means of nitrogen, solutions kept in thermostats were forced into burets, B and C, and then the measured quantity of each was forced into the electrode chamber, A, and immediately stirred by the nitrogen thru F for several seconds, F was closed and mercury from M was allowed to force sufficient of the solution thru J to make a circuit thru G with the calomel electrode—by rapid manipulation it was found possible to make the first observation of the electromotive force within one minute after the solutions were admitted to the electrode. After each reading J was closed. A little mercury was permitted to enter A before each subsequent reading, thus securing the flow while the reading was being made.

## Results

For approximately molar solutions of acetaldehyde and chloral hydrate in normal sodium hydroxide the velocity of change in the observed electromotive force was very large. For this concentration with acetaldehyde the results check those given by Baur[1]. The results with the more dilute solutions of acetaldehyde in sodium hydroxide were as follows:

| + .071 molar acetaldehyde, | | | | .0105 normal sodium hydroxide | | | |
|---|---|---|---|---|---|---|---|
| 2 min | −.1180 | 2 min | −.1186 | 3 min | −.1223 | 2 min | −.1179 |
| 4 | .1255 | 4 | .1286 | 5 | .1263 | 5 | .1183 |
| 7 | .1280 | 6 | .1300 | 17 | .1285 | 9 | .1199 |
| 10 | .1179 | 12 | .1290 | 29 | .1275 | 19 | .1193 |
| 22 | .1112 | 30 | .1253 | 107 | .1229 | 89 | .1110 |
| | | 114 | .1245 | | | | |

The mean minimum results for the concentrations studied were

| Acetaldehyde | Sodium hydroxide | E.M.F. |
|---|---|---|
| .071 molar | .0105 normal | −.128 volts |
| .017 | .0105 | −.113 |
| .0121 | .00525 | −.092 |
| .0263 | .0525 | −.155 |
| 1.0 | 1.0 | −.239 |

[1] Baur: Ber., 34. 377 (1901).

An attempt was made to determine the effect of the added oxidized state as would be expected from the reactions studied by Evans[1]. For this reason the observations were made in the .0263 normal sodium hydroxide to determine the effect due to the addition of acetate and of oxalate. The average minimum values were,

| | | |
|---|---|---|
| .054 molar acetaldehyde | | −.153 |
| .054 " " | + sodium acetate, .020 N | −.158 |
| .076 molar acetaldehyde | | −.163 |
| .076 " " | + potassium oxalate, .020 N | −.160 |

The variations in the presence and absence of the added salt with time were the same.

Since it was not possible to secure reproducible results in acid solutions of acetaldehyde, chloral hydrate was studied. The decomposition of chloral hydrate in water was observed by titrating the acid formed by 100 ml. of the following solutions:

| Chloral hydrate | Ml. .014 base 1/3 hr. | 2 hr. | 20 hr. | Maximum $H^+$ |
|---|---|---|---|---|
| .0140 molar | 1.4 | 1.4 | 2.2 | .0003 N |
| .0280 | 2.6 | 2.7 | 2.8 | .0004 |
| .0560 | 2.7 | 3.9 | 4.2 | .0006 |

The titration of hundredth normal acid after it had stood several days in the presence of chloral hydrate indicated that none of the chloral hydrate had decomposed.

The values given below are representative of the observations made during the first few minutes. Since the velocity of change is very great, the time is indicated in seconds to the nearest multiple of 5. To show the effect of changing acidity, results for .005 molar chloral hydrate only are given, except one series of observations to show the effect in acid solutions of the oxidized state, trichlor acetate.

.0050 molar chloral hydrate, .180 normal sulfuric acid

| | | | | | |
|---|---|---|---|---|---|
| 45 sec. | +.206 | 50 sec. | +.209 | 50 sec. | +.210 |
| 105 | +.229 | 80 | +.228 | 80 | +.223 |
| 135 | +.227 | 180 | +.229 | 110 | +.228 |
| 220 | +.224 | 270 | +.228 | 215 | +.229 |

.005 molar chloral hydrate, .0180 normal sulfuric acid

| | | | | | |
|---|---|---|---|---|---|
| 35 sec. | +.181 | 35 sec. | +.179 | 75 sec. | +.188 |
| 90 | .192 | 90 | .192 | 120 | .196 |
| 140 | .198 | 130 | .194 | 175 | .199 |
| 290 | .203 | 250 | .199 | 220 | .204 |
| 330 | .204 | 495 | .206 | | |

[1] Evans: J. Am. Chem. Soc., **44**, 1543, 1730 (1922).

Same as preceding + .0046 molar sodium trichlor acetate

| | | | | | |
|---|---|---|---|---|---|
| 45 sec. | + .179 | 35 sec. | + .180 | 30 sec. | + .181 |
| 90 | .190 | 85 | .189 | 105 | .196 |
| 165 | .198 | 165 | .196 | 160 | .197 |
| 260 | .202 | 265 | .200 | 215 | .198 |

.0050 molar chloral hydrate, .0062 N barium hydroxide

| | | | | | |
|---|---|---|---|---|---|
| 55 sec. | + .118 | 40 sec. | − .125 | 40 sec. | − .123 |
| 110 | .120 | 90 | .127 | 85 | .128 |
| 160 | .124 | 120 | .125 | 215 | .129 |
| 230 | .123 | 275 | .119 | 330 | .125 |
| 280 | .118 | 420 | .116 | 650 | .106 |
| | | 900 | .102 | 840 | .103 |

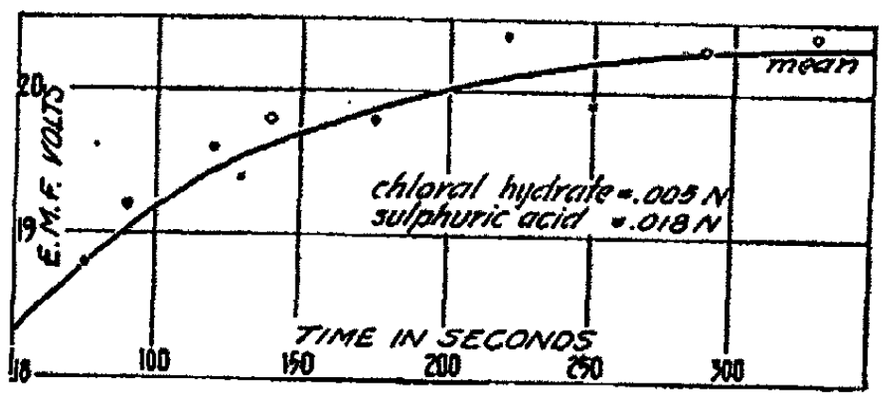



FIG. 2

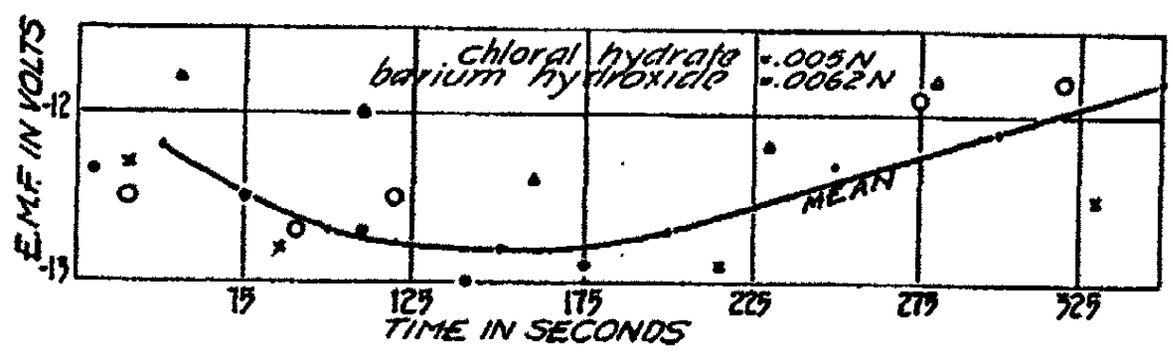



FIG. 3

Median curves to fit the data for the alkaline chloral hydrate solution, and the .018 normal acid solution are given in Figs. 2 and 3.

The velocity of decomposition of alkaline solutions of chloral hydrate was observed. The solutions were allowed to stand in the thermostat for the desired length of time, then the decomposition was stopped by adding an excess of standardized acid, and the excess acid was titrated with barium hydroxide solution, using phenol-phthalein as indicator. Since the reaction at this temperature was very rapid, especially for those in which the concentration of the base was relatively large, the results are not exceedingly accurate. The constants for reactions of the second order were calculated from the standard equations,

$$K_1 = \frac{1}{ta} \cdot \frac{x}{a - x}$$

and,

$$K_2 = \frac{1}{t(a - b)} \ln \frac{b(a - x)}{a(b - x)}$$

A third constant, $K_x$, was calculated on the assumption, for calculation only, that the concentration of the reactive aldehyde was equal to the concentration of the base.

a = concentration of chloral hydrate,
b = concentration of barium hydroxide,
x = decrease in concentration of the base.

For b = a

| t | b | x | $K_1$ | t | b | x | $K_1$ |
|---|---|---|---|---|---|---|---|
| 0 | .0070 | .0000 | | 0 | .0560 | .0000 | |
| 90 sec. | | .00106 | .283 | 60 | | .0263 | .264 |
| 150 | | .00168 | .301 | 120 | | .0363 | .274 |
| 200 | | .00206 | .298 | 200 | | .0425 | .280 |
| 660 | | .00406 | .299 | 325 | | .0471 | .290 |
| 1140 | | .00493 | .290 | | | | |

For b = 2a

| t | b | x | $K_2$ | $K_x$ |
|---|---|---|---|---|
| 0 | .00625 | 0 | | |
| 15 | | .00050 | 1.94 | .42 |
| 60 | | .00139 | 1.80 | .61 |
| 180 | | .00241 | 1.77 | .57 |
| 250 | | .00276 | 2.02 | .51 |
| 0 | .01135 | 0 | | |
| 40 | | .00304 | 2.00 | .80 |
| 50 | | .00339 | 1.94 | .78 |
| 75 | | .00420 | 2.07 | .69 |

For a = 2b

| t | b | x | $K_2$ | $K_x$ |
|---|---|---|---|---|
| 0 | .00595 | 0 | | |
| 40 | | .00037 | .137 | .27 |
| 60 | | .00039 | .097 | .21 |
| 110 | | .00056 | .077 | .16 |
| 250 | | .00103 | .068 | .14 |

For acetaldehyde in alkaline solution the following facts only were observed: The base on standing in presence of the aldehyde did not change its concentration. For .054 and .144 acetaldehyde in .0263 normal sodium hydroxide, for the same intervals of time the same fraction of the aldehyde had decomposed when determined by the method given above.

## Discussion of the Results

The oxidized state has no effect on the apparent electromotive force, a contrast to the reversible type of electrode.

The reduced state affects the apparent electromotive force proportionally to its concentration and to the concentration of the hydroyl ion, the same as for a reversible electrode like $H_2S - S°$. The difference in the two curves in Fig. 2 is due to the fact that the reactive form may be formed less rapidly than in the ionization of the hydrogen sulfide. The subsequent rise in the curve in alkaline solution is due to the decomposition of this reactive form. The rise in the curve for acid solutions of chloral hydrate to a maximum is due to the decrease in concentration of this reactive form to a minimum by the formation of the inactive form.

The velocity of decomposition of the chloral hydrate at first appears anomolous, but as shown by the approximation $K_x$, if we assume that the reaction is due to the active form whose equilibrium with the inactive form is determined by the concentration of the base, it may be possible to account for the variations of the constants for a dimolecular reaction.

The velocity of condensation of the acetaldehyde in a solution of a base of definite concentration is apparently a reaction of the first order.

The velocity of reduction, as reported by St. Bugarszky, for aldehydes is inversely proportional to the concentration of the hydrogen ion.

In all the preceding reactions of the reduced state and in the change of electromotive force, the concentration of the hydroxyl ion seems to be one of the determining factors.

By the assumption of the equilibrium reaction

$$R{-}C(H)=O \rightleftharpoons R{-}C{-}OH \rightleftharpoons R{-}C{-}O^- + H^+$$

in which the bivalent carbon is the reactive form, all the preceding admit of simple interpretation,—the key is the fact that the bivalent carbon radical in solution is directly proportional to the concentration of the hydroxyl ion.

Then the apparent electromotive force, $E_a$, would be at 25°C, assuming the effect to be due to the bivalent carbon,

$$E_a = E_o - .06/n \log [RCHO] [OH]$$

The changes of $E_a$ as indicated by the curves for acid and alkaline solutions are due to the velocity of the change to equilibrium. This is reached in acid solutions of chloral hydrate in a few minutes, but in alkaline solutions the chloral hydrate, and the acetaldehyde decrease in concentration due to chemical reaction, and the curves reach a minimum value which would not be the true equilibrium values for the solutions as prepared.

In alkaline solutions, for the determinations made with one concentration of base, the velocity of condensation of the acetaldehyde is proportional to the concentration of the acetaldehyde. This indicates that the determining

factor in the velocity of the reaction may be the formation of the bivalent carbon, and the latter condenses comparatively rapidly.

In neutral solution the chloral hydrate decomposes until a certain degree of acidity is reached. This is due to the decrease in concentration of the bivalent carbon form in the equilibrium reaction as stated above on account of the formation of the formic acid. In molar solutions of a base the velocity of decomposition of chloral hydrate is almost instantaneous, but in the concentrations of base where fairly accurate observations could be made, the concentration of the base seems to be the determining factor. From the above equilibrium reactions this may be interpreted as due to the dissociation of the ionized bivalent carbon form and its reaction with the base or with the water of the solution as an instaneous reaction, thus

$$Cl_3C.CO^- \quad Cl_3C^- + +CO^-$$

or

$$Cl_3C.CO^- + HOH \quad Cl_3CH + HCOO^-$$

## Summary

The apparent electromotive force of acetaldehyde and chloral hydrate was determined as affected by the concentration of the hydroxyl ion.

The velocity of decomposition of chloral hydrate in dilute alkaline solutions was studied.

A theory was advanced to correlate the observations,—the apparent electromotive force is due to the bivalent carbon radical in solution as the reduced state, which for this state has all the properties of the reduced state in an electrode that satisfies the conditions of a reversible electrode, but the oxidized state is passive.

*University of Nebraska,*
*Lincoln, Nebraska.*

# STUDIES IN ADSORPTION. XIII.
# SCHULZE-HARDY LAW AND ADSORPTION

BY N. R. DHAR AND S. GHOSH

In a previous report[1] of this series we made the following observations:—"It is of interest to note that those substances, which can form complex salts with the adsorbent are likely to be adsorbed most. Thus Ishizaka[2] has shown that potassium salicylate, potassium ferrocyanide and potassium oxalate are adsorbed most by $Al(OH)_3$. Similar results are obtainable with $Fe(OH)_3$. Evidently the phenomenon of adsorption is most marked when there is some sort of chemical affinity between the adsorbent and the substance, which is being adsorbed".

"It appears that hydrated manganese dioxide, which behaves like $H_2MnO_3$ and is also acid to litmus can adsorb large quantities of OH ions, because an acidic substance has naturally a great affinity for OH ions".

"We have observed that the basic portion adsorbed by hydrated manganese dioxide from substances like $BaCl_2$, $CuSO_4$, $Al_2(SO_4)_3$, $AgNO_3$, etc., cannot be removed by washing, whilst the basic portion adsorbed by hydrated manganese dioxide from NaCl, KCl, etc., can be removed slowly but completely by washing. Consequently the adsorption of the basic portion of these electrolytes is more or less permanent. Exactly similar results are obtained with hydrated silica, the basic portion adsorbed from NaCl, KCl, etc., can be removed slowly but completely by washing, whilst the basic portion adsorbed from $CuSO_4$, Alum, etc., cannot be removed by washing. Just as manganese dioxide is capable of adsorbing both acids and bases, similarly silica can adsorb both acids and bases and a base is more adsorbed than an acid, because silica is acidic in nature. The amount of adsorption of acids by silica is very small and is only a few percent of the total quantity of the acid taken. This adsorption is more or less due to the surface effect, and is allied to the adsorption of substances by charcoal, but the adsorption of bases by silica is connected with chemical affinity and is more permanent".

"Moreover it has been observed that the bigger the particles in a medium, the greater is its adsorption by an adsorbent".

"From our experiments on adsorption we find that substances like freshly precipitated $Fe(OH)_3$, hydrated $MnO_2$, etc., have marked adsorptive power and are in certain respects comparable to charcoal, whilst substances like $As_2S_3$, $Sb_2S_3$, $BaSO_4$, etc., have very slight adsorptive power, though all these substances can adsorb appreciably electrolytes in the course of their formation. Consequently the uncharged substances like $As_2S_3$, $Sb_2S_3$, etc., cannot adsorb the precipitating ions to any appreciable amount. Hence the amount of different ions adsorbed by $As_2S_3$, $Sb_2S_3$, etc., in the process of

[1] J. Phys. Chem., 28, 457 (1924).
[2] Z. physik. Chem., 83, 97 (1913).

coagulation is more or less equivalent, as was shown by Whitney and Ober[1] and Freundlich[2]. On the other hand, the neutralized substances like hydrated $MnO_2$, $Fe(OH)_3$, etc., are capable of adsorbing appreciably the precipitating ions; hence in these cases the amount of ions adsorbed by a coagulating sol is bound to be different and are not in equivalent proportion".

"We are of the opinion that charge reversal, amount of adsorption and complex formation go hand in hand and depend upon the chemical affinity existing between the adsorbent and the substance which is being adsorbed".

In the same paper it was also observed that "In Weiser and Sherrick's[3] experiments on the adsorption of substances by $BaSO_4$ in the course of precipitation it is found that those ions which form sparingly soluble barium salts are adsorbed most, because sparingly soluble salts are more allied to barium sulphate". More or less similar results were obtained by us[4] in the adsorption of electrolytes by $BaSO_4$, obtained by the interaction of $Ba(OH)_2$ and $H_2SO_4$. Very recently Beekley and Taylor[5] have got similar results with AgI as the adsorbent. They have shown that less soluble salts are more strongly adsorbed and more soluble salts are weakly adsorbed by AgI.

In the same paper from a survey of the experimental results on adsorption and coagulation we have given a new interpretation of the Schulze-Hardy law when applied to adsorption experiments. Recently our interpretation of the Schulze-Hardy law has been adversely criticized by Weiser[6]. Our interpretation of the Schulze-Hardy law is that in general an ion, which has a small coagulating power for a colloid, is most adsorbed by the colloid in question. Inversely the greater the coagulating power of an ion the less is its adsorption. Hence it follows that an ion of higher valency is less adsorbed than an ion of lower valency. We shall prove in the following pages that this view of the Schulze-Hardy law is both theoretically and experimentally sound.

We shall first show that the interpretation of the Schulze-Hardy law hitherto held that the greater the valency of an ion the greater is its amount of adsorption is fallacious from the following arguments:—

(a) From experiments on coagulation of many sols with different electrolytes it is now established at least qualitatively that the greater the valency of the oppositely charged ion the greater is its coagulating power. This is really what is known as the Schulze-Hardy law, and this deduction is quite sound as it is based on experiments.

(b) Several workers in this field notably Freundlich[7], Bancroft[8], Weiser[9] and others have tacitly assumed that the greater the adsorbability of an ion the greater would be its coagulating power.

---

[1] J. Am. Chem. Soc., 23, 842 (1901).
[2] Kolloid-Z., 1, 321 (1907).
[3] J. Phys. Chem., 23, 205 (1919).
[4] Kolloid-Z., 35, 144 (1924).
[5] J. Phys. Chem., 29, 942 (1925).
[6] J. Phys. Chem., 29, 955 (1925).
[7] loc. cit.
[8] J. Phys. Chem., 19, 349 (1915).
[9] loc. cit.

We shall show that this assumption has very little experimental support even in the adsorption of ions of the same valency not to speak of ions of different valencies.

Combining this assumption (b) which is not yet experimentally proved, with the deduction (a) which is experimentally sound, Freundlich and other workers in colloid chemistry have come to the conclusion that an ion of higher valency, which has a high coagulating power, is more adsorbed than an ion of low valency, which has small coagulating power.

We are of the opinion that this deduction is both experimentally and theoretically unsatisfactory. We believe that the Schulze-Hardy law that the greater the valency of an ion the greater is its coagulating power is generally applicable for the following reasons:—

Since the coagulation of an equal amount of a colloid by ions of different valencies, is at first an electrical phenomenon, it will be clear that for the charge neutralisation of a fixed amount of any colloid, the absolute amount of ions, expressed in gram-moles, necessary in the case of monovalent ions will be greater than that of bi- or trivalent ions, simply because the net charge on a bi- or trivalent ion is greater than that on a monovalent ion. It is apparent, therefore, that only for neutralization of charge on a sol, the greater the coagulating power of an ion the less would be its amount of adsorption.

Hence we are of the opinion that in the coagulation of a sol the valency factor of an ion is more important than its adsorbability. Previous workers in this field have given an undue importance to the question of adsorbability, which is no doubt of a great importance but is certainly not as great as that of valency. In this connection the following lines from an article by Freundlich[1] would be of interest:—

"It follows necessarily that the coagulative power of a given salt depends greatly both on the valency and on the adsorption coefficient, because with different (ionic) values, either of valency or adsorption, very different concentrations are necessary in the solution in order that the equivalent quantity of the (active) ion shall be adsorbed".

In order to prove our case we have to give a summary of the results obtained in adsorption experiments hitherto carried on.

## Arsenious Sulphide

From the researches of Linder and Picton[2], Whitney and Ober, Freundlich[3], and Weiser on the coagulation of arsenious sulphide sol by different electrolytes, we find that the actual amount of adsorption expressed in millimoles is greater in the case of univalent ions like K, neufuchsin and aniline than in the case of bivalent ions like Ba, Sr, Ca, $UO_2$ or the trivalent ion Ce, which shows the least adsorption. It will be interesting to observe that the adsorption of ions per gram of $As_2S_3$ is small and varies from 0.021 to 0.082

[1] Burton: "Physical Properties of Colloidal Solutions", 182 (1921).
[2] J. Chem. Soc., **67**, 63 (1895).
[3] Z. physik. Chem., **73**, 385 (1910).

millimoles. This is certainly because as we have already emphasised that $As_2S_3$ is not a good adsorbent and the uncharged substance cannot adsorb the precipitating ions to a marked extent as will be shown from the direct experiments of Freundlich on the adsorption of electrolytes by a powder of $As_2S_3$. Hence the amount of different ions adsorbed by $As_2S_3$ in the process of coagulation is more or less equivalent as has been proved by different workers.

In this connection, it will be interesting to note that Weiser has made the following observations in one of his papers[1] on the adsorption of electrolytes by arsenious sulphide sol.

"The observations recorded in Table XI show conclusively that concentration of Li below the precipitation value have a marked effect on the adsorption of Ba". Thus at the precipitating concentration of a mixture, containing 1/8 value of precipitating concentration of LiCl alone, the adsorption of Ba ion is lowered more than 25 per cent; whilst from a mixture containing one half the precipitation value of LiCl alone the adsorption of Ba is decreased 53 per cent. . . . The high precipitation value of LiCl cannot be due to a very low adsorption of Li ion, which would displace but little Ba ion at concentrations below the precipitation value; but is due to a fairly marked adsorption of Li ion associated with appreciable adsorption of the stabilizing chlorine ion within the concentration limits investigated".

Several years ago Freundlich[2] carried on some experiments on the adsorption of different electrolytes by powdered $As_2S_3$ and he found that the adsorption of ions in millimoles per gram of $As_2S_3$ from such electrolytes as $NH_4Cl$, $(NH_4)_2SO_4$, $Ce(NO_3)_3$, $UO_2(NO_3)_2$, para-chloraniline hydrochloride, etc. is very small and varies from 0.013 in the case of $NH_4Cl$ to 0.023 in the case of para-chloraniline chloride for almost equal concentrations of the above electrolytes; whilst with morphine chloride, strychnine nitrate, neufuchsin, etc., the adsorption is much greater and varies from 0.068 to 0.050. Hence it is evident from the above results that the chemical affinity of $As_2S_3$ is more pronounced in the case of morphine hydrochloride, strychnine nitrate, neufuchsin, etc., than in the cations of other electrolytes.

It must be emphasised now that the adsorption of different ions by powdered $As_2S_3$ is essentially due to its chemical affinity for the ions in question. As these experiments were conducted with powdered $As_2S_3$, the question of charge neutralisation by the adsorption of ions cannot enter in these cases This important point seems to have been missed by several workers in this field because they have attempted to correlate the coagulating power of an ion and its adsorption from experiments carried on with the powdered substance and not the sol, and this is entirely unsatisfactory.

On comparing the results on adsorption obtained with the sol and with the powder of $As_2S_3$, we find that in general the adsorption of the same ion is greater with the sol than with the powder. The difference is mainly due to

[1] J. Phys. Chem., 28, 232 (1924).
[2] Z. physik. Chem., 73, 385 (1910).

the amount of the ion necessary to neutralize the charge on the sol. From the foregoing results on the coagulation and adsorption by $As_2S_3$ sol as well as by powdered $As_2S_3$ we find that in general an ion of a higher valency is less adsorbed than an ion of a lower valency when the amount of adsorption is expressed in millimoles. In other words, when the adsorption is expressed in milliequivalents, the amount of adsorption is practically equal as has been first observed by Whitney and Ober. There is nothing in the experiments with $As_2S_3$ sol to show that the greater the valency of an ion the greater is the amount of its adsorption.

### Antimony Sulphide

In a previous paper[1] we have shown that the adsorption of Ba ion by $Sb_2S_3$ sol is decreased to the extent of 55 percent by the presence of K ions below the precipitating concentration of KCl. We have also observed that the adsorption of K ion by $Sb_2S_3$ is also decreased by the presence of Ba ion. We have also proved that the adsorption of K (0.2571 millimole) ion expressed in millimoles is about 8 times that of Ba ion (0.0334 millimole) under identical conditions.

A very interesting fact has also been noticed that the sum of the adsorptions by $Sb_2S_3$ of K and Ba ions expressed in equivalents is greater than the adsorption of Ba ions by $Sb_2S_3$, when coagulated by $BaCl_2$ alone, but less than the adsorption of K ion when coagulated by only KCl. These results conclusively prove that univalent ions are more adsorbed than bivalent ones and are in support of our view that less the coagulating power of an ion the greater the adsorption.

### Mercuric Sulphide

Freundlich and Schucht[2] have obtained the results given in Table I with a sol of mercuric sulphide.

TABLE I

| Cation | Concentration of the sol grams per litre. | Coagulating power.* | Adsorption in millimole per gram of Hgs. |
|---|---|---|---|
| $NH_4$ | 13.74 | 0.098 | >0.05 |
| Ag | 11.74 | 3.57 | 0.02 |
| Neufuchsin | 13.74 | 10.31 | 0.008 |
| Brilliant Green | 8.38 | 20.83 | 0.004 |
| Auramin | 10.05 | 10.64 | 0.011 |
| Methylene blue | 14.96 | 10.31 | 0.0077 |
| Ba | 8.29 | 1.96 | 0.022 |
| $Cu(Cu(NO_3)_2)$ | 8.26 | 6.67 | 0.015 |
| $Cu(CuSO_4)$ | 14.43 | 3.85 | 0.011 |
| Ce | 10.45 | 12.19 | 0.004 |

*Coagulating power is the inverse of precipitation value in millimoles.

[1] Ghosh and Dhar: J. Phys. Chem., 29, 435 (1925).
[2] Z. physik. Chem., 85, 641 (1913).

Hence the order of the coagulating powers for the different electrolytes is Brilliant green > Ce > auramine > neufuchsin, methylene blue > Cu ( $Cu(NO_3)_2$ ) > Cu ($CuSO_4$) > Ag > Ba > $NH_4$, beginning with the electrolyte of the highest coagulating power; whilst the order of the adsorption value is $NH_4$ > Ba > Ag > Cu ( $Cu(NO_3)_2$ ) > $Cu(CuSO_4)$, auramine > neufuchsin > methylene blue > Ce > Brilliant green, beginning with the ion adsorbed most. From these results it is clear that the trivalent Ce ion, which has a very high coagulating power, is least adsorbed, whilst the monovalent ions like Ag, $NH_4$, etc., with low coagulating powers show greater adsorption. Hence these results of Freundlich and Schucht are in direct opposition to the views hitherto held that the greater the valency the greater the amount of adsorption, but are in support of our generalization that the greater the amount of adsorption the lower the valency. Though the results obtained by Freundlich and Schucht are not exactly comparable because they used sols of slightly different concentrations with different electrolytes, yet the general accuracy of our conclusion is beyond doubt as shown by these results.

In the foregoing pages it was emphasised that several workers have tacitly assumed that the greater the adsorbability of an ion the greater would be its coagulating power. The experimental results on HgS do not support this assumption even in the case of ions of the same valency not to speak of ions of varying valencies. Thus amongst the two simple univalent cations Ag and $NH_4$ the coagulating power of Ag ion is about thirty-five times greater than that of $NH_4$ ion, but the amount of adsorption is more than double with $NH_4$ than with Ag. Now, when we compare the coagulating powers of the four cations from the organic dyes the following order is obtained:—Brilliant green > auramine > methylene blue > neufuchsin. Their adsorptions are in the following order auramine > neufuchsin > methylene blue > Brilliant green. In the case of the divalent ions Ba and Cu, the coagulating power of Ba is less and the adsorption is greater than those of Cu obtained from either $Cu(NO_3)_2$ or $CuSO_4$. Hence it is clear that the assumption that the greater the adsorbability of an ion the greater is its coagulating power is not at all in accord with experimental results.

In this connection, it will be interesting to observe that the adsorption of the cations by a sol of HgS from the organic dyes is much less than that of other univalent cations. Their coagulating powers are much higher than those of other univalent ions; in other words, the univalent cations from dyes behave as polyvalent ions not only for the coagulation of HgS sol but also for a $As_2S_3$ sol as has been shown by Freundlich. We are of the opinion that the explanation of this particular behavior is the following:—

It is well known that many of these dyes are of a colloidal nature though they conduct electricity. We also know that the charge on a colloid particle is much greater than that on an ion. Moreover, we know from the Schulze-Hardy law that a polyvalent ion carrying several unit charges is a far better coagulant than an univalent ion; consequently the ionic micelles given out by an organic dye would behave as polyvalent ions, with a high coagulating power.

In a previous paper we have shown that the amount of adsorption by $BaSO_4$ is greater, the greater the size of the particles of the substance which is going to be adsorbed. Consequently the cations of the colloidal dyes are likely to be adsorbed in greater quantities than other simple univalent cations.

Freundlich determined the coagulating powers of several cations from dye stuffs on a sol of arsenious sulphide. He also determined the adsorption of these cations by powdered $As_2S_3$ as has already been reported. He observed that from dilute solutions of alkaloids or dyestuffs a great deal of adsorption of the organic cations takes place even with powdered $As_2S_3$ in comparison with the adsorptions of the other univalent ions like $NH_4$, Ag, etc. Moreover, it has been repeatedly observed that charge reversal can be readily effected by cations from alkaloids and dye stuffs. These results strongly support our view that amount of adsorption and charge reversal are essentially dependent on the chemical affinity of the adsorbent for the different cations.

The order of the coagulating power of different cations towards a sol of $As_2S_3$ is Ce > Al > neufuchsin > crystal violet > quinine sulphate > morphine chloride > $UO_2$ > Ba > Mg > p-chloraniline chloride > aniline chloride > strychnine nitrate > H > K > Na > Li—beginning with the ion of the highest coagulating power. It will be seen that though Ce, Al, etc., are less adsorbed by powdered $As_2S_3$ than any of the organic cations, the coagulating powers of trivalent ions Ce and Al are greater than those of the organic cations. Moreover, the coagulating powers of the bivalent ions like Ba, Mg, $UO_2$, etc., are greater than many organic cations like strychnine nitrate, aniline chloride, etc. Hence the contention that the greater the adsorbability the greater the coagulating power is not applicable to these cases.

It should be clearly pointed out here that no strict comparison between the coagulating power of an ion and its adsorption could be made from the experiments of Freundlich on $As_2S_3$, because in the majority of the adsorption experiments he has used a powder and not a sol of $As_2S_3$.

### Ferric Hydroxide

The adsorption and coagulating powers of different acids by a sol of $Fe(OH)_3$, have been determined by Weiser and Middleton[1]. Their results are given in Table II.

TABLE II

| Anion | Coagulating power | Adsorption in millimoles per gram of $Fe_2O_3$. |
|---|---|---|
| Phosphate | 3.42 | 0.5721 |
| Citrate | 5.99 | 0.5081 |
| Tartrate | 4.21 | 0.6232 |
| Oxalate | 3.81 | 0.4364 |
| Sulphate | 4.12 | 0.3804 |
| Iodate | 1.67 | 0.7512 |
| Dichromate | 10.00 | 0.1559 |

[1] J. Phys. Chem., **24**, 30 (1920).

The above authors have concluded "It is evident that there is a tendency for the ions with the lowest precipitation values to be adsorbed the least and vice versa". Consequently it is clear from the experimental results of Weiser and Middleton that our conclusion that the greater the coagulating power the less the adsorption is experimentally sound.

Sen, in a thesis, has made a systematic study of the adsorption of different acids by freshly precipitated hydroxides of iron, aluminium, and chromium and he obtained the results given in Table III with freshly precipitated $Fe(OH)_3$.

TABLE III

| Acid | Adsorption per gram adsorbent |
|---|---|
| Citric | 0.8603 |
| Oxalic | 1.0325 |
| Tartaric | 0.9585 |
| Sulphuric | 0.8448 |

When the above acids are shaken with precipitated $Fe(OH)_3$ sols of positively or negatively charged $Fe(OH)_3$ are obtainable. Therefore, in all the adsorption experiments Sen has used a normal solution of KCl or $NH_4Cl$ to coagulate the sols thus formed and in all cases the change in hydrogen ion concentration has only been estimated. Hence these results with precipitated ferric hydroxide are not comparable with those of Weiser and Middleton obtained with a sol of ferric hydroxide. But one fact comes out very prominently from these results that $Fe(OH)_3$ is a better adsorbent of acids and salts than $As_2S_3$. Moreover, the large amount of adsorption of the acids is mainly due to the chemical affinity of ferric hydroxide for these acids. Though a large amount of adsorption of acids is observed with precipitated $Fe(OH)_3$ it is useless to correlate this adsorption with the coagulating power of the electrolyte, because we are convinced that this high adsorption has nothing to do with the question of charge neutralization of the sol, but is essentially due to the chemical affinity of $Fe(OH)_3$ for the above acids.

### Aluminium Hydroxide

In the adsorption of electrolytes by a sol of $Al(OH)_3$ or by precipitated $Al(OH)_3$, there is divergence amongst the results of different investigators. The following results are obtained by Gann[1] for a sol of $Al(OH)_3$, Table IV.

TABLE IV

| Anion | Coagulating power | Adsorption in millimoles per gram $Al_2O_3$ |
|---|---|---|
| Salicylate | 0.125 | 0.30 |
| Picrate | 0.25 | 0.18 |
| Oxalate | 2.77 | 0.18 |
| Ferricyanide | 10.00 | 0.09 |
| Ferrocyanide | 12.50 | 0.073 |

[1] Kolloidchem.-Beihefte, 8, 63 (1916).

It follows, therefore, from these results that the greater the coagulating power the less is the amount of adsorption and the greater the valency the less is the amount of adsorption.

On the other hand, the results obtained by Weiser and Middleton[1] are different from those of Gann. They are given in Table V.

TABLE V

| Anion | Coagulating power | Adsorption in millimoles per gram $Al_2O_3$ |
|---|---|---|
| Ferrocynaide | 10.64 | 0.3202 |
| Thiosulphate | 5.32 | 0.4096 |
| Ferricyanide | 7.52 | 0.4046 |
| Sulphate | 3.75 | 0.4184 |
| Oxalate | 2.86 | 0.5710 |
| Chromate | 1.54 | 0.4352 |
| Dithionate | 1.23 | 0.3284 |
| Dichromate | 1.13 | 0.3185 |
| Phosphate | 2.89 | 0.8088 |

From the above results also it is evident that in the majority of cases the greater the coagulating power the less is the adsorption. It will be evident from the above results that $Al(OH)_3$ sol is a very good adsorbent for different ions, although Ishizaka has shown that 'grown alumina' can absorb ions to the extent only of 0.002 to .05 millimole per gram of the adsorbent. On the other hand Sen, has obtained the following results in the adsorption of acids by freshly precipitated $Al(OH)_3$:—

| Acid | Adsorption in millimoles |
|---|---|
| Citric | 0.783 |
| Oxalic | 0.952 |
| Tartaric | 0.933 |
| Sulphuric | 0.896 |

In this case also the amount of adsorption due to chemical affinity is more pronounced than that due to charge neutralisation, because the precipitated $Al(OH)_3$ can adsorb large quantities of acids.

From the above it will be seen that the results obtained by various investigators with a sol of $Al(OH)_3$ and different electrolytes are not concordant. In order to throw further light on the question of adsorption of different ions by $Al(OH)_3$ experiments on adsorption of substances by a $Al(OH)_3$ sol are in progress in this laboratory.

### Chromium Hydroxide

No experiments are available on the adsorption of different electrolytes by a sol of $Cr(OH)_3$. Sen has, however, determined the adsorption of different acids by precipitated $Cr(OH)_3$, and he obtained the following results:—

[1] J. Phys. Chem., **24**, 630 (1920).

| Acid | Amount adsorbed in millimoles |
|---|---|
| Citric | 2.196 |
| Tartaric | 3.170 |
| Sulphuric | 3.919 |
| Oxalic | 4.106 |

These results show that acids are very highly adsorbed by $Cr(OH)_3$ and its adsorptive power is greater than that of either $Fe(OH)_3$ or $Al(OH)_3$.

In one of his recent papers Weiser has shown that as the concentration of $K_2C_2O_4$ is increased above the precipitation value the amount of adsorption of $C_2O_4$ ion also increases. This only proves that freshly precipitated $Cr(OH)_3$ has a great affinity for oxalate ions.

Consequently from the experimental results of Sen and of Weiser we conclude that the adsorption of the oxalate ion by freshly precipitated $Cr(OH)_3$ due to chemical affinity will be more prominent than that due only to charge neutralisation of a sol of $Cr(OH)_3$. Hence it is absolutely useless to conclude that oxalate ion, because of its higher valency is more adsorbed than chloride ion as has been done by Weiser, as nobody as yet determined the adsorption of chloride ions by a sol and by freshly precipitated $Cr(OH)_3$ in order to show whether the adsorption of chloride ions by precipitated $Cr(OH)_3$ due to chemical affinity is more pronounced than the adsorption necessary only for charge neutralization of the sol.

### Manganese Dioxide

In previous papers[1] we found that the adsorption of ions by manganese dioxide in the course of its formation is in the following order:—

$Ag > Na > Li > Cu > Cd > Ba > Ni, Zn > UO_2 > Th > Al$. This shows that in general ions of lower valency are more adsorbed than ions of higher valency in the precipitation of manganese dioxide.

We also measured the adsorption of cations by precipitated manganese dioxide and the order of adsorption is the following:—

$$Ag > Cu > Cd > Zn, Mg > Ba > Sr, Ca > Al$$

Very recently we have again measured the adsorption of different cations by a sol of manganese dioxide as well as by precipitated manganese dioxide of a great purity.

The sol was prepared by the interaction of $KMnO_4$ and $H_2O_2$ and dialysed for a week and completely freed from alkali, and it contained 1.6 grams $MnO_2$ per litre. 20 c.c. of this sol were taken and 10 c.c. of M/10 solutions of different electrolytes were added and the volume was always made up to 50 c.c. The following results are obtained:—

[1] Ganguli and Dhar: J. Phys. Chem., **26**, 701, 836 (1922); Chatterji and Dhar: Kolloid-Z., 33, 18 (1923).

| Cations | Adsorption in millimole per gram of $MnO_2$ |
|---|---|
| K | 5.514 |
| Ag | 5.85 |
| $Cu(CuSO_4)$ | 3.90 |
| $Cu(CuCl_2)$ | 5.095 |
| Ba | 1.98 |
| Al | 0.03 (approx.) |

The order of adsorption of cations by a pure sol of manganese dioxide is Ag > K > Cu > Ba > Al.

From the foregoing results obtained with a pure sol of $MnO_2$, we can conclude that the higher the valency of an ion the less is the amount of its adsorption. This result is in direct opposition to the view hitherto held that an ion of a higher valence would be more adsorbed than that of a low valence.

From our recent experiments with freshly precipitated, well-washed and an air-dried sample of hydrated manganese dioxide the following results are obtained:—

| Cation | Amount adsorbed in millimole per gram of the adsorbent |
|---|---|
| K | 1.159 |
| Ag | 1.518 |
| $Cu(CuSO_4)$ | 1.131 |
| $Cu(CuCl_2)$ | 1.048 |
| Ba | 0.386 |
| Al | 0.083 |

The order of adsorption of cations by pure hydrated manganese dioxide is Ag > K > Cu > Ba > Al. In this case also we find ions of higher valency are less adsorbed than ions of lower valency. These results as obtained now are in agreement with those already published.

In this connection we have to emphasise the fact that the adsorption of ions is much greater by a definite weight of the adsorbent in the course of its formation than that obtained when the same weight of the absorbent prepared long ago is used. We have repeatedly observed that sols of $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$, $MnO_2$, etc., are much better adsorbent of ions than the precipitated substances. Moreover, the adsorbability of ions decreases with the ageing of the precipitates. When a sol is coagulated by an electrolyte, the neutralisation of the charge takes up a definite quantity of the oppositely charged ion, and if the neutral particles thus formed have a very slight chemical affinity for the coagulating ion we should always find that the adsorption for different ions expressed in equivalents should be practically equal just as we get in the case of $As_2S_3$ sol to a certain extent. When the adsorption is expressed in moles per gram of the adsorbent, as has been done in this paper we ought to find that the greater the valency of the ion the less is its adsorption.

We have systematically expressed the amount of adsorption of ions in millimoles, and not in milliequivalents as has been done by other workers.

It is easy to conceive that in the coagulation and adsorption by sols, ions take part as a whole and not in parts, and consequently the expression of the results of adsorption and coagulation in millimoles and not in milliequivalents seems more sound and the results of coagulation and adsorption when expressed in millimoles seem more readily conceivable.

We have already emphasised that many authors notably Freundlich, Weiser and others have assumed that the greater the adsorbability of an ion the greater will be its coagulating power. This assumption seems apparently reasonable specially with ions of the same valency, because along with the electrical attraction of the oppositely charged ion towards the sol particles, the chemical affinity between the sol and the coagulating ion may help in the coagulation of the sol because we know that the greater the chemical affinity of an ion towards an adsorbent the greater is its adsorbability. But unfortunately the experimental results available in this field do not support this assumption and it seems likely that there is some unknown factor, which counteracts the effect of chemical affinity of an ion for a sol in facilitating its charge neutralization and coagulation. The assumption that greater the adsorbability the greater the coagulating power will be disproved from the following experimental results even in the case of ions of the same valency:—

| Sol | Anion | Adsorption in millimole per gram of the adsorbent | Coagulating power | Author |
|---|---|---|---|---|
| $Fe(OH)_3$ | $SO_4$ | 0.3804 | 4.12 | Weiser and Middleton |
| " | $C_2O_4$ | 0.4364 | 3.81 | " |
| $Al(OH)_3$ | $SO_4$ | 0.4984 | 3.72 | " |
| " | $C_2O_4$ | 0.5710 | 2.86 | " |
| $Al(OH)_3$ | Picrate | 0.18 | 0.25 | Gann |
| " | Salicylate | 0.30 | 0.125 | " |

It is well known that a solution of $K_2C_2O_4$ is more hydrolysed and contains more $OH'$ ions than a solution of $K_2SO_4$ of the same concentration. Consequently in presence of $K_2C_2O_4$ the positively charged $Cr(OH)_3$ sol will be more unstable than in presence of the same concentration of $K_2SO_4$. Hence if we take into account the hydrolysis and the hydrogen ion concentration in solutions of $K_2C_2O_4$ and $K_2SO_4$ a solution of $K_2C_2O_4$ should coagulate a sol of $Cr(OH)_3$ in a smaller quantity than $K_2SO_4$. Hence the suggestion of Weiser based on hydrolysis to explain the difference in the behavior of $K_2C_2O_4$ and $K_2SO_4$ is of no avail.

Ishizaka has determined the coagulating power of various anions towards a sol of $Al(OH)_3$ and he has also determined the adsorption of the same anions by "grown alumina". He has observed that potassium salicylate is about nine times more effective coagulant than KCl, the coagulating power of salicylate ion is 187.7 whilst that of chloride ion is 21.9.

From the adsorption curves obtained by Ishizaka of various ions with 'grown alumina' we find that the adsorption of 0.02 millimole is reached at concentrations 0.046M in the case of chloride and 0.001M in the case of salicylate. Now, if the view that the greater the adsorbability of an ion the greater would be its coagulating power be correct, the coagulating power of the salicylate ion should be 46 times greater than that of the chloride ion, but in actual experiment we find that the ratio of the two coagulating powers is nine, instead of the calculated value 46.

In the case of substances like $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, $MnO_2$ etc., the chemical affinity of these substances for the coagulating ions is much more pronounced than in the cases of $As_2S_3$, $Sb_2S_3$ etc. Consequently the correlation between the coagulating powers or the valencies of ions with their amount of adsorption in the cases of sols like $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$, $MnO_2$, etc., is less satisfactory than in the cases of $As_2S_3$, HgS and $Sb_2S_3$ sols because the precipitates of the latter class of substances have a small chemical affinity for their coagulating ions.

If by any means we can find out the amounts of adsorption of an electrolyte by a definite weight of the sol and by its freshly obtained precipitate as soon as it is formed, we shall find that this difference of the two adsorption values expressed in moles would be greater in the case of univalent ions than polyvalent ions, because this difference arises from the adsorption due only to charge neutralisation of a sol and to this difference only the Schulze-Hardy law should be rigidly applicable.

## Barium Sulphate

From our experiments on the adsorption of different anions by $BaSO_4$ obtained by the interaction of equivalent amount, of $Ba(OH)_2$ and $H_2SO_4$, we obtain the following order of adsorption:—$Cr_2O_7'' > S_2O_3'' > BrO_3' > AsO_3''' > C_2O_4'' > IO_4' > IO_3' > MnO_4' > NO_2' > Fe(CN)_6'''' > Fe(CN)_6''' > Cl' > CNS' > Br' > I'$ whilst Weiser and Sherrick working with different barium salts and $K_2SO_4$ obtained the following order:—

$$NO_3' > NO_2' > ClO_3' > Fe(CN)_6'''' > MnO_4' > Cl' > Fe(CN)_6''' > Br' > CN' > CNS' > I',$$

the results are expressed in millimoles. It will be observed from the above results that in general monovalent and bivalent anions are more adsorbed than tri- or tetravalent anions. The adsorption series as obtained by us or by Weiser and Sherrick are not in complete agreement with our interpretation of the Schulze-Hardy law, because the positively charged $BaSO_4$ is capable of adsorbing positive ions as well, and the neutral molecule of $BaSO_4$ can also adsorb the negative ion, the positive ion or the neutral molecule of the electrolyte.

Our experiments on the precipitation of $BaSO_4$ in the presence of KCl and $K_2C_2O_4$, show that the adsorption of $C_2O_4''$ ion is greater than that of $Cl'$ ion, though according to our view of the Schulze-Hardy law it should be otherwise. We have found that along with the adsorption of $C_2O_4''$ ion by $BaSO_4$ appreci-

able quantities of K ions are also adsorbed. The positively charged $BaSO_4$ can adsorb K ions from $K_2C_2O_4$ and hence more of the oxalate ion would be necessary for the charge neutralisation and precipitation, whilst in the case of KCl no K ion is adsorbed. Hence a small amount of Cl ion is enough for charge neutralisation. From the following experimental results it will be seen that Na ions from $Na_3AsO_3$ and K ions from $K_2C_2O_4$ are adsorbed by $BaSO_4$:—

| Electrolyte | Original concentration | Percentage of adsorption |
|---|---|---|
| $Na_3AsO_3$ | 0.08833 M | 3.7 |
| $K_2C_2O_4$ | 0.06894 M | 2.0 |

It is evident, therefore, that a colloid can actually adsorb an ion carrying the same charge as the sol and this adsorption stabilises the sol. Consequently if the amount of this adsorption is large, deviations from Schulze-Hardy law will take place.

Freundlich has repeatedly emphasised that when there is no complication, the values of $a$ and $n$ in his exponential formula $x = ac^n$, should be the same for all electrolytes. In other words, according to Freundlich, the adsorption curve of ions with a certain sol should be the same irrespective of the valency of the coagulating ion. If we accept this view of Freundlich, which has been questioned by Wo. Ostwald[1], it follows that the amount of adsorption of a trivalent ion and an univalent ion should be equal at the same original concentration; consequently, it has not been proved at all that an ion of higher valency is adsorbed more than an ion of lower valency.

Curiously enough the majority of experiments on adsorption and coagulation carried on by different investigators are strongly in support of our view that the smaller the coagulating power of an ion the greater is its amount of adsorption. Thus the experiments of Freundlich and Schucht on the coagulation and adsorption by a sol of mercuric sulphide our experiments on $Sb_2S_3$, the coagulation and adsorption experiments of Gann on $Al(OH)_3$ sol and on $Fe(OH)_3$ sol by Weiser and Middleton, and our experiments on a sol of manganese dioxide conclusively prove that the greater the valency of an ion the less is its amount of adsorption and the smaller the coagulating power of an ion the greater is its amount of adsorption.

Another interesting fact which is observed from a survey of the experimental results is this:—

Our experiments on the adsorption of cations by precipitated hydrated $MnO_2$ conclusively prove that even with the precipitate, an ion of higher valency is adsorbed much less than an ion of lower valency.

When comparisons are made in the adsorption of ions like $NH_4$, Ba, $UO_2$, Ce, etc., by powdered $As_2S_3$ we also find that there is a general tendency of the ions of lower valency to be adsorbed more than ions of higher valency at equal concentrations of the electrolytes. It is evident that in these cases the question of charge is unimportant, because the adsorbents are neutral sub-

[1] Kolloid-Z., 26, 28, 69 (1920).

stances. It is very difficult to explain these facts in the present state of our knowledge on the mechanism of adsorption, but we are throwing out the following tentative suggestion:—

If we consider that the chemical affinity of K and Ba ions for hydrated manganese dioxide to be practically equal and if we assume that two K ions are adsorbed by an unit surface of hydrated manganese dioxide, the force of repulsion between these two ions is $e^2/r^2$, where $e$ is the charge on an univalent ion r, the distance between the ions. Hence the force of repulsion between two bivalent ions will be $4e^2/r^2$ on the assumption that two barium ions could be taken up by an unit surface of $MnO_2$. Since the force of repulsion for a bivalent ion is 4 times greater than that for a monovalent ion, it is reasonable to expect that less of Ba ions would be adsorbed than K ions on an unit surface of the hydrated manganese dioxide under otherwise identical conditions.

Many authors have deduced the adsorbability of different ions from their coagulating powers towards a certain sol. It is well known that in alkaline medium albumin is negatively charged and cations are effective in coagulating albumin, whilst in the presence of acids the albumin is positivelty charged and the anions are effective. Bancroft[1] has arranged cations and anions in series of gradually increasing or decreasing adsorptive power from the coagulating powers of the anions on a positively charged sol, and from those of the cations on a negatively charged sol.

In view of the facts brought forward in this paper these adsorption series obtained from the coagulating powers seem untrustworthy.

**Summary**

1.. The generally accepted view that an ion, which is highly adsorbed also possesses a high coagulating power is not supported by experiments on adsorption.

2. There is no justification for the assumption that the greater the valency and hence the coagulating power of an ion the greater is its adsorption.

3. On the other hand, experiments on the coagulation and adsorption of different ions by sols of HgS, $Sb_2S_3$, $Al(OH)_3$, $Fe(OH)_3$, $MnO_2$ etc., strongly support our view that the greater the valency of an ion the less is its amount of adsorption and smaller the coagulating power of an ion the greater is its amount of adsorption.

4. It has been shown that the large amount of adsorption of ions associated with the coagulation of the sols like $MnO_2$, $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$ etc., is mainly due to a marked chemical affinity of these substances for different ions.

5. It seems very likely that the valency of an ion is a more important factor in coagulation than its adsorbability.

*Chemical Laboratory,*
*University of Allahabad,*
*Allahabad, India*
*September 23, 1925.*

[1] J. Phys. Chem., 19, 349 (1915).

# VAPOR PRESSURE LOWERING AS A FUNCTION OF THE DEGREE OF SATURATION. II

BY ISAAC BENCOWITZ* AND HENRY T. HOTCHKISS, JR.

## Introduction

Despite the fact that concentration is a variable of primary importance, no uniform mode of expressing the ratio of the quantity of one substance to another, or to their sum has ever been employed. For analytical purposes the choice of a system of units is more or less a matter of expediency, but in the study of the theory of solutions a method of expressing concentrations which is of theoretical significance is essential. Several ratios have been proposed and used in an attempt to fulfill this requirement, but none has been found to be on a sound basis. Thus the "volume-normal" system, i.e. number of moles per litre of solution, had theoretical significance because van't Hoff's discovery[1] of the analogy between the osmotic pressure of solutions and the behavior of gases. Later Morse and Fraser[2] in order to bring this very analogy in closer agreement with the experimental facts, introduced the "weight-normal" system, i.e. number of moles of solute in 1000 gms. of water. Since then, it has been definitely shown[3] that no parallelism between the gas and the osmotic pressure of solutions exists. The theoretical foundations on which these two systems had been based were thus shown not to be sound. The methods themselves, however, remain and are frequently used. Of the two, the "weight-normal" system is preferred by many investigators[4] on various grounds.

Duhem[5] expressed the concentration in moles of the dissolved substance per mole of solvent. In all these systems one of the components is designated as solute and the other as solvent. A more symmetrical manner of expressing the concentration is the "mole-fraction". This system assumes a theoretical significance because of Raoult's law. But this law supposedly valid in the case of infinitely dilute solutions cannot accurately define even the so-called "ideal" solutions[6]. Rodebush[7] states "that even in the most dilute solutions that we can study, the attraction between ions causes a negative deviation from Raoult's Law". The mole-fraction, however, has numerous theoretical

---

* National Research Fellow in Chemistry.

[1] Z. physik. Chem., **1**, 481 (1887).

[2] Am. Chem. J., **34**, 1 (1905); **37**, 324, 425, 458 (1906); **38**, 175 (1907); Morse: "The Osmotic Pressure of Aqueous Solutions", p. 97 (1914); Findlay: "Osmotic Pressure" (1913); Bancroft: J. Phys. Chem., **10**, 320 (1916).

[3] Lewis: J. Am. Chem. Soc., **30**, 660 (1910); Kendall: **43**, 1391 (1921); Hildebrand: "Solubility", p. 24 (1924).

[4] Lewis and Randall: "Thermodynamics", p. 33 (1923); Philip: J. Chem. Soc., **91**, 711 (1907).

[5] Duhem: "Mécanique chimique", **3**, 4 (1898).

[6] Hildebrand: "Solubility", p. 27 (1924).

[7] J. Phys. Chem., **28**, 1115 (1924).

and practical advantages[1]. Still another method which has been found useful in expressing solubility, is number of gram-moles of water required to dissolve one gram-mole of solute[2]. The mole-fraction, however, has numerous advantages in the theoretical application of thermodynamics to the theory of solutions[3].

All these various ways of expressing concentrations are arbitrary, from a theoretical point of view. The only criterion for the choice of the method to be employed seems to be its usefulness. Such a criterion is scientifically illogical and all functions in which the concentration expressed in any of these ways appears as a variable become arbitrary.

If it were possible to express the concentration in such a manner that it would become a function of the solution as much as any other property of the solution, then the method of expression would be of fundamental significance. Now if we designate the concentration thus expressed by $S$, and the solution forces by $X$, we can write,—

$$S = f(X) \qquad (1)$$

and if we take any other property, $A$, of a solution we can write

$$A = \varphi(X) \qquad (2)$$

so that if it were possible to express $A$ as a function of $S$ we would obtain,

$$A = F(S) \qquad (3)$$

Relation (3) is bound to be a fundamental expression and it may tell us something concerning the forces of solution $X$. There is nothing arbitrary about this function, inasmuch as both variables are functions of $X$.

## Vapor Pressure Lowering and Degree of Saturation

The degree of saturation is the concentration of a solution expressed in terms of the solubility. Thus if the concentration of a solution is given as $n$ gms. (or moles) per $W$ gms. (or moles) of solvent, and the concentration of a saturated solution as $N$ gms. (or moles) per $W$ gms. (or moles) of solvent, the degree of saturation $S$, is then given by:

$$S = n/N \quad .$$

The degree of saturation is therefore the concentration of a solution expressed *in terms of solubility*. The concentration thus expressed is fundamental, and obviously, is as much a function of the solution forces as the solubility. And all relations expressing any property of the solution as a function of the degree of saturation will be essentially fundamental.

Applying the concept of the degree of saturation to vapor pressure lowering, the following relation was developed[4].

$$\log \triangle P = K\left[\frac{1}{T} - a\left(1 - \frac{\log S}{b}\right)\right] \qquad (4)$$

---

[1] Lewis and Randall: loc. cit.; Bjerrum: Z. physik. Chem., 104, 406 (1923); John Johnston: J. Phys. Chem., 29, 882 (1925).

[2] Gladstone and Pound: J. Chem. Soc., 127, 2660 (1925).

[3] Lewis and Randall: loc. cit.; John Johnston: J. Phys. Chem. 29, 882 (1925).

[4] Bencowitz: J. Phys. Chem., 29, 1432 (1925).

The similarity between solubility and vapor pressure is best shown in the following quotation from Nernst[1]. "The far-reaching analogy which exists between the process of solution and that of evaporation, and to which repeated reference must be made, is also shown in the fact that just as the vapor pressure of a solvent is depressed by the addition of a foreign substance $B$, so also is the solubility of $A$ in a second solvent diminished by the addition of a foreign substance $B$". In the case of *non-volatile solutes*, this statement is not valid inasmuch as we do know of instances where the addition of a foreign substance $B$ increases the solubility[2] whereas no instances are known where the same is true of the vapor pressure. The solubility and vapor pressure are, therefore, hardly identical, but they are, no doubt, similar processes. Equation (4) is therefore identical with (3) since the two variables the vapor pressure lowering, $\triangle P$, and the degree of saturation, $S$, are both functions of the same solution forces. This relation is of a fundamental nature.

Equation (4) was obtained in the following manner on the basis of three postulates:

*Postulate* 1. When the log of the vapor pressure lowering $\triangle P$ for any degree of saturation $S$ is plotted against the reciprocal of the absolute temperature $T$, a straight line should be obtained.

$$\left[\frac{\partial \log \triangle P}{\partial (1/T)}\right]_S = K$$

*Postulate* 2. The value of the constant $K$ is independent of the degree of saturation.

*Postulate* 3. When the log of the degree of saturation $S$ is plotted against the reciprocal of the absolute temperature at constant vapor pressure lowering ($\triangle P$ = 1 mm.) a straight line should be obtained, i.e.,

$$\left[\frac{\partial \log S}{\partial (1/T)}\right]_{\triangle P = 1\ mm} = \text{Const.}$$

The experimental proof of these three postulates as well as the mathematical derivation is given in the first paper[3]. In the present paper additional experimental evidence will be given in corroboration of equation (4) and of Postulate 1.

**Generalization 1.**

According to the first postulate,

$$\left[\frac{\partial \log \triangle P}{\partial (1/T)}\right]_S = K$$

which upon integration gives for the limits $\triangle P'$ and $\triangle P''$,

$$\log \frac{\triangle P'}{\triangle P''} = K\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad (6)$$

[1] Nernst: "Theoretical Chemistry", 5th English Ed., p. 147 (1923).

[2] K. Linderstrom-Lang: Compt. rend. Trav. Lab. Carlsberg, 15, 1 (1924). See Eucken, Jette and LaMer: "Fundamentals of Physical Chemistry," 342 (1925).

[3] Bencowitz: loc. cit.

A similar expression where $S = 1$, i.e. for the vapor pressure lowering of a saturated solution at $T_1$ and $-T_2$ is,

$$\log \frac{\Delta P_S'}{\Delta P_S''} = K\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad (7)$$

TABLE I

Ratios of Vapor-pressure Lowering at any Degree of Saturation to that of a Saturated Solution at the Same Temperature

| Name of Substance | t | $\Delta P_s$ | $\Delta P_1$ | $\Delta P_1/\Delta P_s$ | $\Delta P_2$ | $\Delta P_2/\Delta P_s$ |
|---|---|---|---|---|---|---|
| $NaBr \cdot H_2O$ | 50 | 40.65 | 21.8 | 0.4456 | 9.75 | 0.1991 |
| | 60 | 80.54 | 36.1 | .4488 | 16.1 | .2004 |
| | 70 | 131.5 | 58.4 | .4436 | 26.3 | .2000 |
| | 80 | 200.0 | 88.0 | .4405 | 39.4 | .1972 |
| | 90 | 301.3 | 133.5 | .4426 | 60.0 | .1991 |
| | | | | *A.D. = 0.5% | | A.D. = 0.1% |
| $K_2CO_3 \cdot 2H_2O$ | 30 | 18.11 | 7.60 | .4198 | 3.20 | .1766 |
| | 40 | 31.62 | 13.59 | .4249 | 5.78 | .1807 |
| | 50 | 53.95 | 23.07 | .4246 | 9.93 | .1828 |
| | 60 | 95.06 | 39.63 | .4169 | 16.86 | .1774 |
| | 70 | 149.6 | 63.53 | .4246 | 26.91 | .1799 |
| | 80 | 235.5 | 100.0 | .4246 | 42.46 | .1803 |
| | 90 | 367.2 | 153.8 | 0.4188 | 64.86 | .1766 |
| | | | | A.D. = 0.7% | | A.D. = 1.1% |
| $K_2CrO_4$ | 40 | 8.61 | 3.89 | .4524 | 1.77 | .2055 |
| | 50 | 14.90 | 6.79 | .4560 | 3.11 | .2090 |
| | 60 | 24.77 | 11.22 | .4529 | 5.13 | .2070 |
| | 70 | 38.91 | 17.74 | .4560 | 8.18 | .2104 |
| | 80 | 60.25 | 27.55 | .4571 | 12.62 | .2094 |
| | 90 | 92.05 | 41.30 | .4488 | 18.45 | .2005 |
| | | | | A.D. = 0.5% | | A.D. = 1.3% |
| $BaCl_2 \cdot 2H_2O$ | 50 | 9.50 | 4.82 | .5069 | 2.11 | .2218 |
| | 60 | 16.22 | 8.36 | .5152 | 3.73 | .2286 |
| | 70 | 26.61 | 14.09 | .5157 | 6.33 | .2377 |
| | 80 | 44.67 | 22.91 | .5140 | 10.23 | .2291 |
| | 90 | 68.87 | 35.65 | .5145 | 16.29 | .2366 |
| | | | | A.D. = 0.5% | | A.D. = 2.0% |
| $(NH_4)_2SO_4$ | 30 | 6.15 | 3.10 | .5035 | 1.56 | .2530 |
| | 40 | 11.20 | 5.66 | .5058 | 2.86 | .2559 |
| | 60 | 32.96 | 16.33 | .4954 | 8.18 | .2483 |
| | 70 | 52.24 | 26.18 | .5012 | 13.24 | .2535 |
| | 80 | 82.60 | 41.50 | .5034 | 20.75 | .2512 |
| | 90 | 124.7 | 62.23 | .4943 | 31.12 | .2511 |
| | | | | A.D. = 0.7% | | A.D. = 0.7% |

* A.D. = The average deviation from the average.

TABLE I (continued)

| Name of Substance | t | $\Delta P_s$ | $\Delta P_1$ | $\Delta P_1/\Delta P_s$ | $\Delta P_2$ | $\Delta P_7/\Delta P_s$ |
|---|---|---|---|---|---|---|
| $MgCl_2 . 6H_2O$ | 40 | 37.16 | 14.19 | 0.3733 | 5.36 | 0.1386 |
| | 60 | 112.7 | 41.88 | .3715 | 15.56 | .1380 |
| | 80 | 290.4 | 107.9 | .3715 | 39.63 | .1365 |
| | | | | A.D. = 0.16% | | A.D. = 1.2% |
| $SrCl_2 . 6H_2O$ | 30 | 9.77 | 3.96 | .4074 | 1.62 | .1663 |
| | 40 | 19.41 | 7.92 | .4083 | 3.25 | .1675 |
| | 50 | 35.97 | 14.62 | .4065 | 5.96 | .1656 |
| | 60 | 67.30 | 27.48 | .4083 | 11.20 | .1663 |
| | | | | A.D. = 0.6% | | A.D. = 8% |
| $SrBr_2 . 6H_2O$ | 50 | 57.55 | 21.38 | 0.3715 | 8.57 | 0.1479 |
| | 60 | 105.9 | 39.35 | .3715 | 14.86 | .1403 |
| | 80 | 316.2 | 118.9 | .3758 | 45.50 | .1439 |
| | | | | A.D. = .5% | | A.D. = 1.0% |
| LiCl | 40 | 20.65 | 8.00 | .3873 | 3.57 | .1730 |
| | 50 | 35.89 | 14.45 | .4027 | 6.21 | .1730 |
| | 60 | 63.38 | 25.59 | .4036 | 10.89 | .1718 |
| | 65 | 79.08 | 32.21 | .4074 | 14.06 | .1758 |
| | 70 | 100.5 | 42.17 | .4198 | 17.99 | .1791 |
| | 75 | 129.4 | 53.96 | .4169 | 22.91 | .1770 |
| | | | | A.D. = 2.0% | | A.D. = 1.3% |
| $NH_4Cl$ | 40 | 13.46 | 7.13 | .5296 | | |
| | 50 | 24.77 | 13.24 | .5358 | | |
| | 60 | 43.55 | 23.50 | .5395 | | |
| | 70 | 72.78 | 38.46 | .5284 | | |
| | 80 | 118.3 | 64.86 | .5483 | | |
| | | | | A.D. = .1% | | |
| KI | 40 | 17.30 | 8.12 | .4699 | 3.76 | .2172 |
| | 50 | 32.88 | 15.74 | .4787 | 7.21 | .2193 |
| | 60 | 58.75 | 27.60 | .4699 | 12.88 | .2193 |
| | 70 | 95.72 | 45.60 | .4765 | 21.53 | .2249 |
| | 80 | 159.2 | 75.17 | .4721 | 34.99 | .2193 |
| | 90 | 252.3 | 118.9 | .4710 | 55.08 | .2183 |
| | | | | A.D. = 0.6% | | A.D. = 0.8% |
| RbCl | 30 | 9.50 | 4.46 | .4688 | 2.08 | .2193 |
| | 40 | 17.22 | 8.09 | .4699 | 3.80 | .2208 |
| | 50 | 30.76 | 14.52 | .4721 | 6.92 | .2249 |
| | 60 | 53.57 | 25.07 | .4678 | 11.70 | .2183 |
| | 70 | 87.70 | 40.55 | .4624 | 19.05 | .2173 |
| | 80 | 136.8 | 64.27 | .4699 | 30.13 | .2203 |
| | 90 | 210.4 | 98.85 | .4699 | 46.78 | .2223 |
| | | | | A.D. = 0.7% | | A.D. = 0.9% |

TABLE I (continued)

| Name of Substance | t | $\Delta P_s$ | $\Delta P_1$ | $\Delta P_1/\Delta P_s$ | $\Delta P_2$ | $\Delta P_2/\Delta P_s$ |
|---|---|---|---|---|---|---|
| KCl | 20 | 2.58 | 1.38 | .5370 | 1.43 | .2723 |
| | 30 | 5.13 | 2.73 | .5321 | 1.31 | .2559 |
| | 40 | 9.75 | 5.03 | .5165 | 2.44 | .2500 |
| | 60 | 30.20 | 15.14 | .5012 | 7.53 | .2495 |
| | 70 | 49.20 | 25.18 | .5117 | 12.36 | .2512 |
| | 80 | 81.28 | 40.74 | .5012 | 20.05 | .2466 |
| | 90 | 123.3 | 62.95 | .5105 | 31.26 | .2535 |
| | | | | A.D. = .2% | | A.D. = 2.0% |
| $BaBr_2 . 2H_2O$ | 40 | 15.96 | 6.73 | 0.4217 | 2.84 | .1778 |
| | 60 | 46.66 | 19.63 | .4207 | 8.32 | .1782 |
| | 80 | 120.30 | 50.93 | .4217 | 21.58 | .1786 |
| | | | | D.A. = .1% | | D.A. = .1% |
| $ZnSO_4 \cdot H_2O$ | 70 | 30.34 | 15.21 | .5012 | 7.62 | .2512 |
| | 80 | 44.77 | 22.39 | .5000 | 11.17 | .2495 |
| | 90 | 64.27 | 32.14 | .5000 | 16.11 | .2506 |
| | | | | A.D. = 0.8% | | A.D. = .2% |
| $NaBr . H_2O$ | 50 | 47.87 | 21.62 | .4519 | 9.82 | .2051 |
| | 60 | 79.80 | 35.81 | .4488 | 16.00 | .2005 |
| | 80 | 192.7 | 87.5 | .4539 | 39.45 | .2046 |
| | 90 | 292.4 | 131.8 | .4508 | 59.28 | .2028 |
| | | | | A.D. = .3% | | A.D. = .8% |
| $NaI . 2H_2O$ | 30 | 22.13 | 9.59 | .4335 | 4.17 | .1883 |
| | 40 | 42.85 | 18.41 | .4375 | 7.44 | .1862 |
| | 50 | 81.65 | 35.72 | .4325 | 15.21 | .1866 |
| | 60 | 152.80 | 66.08 | .4299 | 28.51 | .1854 |
| | | | | A.D. = .5% | | A.D. = .4% |

Subtraction (7) from (6) and dropping logs, we get,

$$\frac{\Delta P'}{\Delta P_s'} = \frac{\Delta P''}{\Delta P_s''}$$

That is, the ratio of the vapor pressure lowering at any degree of saturation, and the vapor pressure lowering of a saturated solution is independent of the temperature. In Table I are given the theoretical and experimental values of these ratios. The experimental values were read off smooth log S − log $\Delta$P curves which passed through the various experimental points. A family of such curves is shown in Fig. 1. The $\Delta P_1$ and $\Delta P_2$ values, given in the third and fifth columns of Table I, were read off these isotherms for Log S = 0.3

and log S = 0.6 respectively. The choice of log S was a matter of convenience. The vapor pressure lowering of a saturated solution, $\triangle P_s$, at each temperature was obtained by extending the straight line log S – log $\triangle$P to log S = 0. These values are given in the second column of Table I. Comparison data of seventeen electrolytes are given. For the other substances the extrapolation must be carried too far to be reliable. It is seen, therefore, that Generalization 1 is substantially corroborated by the experimental data. In only a few cases is the average deviation greater than one per cent.

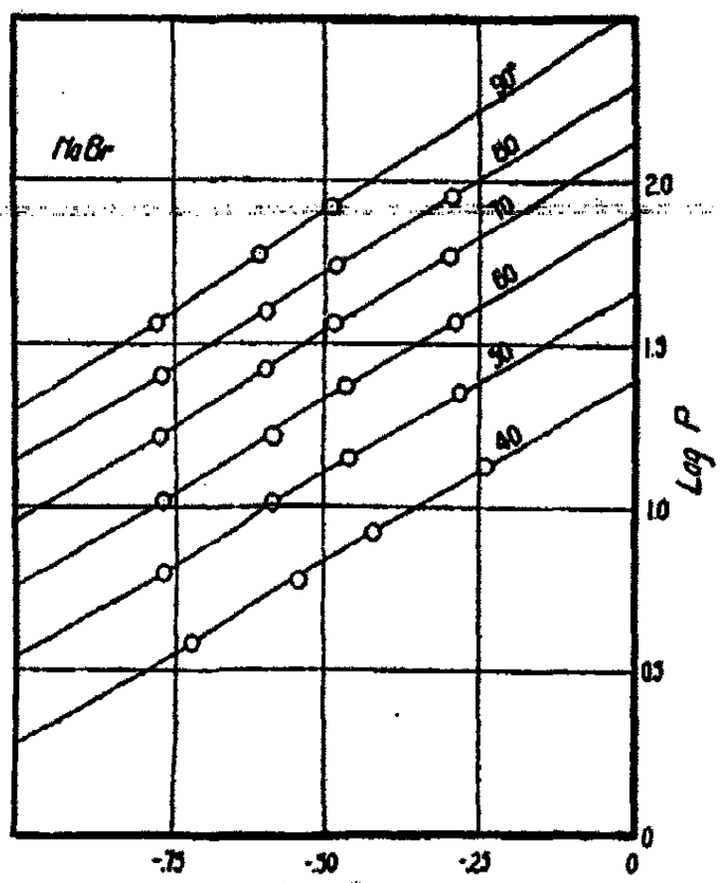



FIG. 1

Log P–log S curves for Sodium Bromide

## Generalization 2

Equation (4) may be written,—

$$\log \triangle P = K\,[1/T - a] + Ka/b \log S \qquad (4)$$

For a saturated solution, since log S = 0, we have

$$\log \triangle P_S = K\,[1/T - a] \qquad (8)$$

subtracting (8) from (4)

$$\log \triangle P/\triangle P_S = Ka/b \log S \qquad (9)$$

which on dropping logs and letting Ka/b = h, becomes

$$\triangle P/\triangle P_s = S^h \qquad (10)$$

TABLE II

Comparison Values of the Ratios $\Delta P/\Delta P_s$ and S

| Name of Substance | t | $\Delta P$ | $S \times 10^2$ | $\Delta P/\Delta P_s$ | $S^h$ | $\Delta P$ | $S \times 10^2$ | $\Delta P/\Delta P_s$ | $S^h$ |
|---|---|---|---|---|---|---|---|---|---|
| $NaI \cdot 2H_2O$ | 30 | 3.90 | 23.69 | *0.1762* | *0.1743* | 9.19 | 47.37 | *0.4112* | *.4040* |
| | 40 | 6.79 | 21.96 | *.1574* | *.1590* | 99.60 | 29.29 | *.2225* | *.2254* |
| | 50 | 11.40 | 19.75 | *.1386* | *.1398* | 16.00 | 26.34 | *.1946* | *.1983* |
| | 60 | 18.40 | 17.53 | *.1202* | *.1209* | 42.99 | 35.04 | *.2802* | *.2810* |
| $MgCl_2 \cdot 2H_2O$ | 40 | 3.20 | 17.40 | *0.08224* | *0.08144* | 19.18 | 60.93 | *0.4930* | *0.4908* |
| | 60 | 8.40 | 16.39 | *.07452* | *.07473* | 22.79 | 32.76 | *.2014* | *.2019* |
| | 80 | 51.60 | 30.25 | *.1776* | *.1800* | 116.1 | 52.94 | *.3998* | *.4018* |
| $SrCl_2 \cdot 6H_2O$ | 30 | 24.0 | 34.07 | *0.2445* | *0.2482* | 41.0 | 51.11 | *0.4196* | *0.4196* |
| | 40 | 17.0 | 15.31 | *.0876* | *.0882* | 42.0 | 30.63 | *.2163* | *.2163* |
| | 50 | 68.0 | 27.62 | *.1890* | *.1892* | 115.0 | 41.44 | *.3196* | *.3198* |
| | 60 | 44.0 | 12.22 | *.0654* | *.0651* | 108.0 | 24.44 | *.1608* | *.1616* |
| NaBr | 50 | 10.1 | 25.27 | *0.2062* | *0.2060* | 14.30 | 34.49 | *0.2919* | *0.2877* |
| | 60 | 10.3 | 17.04 | *.1279* | *.1261* | 37.00 | 51.11 | *.4594* | *.4559* |
| | 70 | 26.1 | 25.04 | *.1984* | *.1976* | 58.5 | 50.09 | *.4448* | *.4453* |
| | 80 | 24.9 | 16.90 | *.1248* | *.1252* | 55.8 | 33.80 | *.2797* | *.2810* |
| | 90 | 36.8 | 16.36 | *.1222* | *.1220* | 59.0 | 40.25 | *.1958* | *.1961* |

TABLE II (continued)

| Name of Substance | t | ΔP | S × 10² | ΔP/ΔP₈ | Sʰ | ΔP | S × 10² | ΔP/ΔP₈ | Sʰ |
|---|---|---|---|---|---|---|---|---|---|
| $K_2CO_3 . 2H_2O$ | 30 | 2.11 | 17.51 | *0.1159* | *0.1140* | 17.20 | 96.33 | *0.9495* | *0.9545* |
| | 40 | 11.10 | 42.74 | *.3470* | *.3465* | 20.00 | 68.38 | *.6252* | *.6226* |
| | 50 | 5.90 | 16.50 | *.1086* | *.1058* | 33.00 | 66.02 | *.6074* | *.5960* |
| | 70 | 14.30 | 15.02 | *.0956* | *.0941* | 80.18 | 60.10 | *.8174* | *.8376* |
| | 80 | 65.50 | 35.76 | *.2781* | *.2775* | 174.0 | 78.68 | *.7387* | *.7415* |
| | 90 | 30.50 | 13.56 | *.0830* | *.0828* | 170.0 | 54.24 | *.4628* | *.4664* |
| $K_2CrO_4$ | 40 | 2.8 | 37.26 | *0.3252* | *0.3196* | 6.2 | 74.70 | *0.7202* | *0.7140* |
| | 60 | 7.5 | 35.28 | *.3028* | *.3003* | 16.6 | 70.58 | *.6700* | *.6689* |
| | 70 | 19.8 | 54.79 | *.5090* | *.4991* | 37.5 | 95.88 | *.9639* | *.9525* |
| | 80 | 17.3 | 33.28 | *.2870* | *.2812* | 38.2 | 66.72 | *.6340* | *.6266* |
| | 90 | 42.8 | 51.94 | *.4649* | *.4692* | 81.3 | 90.87 | *.8833* | *.8956* |
| $BaBr_2 . 2H_2O$ | 40 | 62.40 | 21.90 | *0.1504* | *0.1498* | 13.5 | 11.42 | *0.8458* | *0.8492* |
| | 60 | 15.10 | 40.59 | *.3236* | *.3248* | 25.2 | 16.43 | *.5400* | *.5379* |
| | 80 | 34.90 | 37.09 | *.2890* | *.2896* | 82.8 | 74.18 | *.6855* | *.6903* |
| $ZnSO_4 . H_2O$ | 70 | 51.0 | 16.85 | *0.1681* | *0.1685* | 85.0 | 28.08 | *0.2801* | *0.2808* |
| | 80 | 10.3 | 23.28 | *.2300* | *.2328* | 12.9 | 29.10 | *.2881* | *.2910* |
| | 90 | 11.5 | 17.92 | *.1815* | *.1792* | 19.1 | 29.87 | *.2971* | *.2987* |

The experimental values of the ratio of the vapor pressure lowering and the values of $S^h$ are given in Table II for several salts. In the second and sixth columns are given the experimental vapor pressure lowerings and in columns three and seven the corresponding degrees of saturation. The values for the vapor pressure lowerings of saturated solutions were taken from Table I. In columns four and eight are given the ratios of the vapor pressure lowerings, while in columns five and nine the corresponding values of $S^h$ are given. Owing to the uncertainty introduced in the value of $S^h$ by slight errors in $h$ a more satisfactory test of this generalization is afforded by a study of the graphs of Fig. 2, rather than by an inspection of the data in Table II.

The theory as expressed by equation (10) requires that the log $(\triangle P/\triangle P_s)$ − log S graph be a straight line, and that the slope of this line be equal to $h$. In Fig. 2 are given such graphs for all the electrolytes for which reliable data for $\triangle P_s$ could be obtained by extrapolation of log $\triangle P$ − log S curves. The experimental values of $\triangle P$ were taken from Landolt and Börnstein's tables, and the values of $S$ were obtained by dividing the corresponding concentration by the solubilities. It is of interest to point out that values at different temperatures were used. It is seen that the generalization is in good agreement with the data for many diverse materials.

In Fig. 3 are given the graphs of log $(\triangle P/\triangle P_s)$ against *log S*. The values of $\triangle P_s$ were experimentally determined by Bronsted[1], and the values of $\triangle P$ are those of Tammann[2]. All values are at 100°C. The interesting point about these values is the fact that $\triangle P_s$ and $\triangle P$ were experimentally determined by two different investigators, using different methods. The agreement with the requirements of the theory is a striking confirmation of Generalization 2.

## Theoretical Considerations

The experimental evidence given in this paper and in the first paper confirm conclusively the relations developed. These relations, though developed empirically, must have theoretical significance because of the nature of the independent variables. No attempt, however, will be made here to formulate any theory to fit the equation. It is merely pointed out that the concentration expressed in terms of the degree of saturation leads to fundamental relations which may become important in the theory of solutions.

In connection with this, there are several relations which are interesting. The exponent $h$ in (10) is equal to $ka/b$. The values for these three constants for thirty-one salts are given in the first paper.

$$K = -\left[\frac{\partial \log \triangle P}{\partial (1/T)}\right]_S$$

$$b/a = \left[\frac{\partial \log S}{\partial (1/T)}\right]_{\triangle P}$$

[1] Bronsted: Z. physik. Chem., **82**, 633 (1913).
[2] Tammann: Mém. Acad. Petersburg, (7) **35**, (1887); Z. physik. Chem., **2**, 42 (1888).

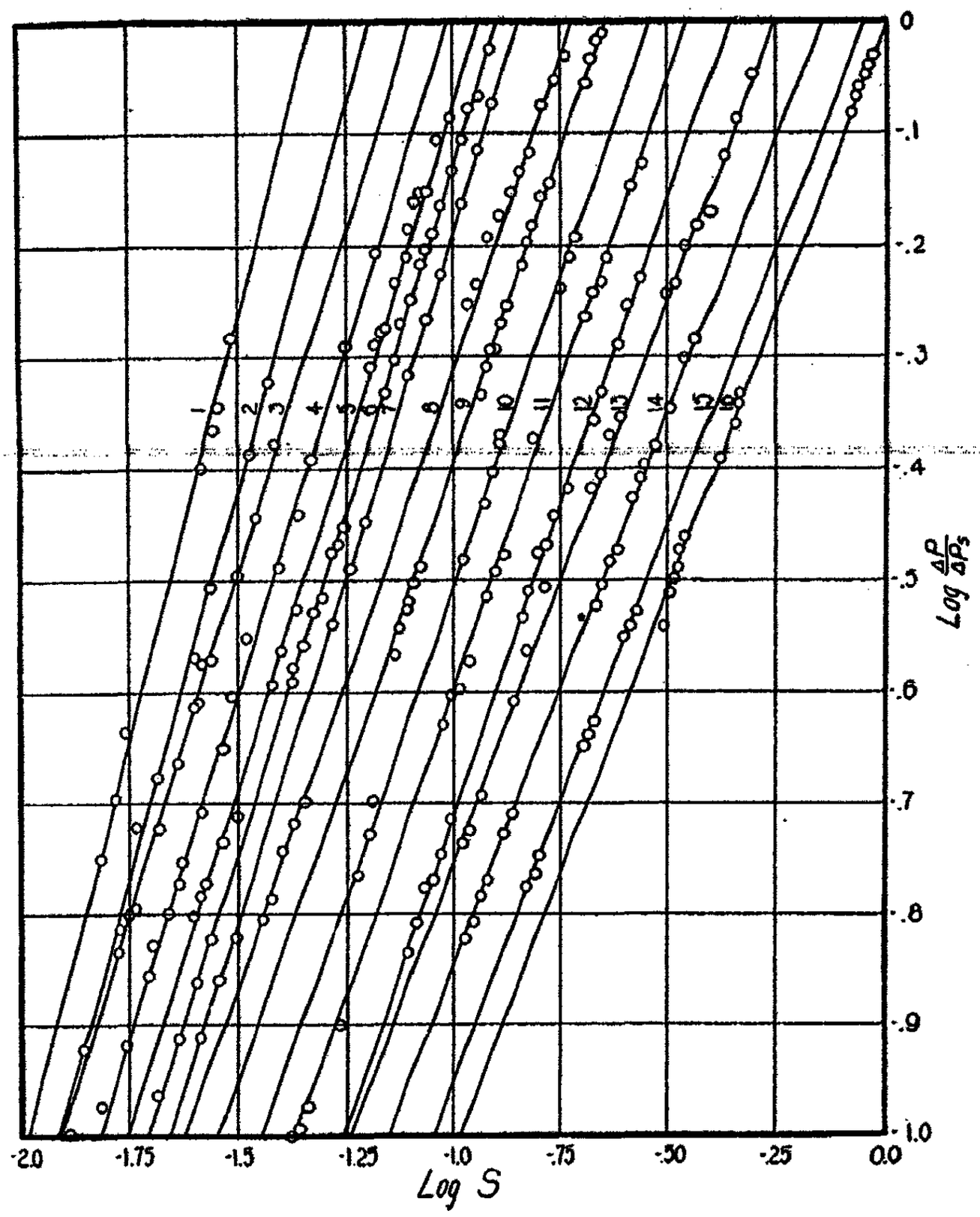



FIG. 2

Log $\frac{\Delta P}{\Delta P_s}$ – log S curves for Sixteen Salts

| No. of Curve | Name of Substance | Log S Scale | No. of Curve | Name of Substance | Log S Scale |
|---|---|---|---|---|---|
| 1 | $MgCl_2$ | Add 1.30 | 9 | $K_2CrO_4$ | Add 0.65 |
| 2 | $SrBr_2$ | " 1.20 | 10 | $Na_2CO_3$ | " 0.58 |
| 3 | $SrCl_2$ | " 1.12 | 11 | RbCl | " 0.45 |
| 4 | NaI | " 1.00 | 12 | KI | " 0.35 |
| 5 | LiCl | " 0.45 | 13 | KCl | " 0.25 |
| 6 | $K_2CO_3$ | " 0.90 | 14 | $(NH_4)_2SO_4$ | " 0.15 |
| 7 | $BaBr_2$ | " 0.85 | 15 | $ZnSO_4$ | " 0.05 |
| 8 | $BaCl_2$ | " 0.70 | 16 | $Na_2SO_4$ | " 0.00 |

but

$$-\left[\frac{\partial \operatorname{Log}\triangle P}{\partial(1/T)}\right]_S \Big/ \left[\frac{\partial \log S}{\partial(1/T)}\right]_{\triangle P} = \left[\frac{\partial \operatorname{Log}\triangle P}{\partial \log S}\right]_T$$

therefore

$$\left[\frac{\partial \operatorname{Log}\triangle P}{\partial \log S}\right]_T = Ka/b = h$$

The values of $h$ are given in Table III. It will be seen that the electrolytes can be divided into three classes, namely

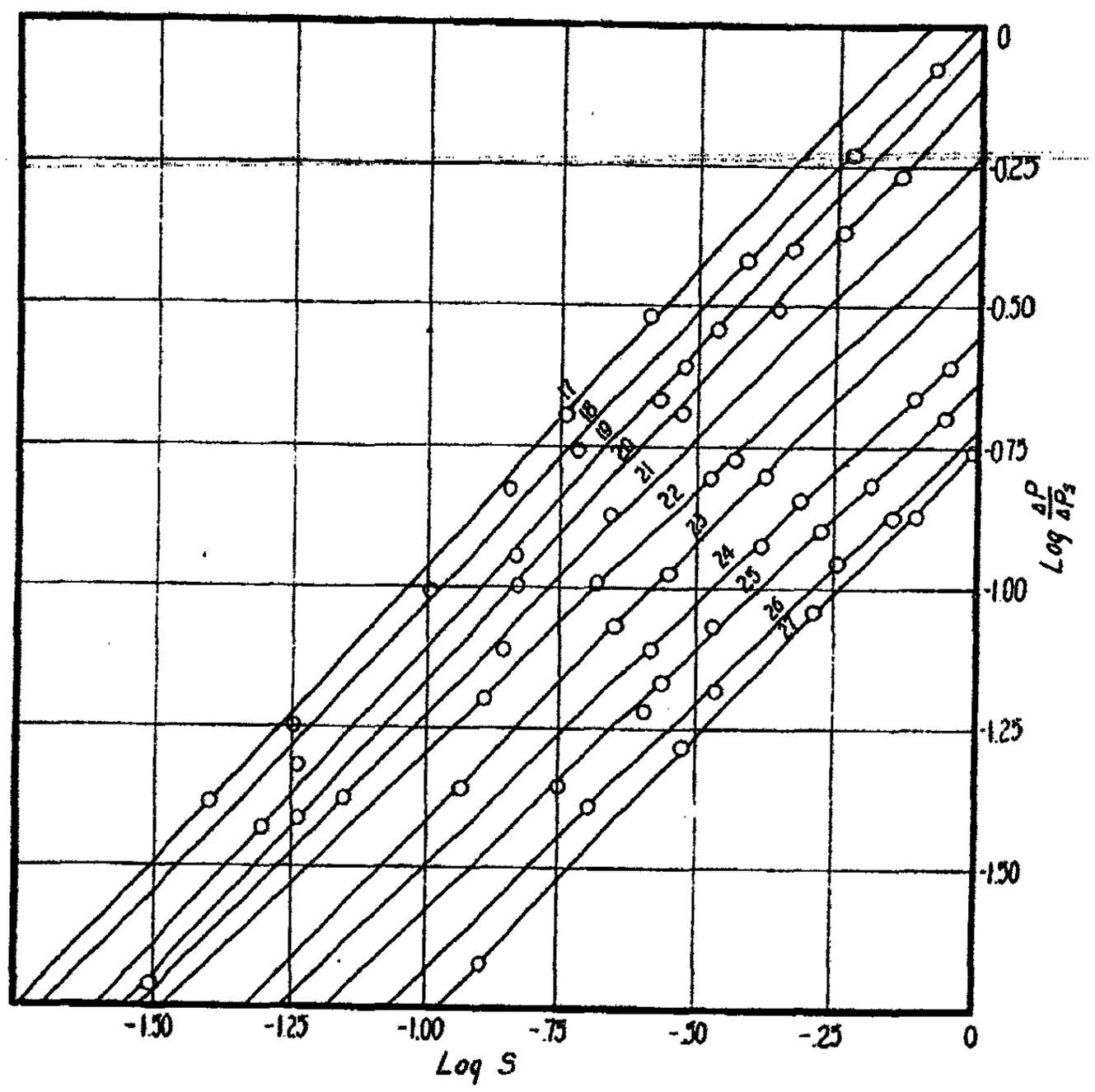



FIG. 3

Log S–log $\frac{\Delta P}{\Delta P_s}$ curves for salts for which datad $\Delta P_s$ are available at 100°C

| No. of Curve | Name of Substance | Log $P/\Delta P_s$ Scale | | No. of Curve | Name of Substance | Log $P/\Delta P_s$ Scale | |
|---|---|---|---|---|---|---|---|
| 17 | NaBr | Substr. | 0.10 | 23 | $NaClO_3$ | Add | 0.55 |
| 18 | KBr | Add | 0.00 | 24 | $K_2SO_4$ | " | 0.25 |
| 19 | KI | " | 0.10 | 25 | $KClO_3$ | " | 0.65 |
| 20 | NaCl | " | 0.10 | 26 | KCl | " | 0.70 |
| 21 | $KNO_3$ | " | 0.50 | 27 | $Na_2SO_4$ | " | 0.75 |
| 22 | $NaNO_3$ | " | 0.45 | | | | |

## TABLE III

### Values of the Exponent h

| Name of Substance | h | | Name of Substance | h | |
|---|---|---|---|---|---|
| $NaNO_3$ | 0.8412 | group I | $NaI \cdot 2H_2O$ | 1.143 | group IIIb |
| $KNO_3$ | .8933 | | $LiBr \cdot 2H_2O$ | 1.152 | |
| $NH_4Cl$ | .8950 | | $K_2CrO_4$ | 1.155 | |
| $ZnSO_4 . H_2O$ | .9971 | group II | $NaClO_3$ | 1.205 | |
| $Na_2SO_4$ | .9976 | | $BaBr_2 \cdot 2H_2O$ | 1.240 | |
| $(NH_4)_2SO_4$ | 1.000 | | $K_2CO_3 \cdot 2H_2O$ | 1.252 | |
| $ZnSO_4 . 6H_2O$ | 1.000 | | $LiBr \cdot H_2O$ | 1.256 | |
| KCl | 1.000 | | $NaBr \cdot H_2O$ | 1.263 | |
| $NH_4Br$ | 1.033 | | LiCl | 1.263 | |
| $Na_2CO_3 \cdot 2H_2O$ | 1.037 | group IIIa | $SrCl_2 \cdot 6H_2O$ | 1.307 | |
| $NaBr \cdot 2H_2O$ | 1.049 | | $CaCl_2 \cdot 2H_2O$ | 1.317 | |
| NaCl | 1.049 | | $SrBr_2 \cdot 6H_2O$ | 1.323 | |
| KBr | 1.060 | | $MgCl_2 \cdot 6H_2O$ | 1.403 | |
| RbCl | 1.094 | | $NiSO_4 \cdot 6H_2O$ | 1.559 | |
| $BaCl_2 \cdot 2H_2O$ | 1.109 | | $CoSO_4 \cdot 7H_2O$ | 1.670 | |
| KI | 1.138 | | $Be_2(SO_4)_3 \cdot 4H_2O$ | 1.698 | |

(1) $h < 1$; (2) $h = 1$; (3) $h \triangle 1$.

Now, when $\triangle P$ is plotted against $S$ characteristic curves are obtained for each group. Where $h$ equals 1, these curves are straight lines. The curves for $(NH_4)_2SO_4$ are shown in Fig. 4a. Where $h$ is less than one, the curves are concave downward. In Fig. 4d are shown such curves for $NaNO_3$. For substances for which $h$ is greater than 1 two modifications exist, as shown in Fig. 4b and 4c. The former are concave upward till a certain degree of saturation is reached, when they become straight lines, while the latter are concave upward continuously. The examples given are $BaCl_2$ and LiCl. Whatever the theoretical significances of these curves may be, they are probably indicative of the molecular constitution of the solution.

### Conclusion

The degree of saturation is the ratio of the number of moles of solute dissolved in a given quantity of solvent to the number of moles of solute that this given quantity of solvent can hold in solution under similar conditions.

The theoretical significance of this ratio is of prime importance when the molecular conditions of an under-saturated and saturated solutions are identical. This is obviously, not the case when the usual solubilities are used inasmuch as the solubility as generally determined is affected both by "self-salting out" as well as adsorption.

Various theories have been suggested to explain the salting-out effect[1]. Whatever the real explanation may be, it is certain that the presence of solute molecules or ions affects the power of the solvent to dissolve. This, no doubt is true when only one kind of solute is present as well as when a second solute is present. This effect is what is termed in this paper and in the preceding paper "self salting-out".

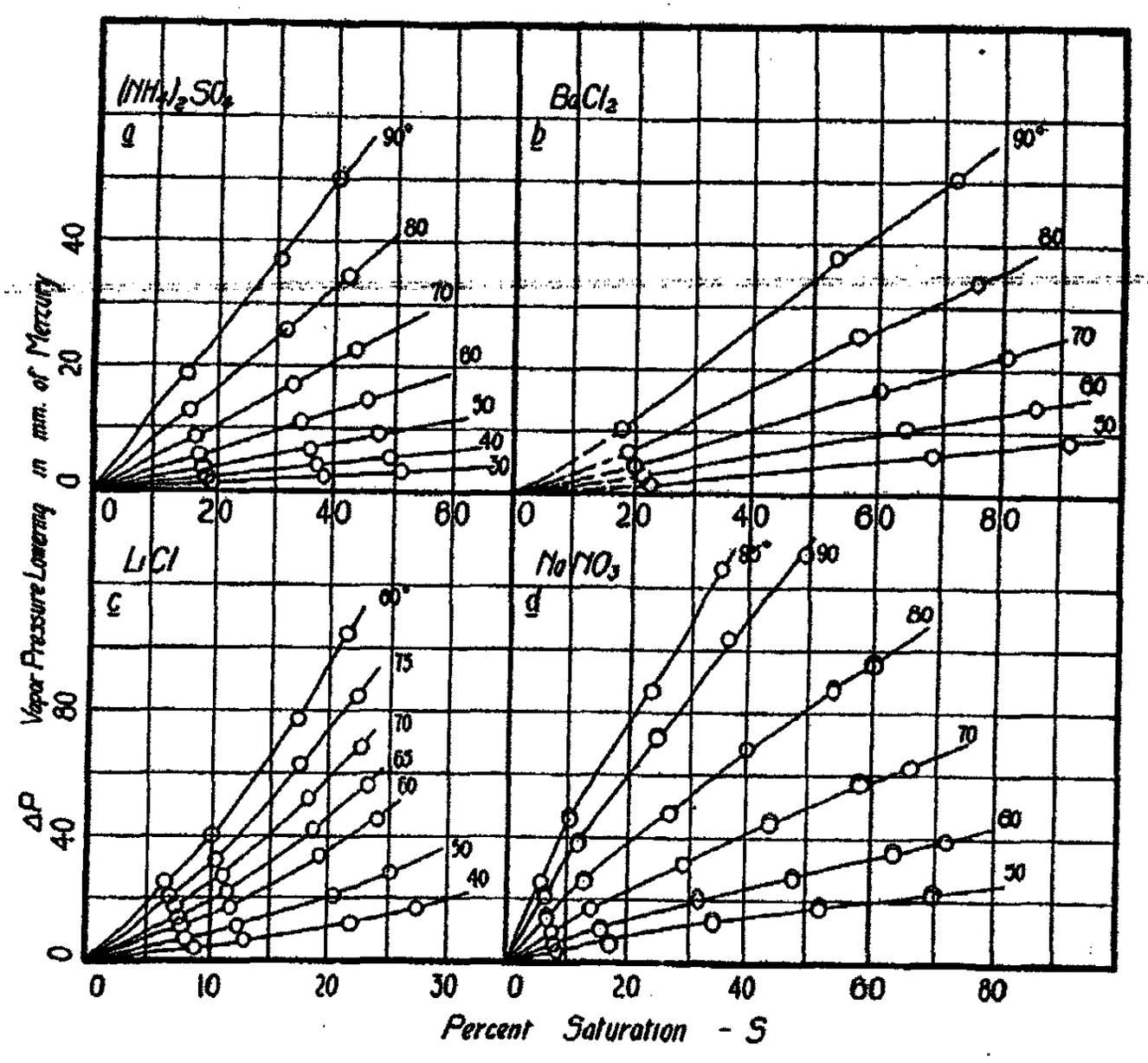



FIG. 4
Typical ΔP-S Curves

It has long been known that salt crystals strongly adsorb a common ion from solution. While this has been appreciated analytically the most convincing evidence has come from the study of the electric charges carried by colloidal particles of insoluble salts. In a recent investigation Fajans and Frankenburger[2] have determined the amount of adsorption of silver ions by

[1] Euler: Z. physik. Chem., 31, 360 (1899); Geffcken: 49, 257 (1904); Levin: 55, 503 (1906); Rothmund: 33, 401 (1900); 69, 523 (1909); Lowry: Trans. Faraday Soc., 1, 197 (1905); Philip: J. Chem. Soc., 91, 711 (1907); McKeown: J. Am. Chem. Soc., 44, 1203 (1922).
A thorough discussion and resumé of this subject is given in the American adaptation of Eucken, Jette and LaMer, loc. cit. (p. 341-348).

[2] Z. physik. Chem., 105, 255 (1923).

silver bromide crystals. Solubility is the concentration of the liquid phase in equilibrium with the solid phase. Solubility so defined must be corrected for adsorption as well as "self-salting" out in order to obtain the "real" solubility. The degree of saturation expressed in terms of this "real" solubility will be different from the degree of saturation used in these papers. We should expect therefore, regular deviations from the relations developed here. These deviations are probably negligible or at any rate are masked by the experimental error. If more accurate date should become available, this deviation will no doubt become apparent. This, however, does not invalidate the relations developed nor does it vitiate the importance of the concept of the degree of saturation.

## Summary

In this paper additional experimental proof was given in confirmation of the two generalizations:—

*Generalization 1*:—The ratio of the vapor pressure lowering $\Delta P$ at any degree of saturation and the vapor pressure lowering of a saturated solution $\Delta P_s$ is independent of the temperature.

*Generalization 2*:—The ratio $\Delta P/\Delta P_s$ is a simple function of the degree of saturation, i.e.

$$\Delta P/\Delta P_s = S^h$$

where

$$h = Ka/b = \left[\frac{\partial \log \Delta P}{\partial \log S}\right]$$

These two generalizations are deducible directly from an equation developed in a previous paper which connects the vapor pressure lowering with the degree of saturation. The equation is

$$\log \Delta P = K\,[1/T - a\,(1 - \log S/b)]$$

where $K$, $a$, and $b$ are constants, $S$ the degree of saturation, $\Delta P$ the vapor pressure lowering, and $T$ the absolute temperature.

*Havemeyer Chemical Laboratory,*
*New York University,*
*New York City.*

# THE PREPARATION AND CONDITIONS OF FORMATION OF THE TWO POSSIBLE TYPES OF EMULSION IN THE SYSTEM CRESYLIC ACID—GELATINE—WATER*

BY ROWLAND MARCUS WOODMAN

It is the belief at present that an emulsifier is capable of promoting the one type of emulsion only with any two given liquids[1].

Weston[2] investigated the efficiency of colloidal clay as an emulsifier of oils and fats, and makes a statement that colloidal clay is capable of facilitating the emulsification of oil in water or of water in oil.

During some work on emulsions, with a view to their application to trees as contact insecticides[3], it was found that certain mixtures of soft soap, cresylic acid, and paraffin oil were completely soluble in water, provided the water were present in excess of a definite amount depending on the relative proportions of soap, cresylic acid and paraffin oil. If the water were below this amount, mixtures of solutions and emulsions were formed; both types of emulsion were suspected, according to the amounts of water added, but, as the system was so complicated, this could not be proved. It was resolved, therefore, to choose some simpler analogous system which would offer every facility for the formation of the two types of emulsion, if these were at all possible.

The system chosen consisted of the two liquids water and "cresylic acid" (a mixture of the three cresols labelled "pure"), the emulsifiers being gelatine (Coignet's Gold Leaf Label, and the same purified by a modification of Loeb's process[4]). The advantages of this system are obvious: gelatine gives a colloidal solution with water and is soluble[5] in cresylic acid; if the type of emulsion formed in a system is conditioned by the fact that the future external phase liquid wets the emulsifier, then the chosen system should, by altering the conditions of experiment, favor both liquids in turn. For in view of the fact that an aqueous gelatine solution forms the continuous phase of many emulsions, water must, on the above hypothesis, wet the particles of gelatine in an aqueous colloidal solution of gelatine; on the other hand, if gelatine dissolves in cresylic acid, it is justifiable to assume that the solute is wetted by the solvent. Hence, in the chosen system, where the gelatine is capable of being wetted by both liquid phases (as shown by simply dipping gelatine into the two liquids), it may be possible to form both types of emulsions by varying the conditions.

*Experimental:* 0.4% solutions of pure gelatine were made in distilled water, and in cresylic acid.

---

* School of Agriculture, University of Cambridge.

[1] Clayton: "Emulsions and Emulsification", 7 (1923).

[2] Weston: Chemical Age, 4, 604, 638, 640 (1921).

[3] Woodman: J. Pomology and Horticultural Science, 5, 43 (1925).

[4] Loeb: "Proteins and the Theory of Colloidal Behaviour", (1922).

[5] Stocke: "Brit. Ass. Colloid Reports", 1, 74 (1917).

The first experiments were made to ascertain (assuming the two types of emulsion possible), if the type formed depended on previous wetting of the emulsifier by one of the liquid phases: definite volumes of aqueous gelatine and cresylic acid, and of distilled water and cresylic acid gelatine solution, were shaken together in stoppered graduated 50 c.c. cylinders and left to cream[1]. The results obtained are given in Table I.

TABLE I

| 1 c.c. of 0.4% aqueous gelatine | 2 c.c. of cresylic acid | 3 c.c. of 0.4% cresylic acid gelatine | 4 c.c. of Water | 5 c.c. of B | 6 c.c. and character of cream | 7 Description of emulsion from Drop Test on cream | 8 % by vol. of disperse phase in cream on basis of full creaming | 9 % by vol. of disperse phase obtained by cracking known vol. of cream |
|---|---|---|---|---|---|---|---|---|
| 10 | — | — | — | 10 | 13 u | W in B | 76.92 | — |
| 25 (1%) | — | — | — | 5 | 8 | B " W | — | — |
| 20 | — | — | — | 10 | 14 8 | B " W | 71.43 | 70 of B |
| 25 (1%) | 5 | — | — | — | u | C " W | — | — |
| 30 | 5 | — | — | — | 7 u | C " W | 71.43 | — |
| 25 | 2 | — | — | — | u | C " W | — | — |
| 200 | 30 | — | — | — | 38 u | C " W | 78.94 | 63.63 of C |
| — | — | 200 | 30 | — | 8 | W " C | — | — |
| 30 | 5 | — | — | — | u | C " W | — | — |
| 30 | 10 | — | — | — | u | C " W | — | — |
| 30 | 15 | — | — | — | u | C " W | — | — |
| 20 | 15 | — | — | — | u | C " W | — | — |
| 10 | 10 | — | — | — | u | C " W | — | — |
| 10 | 15 | — | — | — | u | C " W | — | — |
| 10 | 20 | — | — | — | s | W " C | — | — |
| — | — | 30 | 5 | — | s | W " C | — | — |
| — | — | 30 | 15 | — | s | W " C | — | 28 of C. |
| — | — | 10 | 10 | — | u | C " W | — | — |
| — | — | 10 | 15 | — | u | C " W | — | — |
| — | — | 10 | 20 | — | u | C " W | — | — |
| 32 | 10 | — | — | — | u | C " W | — | — |
| 10 | 10 | — | — | — | s | W " C | — | — |

**Notes on Table I.**

*Column 5.* B is a mixture (1.1 by volume) of toluene and cresylic acid and is less dense than water; W = water; C = cresylic acid.

*Column 6.* Shows the volume of "cream" when the emulsion is apparently fully creamed (3 b); *s* means a supernatant cream; *u* that the cream tends to settle to the bottom.

[1] Woodman: J. Pomology and Horticultural Science", 4, 184 (1925).

*Column 7.* Indicator methods were not of much use in determining the type of emulsion formed, as cresylic acid and water are mutually miscible to some extent. The drop test was found quite applicable, especially when carried out on the creams. The types were also recognizable by their behaviour in a wet pipette, the W in C cream forming a film, difficultly removable by running water, on pipetting up and running out of the pipette. A further differentiation of the two types was afforded by the method of creaming: thus a B in W emulsion creams normally whilst a W in B emulsion tends to "cream" downwards to form an "undercream"; C in W emulsions form undercreams and W in C emulsions ordinary creams. The method of creaming is thus obviously correlated with the densities of the two liquid phases and the type of emulsion formed.

*Column 8.* Assuming that the disperse phase of an emulsion consists of small spheres of the same diameter, the closest packing of the spheres (without distortion), allows 74% of the space occupied to consist of disperse phase. This fact has been applied to emulsion creams (6), and it has been shown experimentally that complete creaming of emulsion mixtures results in the formation of a cream containing approximately the mathematical limit 74% by volume of disperse phase (*e.g.*, for 32 observations[1] the average was 72.28 ± 0.67). This allows two further methods of determining the type of emulsion formed. In the first place, assuming all the disperse phase to be in the cream (which is usually the case for simple one-type systems such as oil—emulsifier—water, where the oil and water are immiscible and the oil is not soluble to any appreciable extent in the continuous medium[2], measurement of the final volume of cream (which is usually well-defined[3]), (6 and 3 b), obtained by shaking known unequal volumes of the two liquid media with emulsifier, allows calculation of the volume percentages in the cream of either liquid, assuming each in turn to be the disperse phase, and that complete emulsification of one liquid has taken place. That percentage which comes within the approximate range 65—80 is then likely to be that of the internal phase liquid, being nearer to the theoretical 74%. In the case where the phase liquids have very different volumes (e.g. 2: 1 or 3: 1), no calculation is necessary, for the volumes of cream widely differ for the two types.

This method was found to be of little use in the present system, as the C in W emulsions were usually unstable, free cresylic acid being present in nearly every case; it was applicable, however, to most emulsions of the opposite type.

*Column 9.* Illustrates the second method of differentiation by means of the emulsion cream, and consists in "cracking" a known volume of the cream obtained after complete creaming, by adding a concentrated acid (hydrochloric, which has not tendency to react with the cresylic acid), and, after waiting a few days, reading off the volume of cresylic acid obtained. If the volume of

[1] Woodman: J. Pomology and Horticultural Science, 4, 184 (1925).
[2] Pickering: J. Chem. Soc., 111, 86 (1917); Woodman: l. c.
[3] Pickering: J. Chem. Soc., 91, 2001 (1907); Woodman: l. c.

cresols approximates to 74% of the cream taken, the emulsion is C in W; if to 26%, then it is W in C. This method was found applicable, as was the first, to most W in C emulsion creams, but failed with most C in W emulsions, apparently because these "broke" long before complete creaming was possible.

### Discussion of Results of Table I

Table I shows that, in the given system, it is quite possible to make the two types of emulsion. Apparently the previous suspension or solution of the emulsifier in one of the liquids does not appear to determine the type of emulsion subsequently formed. Experiments on another system bore this out: a clean cork was filed and ground to a fine state of division, and the cork dust ground with water. The larger particles floated to the surface, leaving an aqueous suspension of very fine cork dust underneath, the dust presumably being wetted by the water. Ten c.c. of this suspension were pipetted off and shaken with 10 c.c. of toluene. A comparatively stable emulsion resulted, which rapidly creamed on standing. The cream finally possessed a volume 12.4 c.c. (*i.e.* 80.65 per cent. of disperse phase, assuming no miscibility of the two media). As the cream rose to the surface, was capable of dilution by water, and as the globules became dark red on dusting a little Sudan III over the surface and shaking, the emulsion was of the oil in water type.

Twenty c.c. of a similarly formed suspension of fine cork dust in toluene were now shaken with 20 c.c. of water. A creamy-looking emulsion resulted, which creamed normally and very quickly, giving 24.75 c.c. of cream, *i.e.* 80.79% of disperse phase. Similar tests to those above proved the emulsion to be of the oil in water type also, though one might assume previous thorough wetting of the emulsifier—cork dust—by the toluene. The emulsion was very unstable, the cream rapidly becoming coarse-grained in character.

The results of these two experiments, together with those of Table I, tend to show that previous wetting of the emulsifier by suspension in one of the liquids is no criterion of the type of emulsion subsequently formed. It must be borne in mind, however, that toluene might exert considerable solvent action on portions of the cork, the emulsifier thus being different (and not a mere suspension of small solid particles of cork), in the two cited cases. A water film might also conceivably replace the toluene film round the cork in the second case, thus explaining the instability noticed; for whereas toluene can replace a water film on a solid surface in a few minutes, water may take weeks to replace entirely a film of an immiscible organic liquid such as toluene[1]. The formation of the same type of emulsion in both experiments would, on the hypothesis of replaceable films, in conjunction with the usual theory of emulsification, have to be put down to a *preferential* wetting of the cork by water.

Table I shows clearly that the relative volumes of the liquid media have a great effect on the type of emulsion formed. Thus a large relative amount of aqueous phase predisposes to the C in W type, and vice-versa, irrespective as

[1] Reynolds: J. Chem. Soc., 119, 460 (1921).

## Table II

10 c.c. aq. solution of pure gelatine.
10 c.c. cresylic acid.

| No. of Expt. | Method of Treatment | Type of Emulsion Formed | c.c. and character of cream | % by vol. of disperse phase in cream on basis of full creaming |
|---|---|---|---|---|
| 1 | Preliminary 10 min. standing before shaking | C in W | u | — |
| 2* | Immediate continuous shaking | W in C | s | — |
| 3† | Stand 15 min. first, then gentle partial rotation before shaking. | C in W | u | — |
| 4* | Stand 30 min., then continuous shaking | W in C | 12.5s | 80.00 |
| 5* | Stand 40 min. and then intermittent shaking at rate of one shake per 30 sec. | W in C | 13 s | 76.92 |
| 6 | Intermittent shaking at rate of one shake per 30 sec. | C in W | u | — |
| 7* | Intermittent shaking at rate of one shake per sec. | W in C | 13 s | 76.92 |
| 8* | Immediate continuous shaking | W in C | s | — |
| 9 | Pipette acid into aq. phase in stream of small drops; gentle partial rotation for a min., and then intermittent shaking—1 per sec. | C in W | u | — |
| 10 | Intermittent shaking—1 per 30 sec. | C in W | u | — |
| 11* | Immediate continuous shaking | W in C | 12.75s | 78.43 |
| 12 | Gentle partial rotation and then continuous shaking | C in W | u | — |
| 13* | Four intermittent shakes—1 per 30 sec. | W in C | 12 s | 83.33 |
| 14* | (0.3%) Two intermittent shakes —1 per 30 sec. | W in C | 12 s | 83.33 |
| 15 | Gentle partial rotation and then intermittent shaking | C in W | u | — |
| 16 | Gentle partial rotation and then continuous shaking | C in W | u | — |
| 17* | Immediate continuous shaking | W in C | 12.5s | 80.00 |
| 18 | One very feeble shake and then vigorous intermittent shaking at rate of 1 shake per 30 sec. | C in W | u | — |
| 19 | One very feeble shake—wait 30 sec.—then vigorous continuous shaking | C in W | u | — |

to which phase first contains the emulsifier. The ranges of results 9 to 15 and 16 to 20, marked by arrows, clearly demonstrate this fact.

Finally, Table I indicates the fact that, in one case, where the same absolute proportions of the two liquids and of the emulsifier are present (results 13, 22 and 18), the two types of emulsion are possible. As no records of the exact methods of preparation of the emulsions in Table I were noted, it was thought necessary to make further experiments to determine the conditions governing the formation of the two types of emulsions in the above special cases.

### Conditions of Formation of the Two Types of Emulsion when the Constituents of the System are always present in the Same Amounts

In the following experiments, ten c.c. of a 0.4% aqueous solution of pure gelatine were shaken with ten c.c. of cresylic acid, the same stoppered cylinder being used in every case. Except where stated otherwise, the aqueous phase was pipetted very slowly and carefully down the cylinder's side to the surface of the cresylic acid, without disturbing the acid. The cylinder's contents were, in different cases, subjected to different treatments previous to emulsification. The results are given in Table II.

### Notes on Table II

The asterisk indicates a W in C emulsion; it was found, in all such cases, that, on shaking, the emulsion wetted the sides of the cylinder to form a continuous film, which ran down to the main body of emulsion, the film draining thinner, without actually breaking, during a considerable period. The W in C type was comparatively slow-creaming, two or three days being necessary for full creaming; the cream rose, as the disperse phase (water), was less dense than the continuous medium. The creams, moreover, were stable, showing little tendency to break; measurement of the volume of the cream, and cracking of the cream, therefore, gave good indications as to the amount and identity of disperse phase.

The emulsions not so marked were of the opposite type and showed different behaviour: on shaking and standing, the film on the cylinder immediately broke and ran up into drops. In few cases (to be quoted later), and then, apparently fortuitously, was all the cresylic acid emulsified, a few drops generally collecting at the surface of the emulsion, most of these drops falling subsequently. The emulsion mixtures started creaming practically immediately, the cream collecting at the bottom (the disperse phase, cresylic acid, being denser than the aqueous continuous medium). The emulsions were unstable and showed great tendency to crack even whilst creaming, a period of six hours to two days usually completing the cracking; this behaviour was probably due to the unemulsified cresylic acid present, and it meant that volume measurements and cracking of the cream did not give reliable data regarding the disperse phase; occasionally, however, the emulsions were stable a sufficient length of time to allow of such data (e.g. Table I, result 7). After

an hour or so, the C in W emulsions usually presented the following appearance: a thin layer of cresylic acid (unemulsified or got by cracking of the emulsion), surmounted by a layer of cream, in turn surmounted by a layer of excess aqueous continuous phase with a drop of cresylic acid at the center of the free surface. The under-creaming and drop test were taken as criteria of the type.

In one case (result 18) the C in W emulsion appeared stable, the emulsion settling slowly to a layer of cream surmounted by excess aqueous phase, no layer of free cresols being present. No. 15 also appeared moderately stable. Both of these, on reshaking, gave emulsions stable enough to allow readings of the volumes of cream, though they were now slow-creaming, as with the W in C type. In both cases there were 14½ c.c. of undercream surmounted by 5½ c.c. of clear aqueous layer, the percentage of disperse phase thus being 68.96. Twenty c.c. of a mixture containing equal volumes of both creams gave, on cracking with 20 c.c. concentrated hydrochloric acid and waiting two or three days for complete separation, 11.75 c.c. (i.e. 58.75%) of cresylic acid, showing the cream to be of the C in W type.

5 c.c. of the cream from each of eight W in C emulsions (i.e. 40 c.c. total), were mixed and cracked with 40 c.c. of concentrated hydrochloric acid; after waiting a few days to ensure complete separation, 13 c.c. of cresylic acid (i.e. 32.5%) were obtained, showing the acid to be the external phase.

It is noteworthy that when any C in W emulsion completely and spontaneously cracked on standing, subsequent reshaking by any method always re-formed the C in W emulsion.

The dagger (Exp. 3) indicates gentle partial rotation. The stoppered cylinder was grasped at each end and gently rotated until its major axis was horizontal; the cylinder was then slowly and gently rotated in a vertical plane backwards and forwards through about 2°, the centre of the major axis acting as a pivot, for at least a minute.

### Discussion of Table II

Results 1 and 2 seem to point to the fact that the period of standing previous to shaking determines the type formed; evidently these results were fortuitous, for results 4, 5 and others proved this hypothesis to be false. Results 3 and 4 tend to show that the formation of the two types is due to the method of treatment previous to shaking. Results 6 and 10 tend to point to the fact that intermittent shaking gives the C in W type. The results were fortuitous, subsequent experiments disproving them; possibly the intermittent shaking was very gentle.

The later experiments were designed to show the effect of vigour of shaking; it will be seen that, in the main, immediate vigorous shaking *e.g.* ordinary continuous or intermittent shaking by hand) gives the W in C type, whilst a preliminary gentle treatment—either by gentle rotation or very gentle shaking—followed later by *any* method of shaking, gives the C in W type.

*Influence of temperature on formation of types:*

In no circumstances tried could the C in W type be prepared at 52°C. when the proportions used were 10 c.c. of 0.4% aqueous gelatine to 10 c.c. of cresylic acid.

*Repetition of Experiments using a cresylic acid solution of gelatine:*

The previous experiments were repeated using a 0.4% solution of gelatine in cresylic acid, and water. The two liquid media were used in different proportions, two experiments in which the methods of shaking were different being done for each proportion. The results are given in Table III.

TABLE III

| c.c. Water | c.c. 0.4% cresylic acid gelatine | Method of Treatment | Type of Cream | Type of Emulsion by Drop Test |
|---|---|---|---|---|
| 20 | 5 | Gentle partial rotation previous continuous shaking | u | C in W |
| 20 | 5 | Vigorous continuous shaking | u | C " W |
| 10 | 5 | do. to 1 | u | C " W |
| 10 | 5 | do. to 2 | u | C " W |
| 10 | 10 | do. to 1 | u | C " W |
| 10 | 10 | do. to 2 | u | C " W |
| 5 | 10 | do. to 1 | u | C " W |
| 5 | 10 | do. to 2 | s | W " C |
| 5 | 15 | do. to 1 | s | W " C |
| 5 | 15 | do. to 2 | s | W " C |

The results indicate that the previous solution of gelatine in the cresylic acid has not much effect on the general trend of the results of the experiments previously carried out. If the cresylic acid is in excess, the W in C type is formed (results 9 and 10), and if the water is in excess (results 1-6), the C in W type is formed, irrespective of the mode of treatment. Results 5 and 6 (agreeing with result 18, Table I show that equal proportions of the two phases give the C in W type irrespective of treatment, the proportions which yield the two types by different treatment now being 5 of water to 10 of cresylic acid gelatine.

Table IV is a collection of results bearing out the whole of the findings previously discussed; results 16-28 were got when using aqueous commercial gelatine solutions (0.4% except when stated otherwise) and results 22-28 when using another sample of cresylic acid (B.D.H. pure). It will be seen that the different samples of cresylic acid give the same results, and that the presence of traces of inorganic constituents in the commercial gelatine apparently had no effect. The commercial gelatine contained 20% of water approximately, the pure sample of the same being anhydrous.

Continuous shaking means ordinary (vigorous) hand shaking.

It will be seen that an excess of one of the liquid phases causes that phase to become the external one (results 1-16); two proportions gave the dual types

of emulsions by different methods of treatment (results 5-14), immediate vigorous shaking giving the stable W in C type, and preliminary gentle partial rotation, or very gentle shaking, giving the C in W type (results 17-28).

It was noticed that, where the dual types could exist for a certain proportion of liquid phases, the resulting type for a definite mode of shaking could be predicted if the gelatine solution were at least a day old.

TABLE IV

| c.c. 0.4% aqueous gelatine | c.c. cresylic acid | Method of Treatment | Type of cream | Type of Emulsion by Drop Test |
|---|---|---|---|---|
| 30 | 15 | Continuous shaking | u | C in W |
| 30 | 15 | Gentle partial rotation then continuous shaking | u | C " W |
| 20 | 15 | Continuous shaking | u | C " W |
| 20 | 15 | Gentle partial rotation then gentle shaking | u | C " W |
| 10 | 10 | Continuous shaking | s | W " C |
| 10 | 10 | do. | s | W " C |
| 10 | 10 | Gentle partial rotation then continuous shaking | u | C " W |
| 10 | 10 | do. | u | C " W |
| 10 | 10 | Very gentle shake—wait 30 sec.—continuous shaking | u | C " W |
| 10 | 10 | do. | u | C " W |
| 10 | 10 | Continuous shaking | s | W " C |
| 10 | 10 | Gentle partial rotation then continuous shaking | u | C " W |
| 10 | 15 | Continuous shaking | s | W " C |
| 10 | 15 | Very gentle partial rotation then gentle shaking | u | C " W |
| 10 | 20 | do. | s | W " C |
| 10 | 20 | Continuous shaking | s | W " C |
| 20 (1%) | 10 | Gentle partial rotation then continuous shaking | u | C " W |
| 40 (1%) | 10 | do. | u | C " W |
| 150 (1%) | 10 | do. | u | C " W |
| 10 | 10 | Continuous shaking | s | W " C |
| 10 | 10 | Gentle partial rotation then continuous shaking | u | C " W |
| 10 | 10 | *Very gentle* continuous shaking | u | C " W |
| 10 | 10 | do. | u | C " W |
| 10 | 10 | Continuous shaking | s | W " C |
| 10 | 10 | do. | s | W " C |
| 10 | 10 | do. | s | W " C |
| 10 | 10 | Gentle partial rotation then continuous shaking | u | C " W |
| 10 | 10 | *Very gentle* continuous shaking | u | C " W |

In Table IV total emulsification of cresylic acid was never obtained, and hence the C in W emulsions were unstable and cracked spontaneously in a period varying from a few hours to a day or so. Subsequent shaking by any method tried always gave the C in W type again, the second emulsion, got in this way, seeming more stable and lasting than the first.

On trying to repeat the experiments with a two-months' old solution of the commercial gelatine (putridity having been prevented by adding a little toluene when the solution was a few days old), it was found that the C in W type of emulsion only could be prepared, however vigorous the shaking given to the system. Two of the C in W emulsions prepared from this old solution were very stable, the undercreams taking about two days to form fully (slow creaming was found to be a sign of complete, or practically complete, emulsification, thus connoting stability). Measurement of the volumes of the undercreams thus allowed estimation of the percentage of disperse phase (77% in both cases), assuming complete emulsification. The undercreams were like sediments of a solid in an extremely fine state of division, and had not the translucent, slightly oily appearance of the supernatant W in C creams.

Two factors, the added traces of toluene, and the age of the gelatine solution, might have accounted for the above phenomenon. It has already been observed, with regard to the second factor, that, with solutions of gelatine less than a day old, difficulty was experienced in forecasting the type of emulsion resultant upon a particular mode of shaking (extraordinary care had to be taken to make the C in W type), and hence the age of the solution apparently exerts a great effect.

The importance of both these factors was tested; a 0.4% solution of commercial gelatine was made, and traces of toluene were added to prevent putrefaction. The types of emulsion possible by all methods of shaking were then noted for the gelatine solution at different ages. At the same time, the

TABLE V

10 c.c. of 0.4% aq. gelatine solution.
10 c.c. of other phase.

| Age of Gelatine Solution reckoned from Time of Making (h.r) | Other Liquid Phase | Temp. | Types of Emulsion found possible by *any* method of Hand-shaking |
|---|---|---|---|
| 2 | Cresylic acid | room | W in C; C in W |
| 24 | do. | do. | W in C; C in W |
| 49 | do. | do. | W in C; C in W |
| 50-51 | o-cresol | do. | W in o-C; o-C in W |
| 50-51 | m-cresol | do. | W in m-C; m-C in W |
| 50-51 | p-cresol | do. | W in p-C; p-C in W (stable) |
| 168-170 | cresylic acid | do. | W in C (*very* unstable); C in W |
| 336 | do. | do. | C in W only |
| 336-338 | do. | 52°C | W in C (*very* unstable) only |

possibility of the formation of both types when using pure o-, m- and p-cresols[1], instead of the cresylic acid, was tested. The effect of temperature on the type formed was also repeated. The results are given in Table V.

The W in C, o-C, m-C or p-C were always stable, giving measurable supernatant creams, except where stated otherwise; the reverse types, except p-C in W, usually were of the type already described, i.e. took a few hours at least to break completely.

The newest solution used was two hours old, as a certain time had to be given to allow the solution to cool to room temperature; with this solution, as with other ones, both types of emulsion were possible, and hence, in this respect at least, the effect of traces of toluene can be neglected.

When the phases were heated to 52° previous to emulsification, the W in C type was the only one possible, agreeing with previous results. If heating a gelatine solution is regarded as a reversal of the ageing effect[2], destruction of the solid network taking place, then the above fact, taken in conjunction with the previously observed tendency of a new gelatine solution to form W in C emulsions—the reverse type being hard to prepare—points to the conclusion that a cool new solution (age = 0 hr.) of gelatine would probably form the W in C type only.

Older solutions of gelatine (170 hr.) still form both types, the W in C type, however, being very unstable and completely breaking in about 15 minutes; with older solutions still (366 hr.), the C in W type alone is possible at ordinary temperatures.

The older solutions did not, in the present instance, give stabler C in W emulsions; this might be correlated with the fact that the gelatine was subjected to hydrolysis even though toluene was present, the solution obviously having a maximum viscosity at about 2-4 days old. (*N.B.* it has been shown that a solution of pure gelatine attains and keeps a maximum viscosity, and does not show signs of putrescence, owing probably to lack of ash[3]; a gel (previously boiled), of the pure gelatine used in the present experiments, inoculated with liquefying bacteria, showed scarcely a trace of their presence after a month[4]. The reason for using commercial gelatine in these last experiments (and hence having to preserve with toluene) was lack of pure sample).

These later results also showed the impossibility of absolutely standardizing the methods of preparation of the two types, for *very* vigorous shaking was found to be necessary to form the water in cresylic acid (or cresol) type. This shaking was given by means of vigorous (and long), shakes, the whole arm from the elbow down taking part, the wrists being stiff. Shaking from the wrist merely (short shakes), however vigorous, gave the reverse type.

[1] Kahlbaum's cresols (liquefied first), kindly provided by F. C. Thompson, Esq., M.Sc., of the Procter Research Laboratory, Leeds.

[2] Woodman: Unpublished data.

[3] Woodman: J. Pomology and Horticultural Science, 4, 95 (1925).

[4] This test was kindly done for me by Mr. H. P. Hale, of the Low Temperature Research Station, Cambridge.

This might be different behaviour from that noticed before (where very gentle shaking was necessary to give the C in W type), or it might be a point previously overlooked.

In some cases tried it was found that reshaking an old creamed W in C emulsion mixture where the proportions of phases were such as to make both types possible, caused reversion to the C in W type; re-shaking a broken or partially broken C in W emulsion mixture by any method also always gave a C in W type.

The results with commercial gelatine as emulsifier were not so trustworthy and standard as those obtained by using pure gelatine.

## General Discussion of Results

An explanation of the formation of the two types of emulsion in the cases quoted is difficult: there are many possible factors to be taken into account, *e.g.*, the relative wetting powers of the two liquid phases for the emulsifier (consideration of surface forces), the possible formation of gelatine cresate or cresates, the partition of gelatine between water and the cresols, the possible non-emulsifiability of one or more cresols, the size of gelatine particles in the two liquid phases, the ageing of solutions and, obviously, the method of preparation, *etc.*

The partial emulsification of o- and m-cresols and the total emulsification of p-cresol point to the fact that, in the case of cresylic acid, no definite cresol remains wholly unemulsified.

The influence of the formation of gelatine cresates or cresate on the type formed cannot be great, for it will be observed that both types can be prepared in certain cases, by altering the mode of shaking, whether the gelatine be first dissolved in the cresylic acid (a condition which should favor formation of cresates) or in the water. The same experiments show that previous wetting of the emulsifier (and, therefore, interfacial forces) by one of the liquid phases, has little apparent effect.

The method of shaking is obviously, in the cases quoted, of great importance in determining the type formed; a tentative, but by no means a definite explanation is given below, taking this fact into account.

In the first place it will be postulated that colloidal solutions may be of two kinds: (a), where the solute molecule is so large as to make the solution colloidal, and (b), where simple (or complex), molecules are in such a state of aggregation as to make the disperse phase particles colloidal in size. Now it is stated that gelatine is soluble in cresylic acid (*loc. cit.*), presumably to give a true solution; but a cresylic acid solution of gelatine has been proved to be capable of forming the external phase of an emulsion, contrary to the general experience, that an emulsifier is usually, in the limit, in a colloidal state of division, and not more finely-divided. It is probably better to assume that the solution of gelatine in cresylic acid is rather colloidal (possibly due to factor (a) above), than true; then the most that can be stated is—even this is

contrary to general experience—that an emulsion can be formed when the emulsifier is capable of forming some type of solution with *both* liquid phases.

As the emulsifier is "soluble" in both liquid phases, there must be some kind of partition coefficient existing between the two liquids. An explanation of the formation of the W in C type by means of vigorous shaking (sometimes only one shake is necessary), whether the gelatine is first dissolved in the cresylic acid or the water, can be based on this notion: a vigorous shake breaks up both liquid phases momentarily into very small droplets, the two liquids being thrown into close juxtaposition; the partition of gelatine then takes place rapidly (possibly hastened by the greater solvent action of small drops), and, because the particles of gelatine in the cresylic acid are probably smaller and much more numerous than in the water, they are adsorbed on the water globules, the cresylic acid coalescing to form the external phase.

In the case of the C in W type the gentle shaking or previous partial rotation does not break the phases into very small droplets (it was noticed that in the case of cresylic acid rotated with aqueous gelatine, the acid not only tended to break, and then into coarse globules), and hence partition of the gelatine is made difficult. Now there is good evidence for believing that a time factor is concerned in the formation, or completion of formation, of the adsorbed layer at the dineric interface of emulsions, (cf. Briggs's work on the value of intermittent shaking[1] and Nugent's work on the inhibition period in the formation of emulsions[2]). An alternative explanation to that provided by Briggs as regards the value of intermittent shaking in formation of emulsions has been given[3]: a time factor has been assumed so that any adsorption at the interface, following a shake, is firmly established if there is a period of waiting before the next shake; continuous shaking, on the other hand, is liable to disturb and loosen the adsorbed emulsifier, and hence more shakes are necessary, the number being correlated with the rapidity of shaking.

It might be thought from this that intermittent shaking would favor adsorption in the present case, and give a C in W type; but ordinary intermittent shaking is vigorous usually and, as one shake only is necessary to give the C in W type, must be avoided as liable to bring about partition of the gelatine. Hence in order to form the C in W type, very gentle shaking, previous partial rotation, or very gently intermittent shaking is necessary; adsorption of gelatine on the cresylic acid globules then commences and becomes firmly established with little fear of immediate partition of the emulsifier, and any further hand-shaking then gives the C in W type, the usual instability of this type being possibly due to the presence of unemulsified cresols consequent on this preparatory procedure, to the solution of the protective layer of gelatine by the cresylic acid external phase, when the gelatine was originally dissolved in the water, and by the water internal phase when originally dissolved in the cresylic acid.

---

[1] Briggs: J. Phys. Chem., **24**, 120 (1920).
[2] Nugent: Trans. Faraday Soc., **17**, 703 (1922).
[3] Woodman: J. Pomology and Horticultural Science, **4**, 95 (1925).

The above explanation of the formation of the C in W type is manifestly feasible when the gelatine is first dissolved in water, because adsorption usually seems to take place from the external medium; in the case where the gelatine is first dissolved in the cresylic acid, and yet a C in W type can be formed, it must be assumed that the adsorbed layer comes from the internal phase itself.

The above-mentioned hypotheses are by no means rigid, yet they give some explanation of the cases of systems where the usual thermodynamic theory—that the phase which wets the emulsifier becomes the external medium—is complicated by the "solubility" of the emulsifier in both phases. Until more work is done on the partition of a large-moleculed substance such as gelatine between solvents in which colloidal aggregation may occur, and on the surface forces of the resultant solutions, little light can be thrown on the subject. The hypotheses, however, can be adopted to explain various phenomena observed:

A new solution of gelatine, with its tendency to give W in C emulsions, is definitely emulsoid, the solid network being negligible; heating an old solution, "a reversal of the ageing process" (destroying the solid structure to give a new definitely emulsoid solution), also tends to predispose to the W in C type, even when the aged solution in the cool will give the reverse type only. Now raising the temperature facilitates the formation of emulsions of oil in soap solution[1], probably by reason of an increase in the rate of adsorption (though not increase in total adsorption), whereas in the case of gelatine as emulsifier, higher temperatures make emulsification more difficult[2], possibly because of lack of solid debris, obtained on shaking, which is necessary to form the desired rigid protective film. If then, a new solution of gelatine is used, or emulsification is caused to take place at a high temperature, the lack of solid particles would be a bar to the adosprtion required to form the C in W type, and emulsification would be possible only after partition of the gelatine, a W in C type resulting.

An old solution of gelatine will, on shaking, give large particles of debris, possibly much too large to be easily dissolved by the cresylic acid, though still very suitable for adsorption purposes. Any shaking would then tend to give a C in W type, as a large proportion of these particles would probably not take place in the partition, the water phase being rich in gelatine. The same consideration applies to C in W emulsions which have completely broken, and W in C types which have partially broken; the aqueous gelatine is old, out of solution, and difficult of solution by the cresylic acid. Reshaking, therefore, effects a new partition exclusive of this solid material, which is in excess in the water phase, and therefore a C in W emulsion results.

[1] Woodman: J. Pomology and Horticultural Science, 4, 95 (1925).

[2] Woodman: Unpublished data.

## Summary

Both types of emulsion are possible in the systems cresylic acid (or o-, m- and p-cresols)—gelatine—water; marked excess of one liquid phase determines the type formed, this liquid becoming the external phase.

In certain cases both types of emulsion are possible when the constituents of the system are not varied in absolute amount, the type formed depending primarily on the mode of preparation, gentle shaking (usually short shakes), or previous partial rotation favouring the C in W type, and vigorous shaking (usually long shakes), the reverse type.

The W in C type is usually more stable than the C in W type—possibly due to the fact that total emulsification of the cresols rarely takes place, the excess disperse phase liquid hastening creaming and cracking.

There are indications that where the proportions of constituents in the system are such as to make the two types of emulsion possible, an absolutely new gelatine solution would give only the W in C type, medium-aged solutions both types, and old solutions the C in W type, these C in W emulsions probably being stabler than others.

In all cases tried where the proportions are such as to make both types possible, a C in W emulsion which has completely broken gave a C in W type on re-emulsification by any manner of hand-shaking; in some cases tried, it was observed that re-shaking a creamed W in C emulsion by any method caused reversal, particularly when the emulsion was old.

A tentative explanation of the above phenomena is given.


*School of Agriculture,*
*Cambridge,*
*England.*
*Dec. 19, 1925.*

3-46

# THE BENZYLATION OF AMINES. PART III

BY DAVID HENRY PEACOCK

In a previous paper[1] attention was drawn to the effect of concentration upon the velocity coefficient of the reaction between amines and benzyl chloride and to the effect of the constitution of the amine upon the character of this concentration effect. In the present paper an attempt is made to indicate the manner in which these alterations in the value of the velocity constant may be produced.

The effect of concentration upon the velocity of reaction between alkyl halides and sodium alkyloxides, phenoxide or naphthoxide has been frequently observed[2]. The observations have been explained on the assumption that ionisation of the alkyloxide, etc., takes place to an extent depending on the dilution, the ions and undissociated molecules then reacting independently with the alkyl halide[3]. If this were the whole explanation the velocity constant in any particular experiment would be expected to alter during the progress of the reaction; this is frequently found not to be the case[4]. The catalytic effect of the sodium halide formed also disturbs the course of the reaction. Burke and Donnan[5] found that in the reaction between alkyl halogen compounds and silver nitrate the velocity constant apparently depended on the concentration of the nitrate group whether present as silver nitrate or alkyl nitrate. Slator and Twiss[6] found that certain alkyl bromides when reacting with sodium thiosulphate gave higher values for the velocity constant in more dilute solution.

Conant and Hussey[7] found that for the reaction between potassium iodide and alkyl chlorides alteration in concentration produced no marked effect upon the value of the velocity constant.

Menschutkin[8], was apparently the first to observe the effect of concentration upon the velocity constant of the reaction between alkyl halogen compounds and amines; for the reaction between allyl and methyl bromides and various amines the velocity constant and the concentration are connected by the relation $KV = \text{const.}$, where V is the dilution. Thus the velocity constant decreased as the dilution increased. Rheinlander[9], found that the velocity constant of the reaction between aniline and the nitrohalogen benzenes increased as the concentrations of the reactants decreased; the effect of altera-

[1] J. Chem. Soc., **127**, 2177 (1925).

[2] Cf. Hecht, Conrad and Bruckner: Z. physik. Chem., **4**, 273 (1889); Cox: J. Chem. Soc., **119**, 142 (1921); Segaller: **103**, 1154 (1913).

[3] Cf. Shroder and Acree: J. Chem. Soc., **105**, 2582 (1914).

[4] Cf. Segaller: loc. cit.

[5] J. Chem. Soc., **85**, 555 (1904).

[6] J. Chem. Soc., **95**, 99 (1909).

[7] J. Chem. Soc., **47**, 476 (1925).

[8] Z. physik. Chem.; **34**, 157 (1900).

[9] J. Chem. Soc., **123**, 3110 (1923).

tion in the concentration of the halogen compound was less marked than that produced by the aniline. Monomethyl aniline showed similar effects but to a smaller extent than did aniline. Owing to the power of forming additive compounds with bases possessed by the nitro compounds of benzene[1], this case is somewhat complicated and is undergoing further examination.

The present author has found that alteration of the concentration of benzyl chloride produced little effect upon the velocity constant of the reaction with amines. Changes in the concentration of the base produced effects depending on the nature of the base. Aniline and o-toluidine showed an increase in velocity constant when the concentration of the base was increased; p-toluidine, p-chloraniline, monoethylaniline showed only a slight alteration in velocity constant; dimethyl aniline, diethylaniline and dimethyl-p-toluidine showed a very marked decrease in velocity constant when the concentration was increased. The activation energy for the reaction also showed changes depending on the concentration of the reactants; within the limits of experimental error it appeared as if the value for the energy of activation approached a limiting value as the concentration of the reactants diminished.

Table I contains the results; those marked (a) are from J. Chem. Soc., 125, 1975 (1924) and those marked (b) from J. Chem. Soc., 127, 2177 (1925).

TABLE I

Velocity Constants for the Reaction with Benzyl Chloride Ethyl Alcohol as Solvent. (a)

| Concentration of Benzyl Chloride | Concentration of Aniline | Temperature | $K \times 10^5$ |
|---|---|---|---|
| 2 M | 4 M | 40° | 354 |
| 1 M | 4 M | " | 383 |
| 1 M | 2 M | " | 300 |
| 0.4 M | 1.6 M | 35° | 157 |
| 0.2 M | 1.6 M | " | 148 |
| 0.2 M | 0.8 M | " | 122 |

In the case of reactions between alkyl halogen compounds and organic bases it does not seem possible to apply the ionic explanation as used for the sodium alkyloxides etc., by Acree (loc. cit.) and others. The formation of reactive complexes between the solvent and the reactants would only explain changes in velocity constant at comparatively high concentration and changes only in one sense; for if an amine A and the solvent S combined thus:—

$$A + S \rightleftharpoons AS$$

[1] Bamberger: Ber., 33, 102 (1900); Sudborough and Picton: J. Chem. Soc., 89, 583 (1906).

TABLE II

Velocity Constants, Aniline, etc., and Benzyl Chloride in Methyl Alcohol at 35° and 45°

| Base | Conc | Concentration of Benzyl Chloride | $k_{35°} \times 10^3$ | $k_{45°} \times 10^3$ | E, calories |
|---|---|---|---|---|---|
| (b) Aniline | 1.6 | 0.4 | 4.25 | 11.2 | 18,780 |
| " " | 1.6 | 0.2 | 4.07 | 10.55 | 18,460 |
| " " | 0.8 | 0.2 | 3.68 | 9.2 | 17,770 |
| " " | 0.4 | 0.2 | 3.62 | 8.5 | 16,550 |
| (b) o-Toluidine | 1.6 | 0.2 | —— | 7.1 | —— |
| " " | 0.8 | " | —— | 5.96 | —— |
| " p-Toluidine | 1.6 | " | 6.21 | 15.1 | 17230 |
| " " | 0.8 | " | 5.99 | 14.7 | 17440 |
| " p-Chloraniline | 0.8 | " | —— | 5.08 | —— |
| " " | 0.4 | " | —— | 5.15 | —— |
| " Monoethyl aniline | 1.6 | " | —— | 1.13 | —— |
| " " | 0.8 | " | —— | 1.13 | —— |
| " Diethyl aniline | 1.6 | " | —— | 0.303 | —— |
| " " | 0.8 | " | —— | 0.400 | —— |
| " " | " | 0.1 | 0.178 | 0.377 | 14550 |
| (b) Dimethyl | 1.6 | 0.2 | 2.23 | 5.06 | 15890 |
| " aniline | 0.8 | " | 2.78 | 6.09 | 15210 |
| " | " | 0.1 | 2.90 | 6.23 | 14430 |
| " | 0.4 | " | 3.13 | 6.99 | 15580 |
| " Dimethyl | 0.8 | 0.1 | 5.75 | 11.5 | 13440 |
| " p-toluidine | 0.4 | " | 6.58 | 12.9 | 13470 |

then [AS] would be proportional to the original concentration of the amine as soon as the concentration of S, the solvent, increased to such an extent that the changes in its concentration produced by the above reaction became negligible. The effect of concentration upon velocity constant is not however negligible at low concentrations and is not always in the same sense. The assumption of the formation of a complex between the two reactants as a precedent to reaction is also insufficient to explain the effects of concentration. Hawkins[1] who examined the freezing point curves for mixtures of allyl bromide and pyridine with various solvents concluded that his results afforded no evidence for the existence of solvent-solute complexes.

The hypothesis of activated molecules offers a qualitative explanation of the observed facts if it be assumed that activation of one linkage or group of atoms can occur without other parts of the molecule being affected and that the energy of activation associated with one part of a molecule can be transferred to another under suitable conditions. A molecule of aniline can be activated in several ways; the 2, 4, 6 positions in the molecules may become reactive or the two hydrogen atoms of the amino group or the nitrogen atom

[1] J. Chem. Soc., 121, 1170 (1922).

may be brought to a state in which it readily becomes pentavalent, forming the nucleus of a positive ion. In the reaction between benzyl chloride and aromatic bases the essential reaction is probably the conversion of the trivalent nitrogen atom into this positive ion; this does not necessarily imply ionic dissociation as the ionisation may be intramolecular. Looked at from another point of view the above statement implies that the "lone pair" of electrons in the trivalent nitrogen atom have to be activated before they become available for the formation of the new bond involved in the formation of pentavalent nitrogen. The similarity in the behaviour of primary, secondary, and tertiary amines with benzyl halogen compounds and with alkyl halogen compounds supports this view. Nuclear substitution produces similar effects upon the rate of reaction of a primary amine and of a tertiary amine with benzyl chloride e.g. p-toluidine and dimethyl p-toluidine react faster with benzyl chloride than do m-toluidine and dimethyl m-toluidine. Similar results have been observed with other halogen compounds of Menschutkin (loc. cit.) and E. R. Thomas[1]. Substitution in the nucleus of benzyl chloride produces similar effects on the rate of reaction with both dimethylaniline and aniline thus, m-nitrobenzyl chloride reacts faster than p- in both cases. The result with aniline could be explained by assuming that reaction primarily occurs with the hydrogen of the amino group but by analogy with dimethylaniline and ethyl methyl aniline it is reasonable to assume that the reaction takes place through a stage in which a pentavalent nitrogen atom is formed. A primary amine, such as aniline reacts in the normal way with benzyl chloride when the nitrogen atom is activated. The other modes of activation of the aniline molecule are not directly useful in this reaction but under ordinary conditions we may assume that all six reactive forms are present in equilibrium in a solution of aniline. When one form is removed by reaction then the equilibrium is displaced and interchange of energy between inactive forms and forms activated in other ways may take place in order to restore the balance.

The possibility of interchange of energy of activation by collision has frequently been postulated in gaseous reactions and does not seem improbable in the case now considered[2]. If activation be assumed to be the result of the absorption of radiation then transference of energy from one active centre to another may take place through the intervention of radiation. However the interchange takes place there is also the possibility of its being governed by quantum considerations. In such a case the assumption is allowable that, as in the case of the photo-electric effect, a quantum of insufficient amount will fail to produce activation whereas energy in excess of that necessary for activation may be converted to kinetic energy. As the probability of an effective collision between an inactive molecule and an activated will depend upon

---

[1] J. Chem. Soc., 103, 595 (1913).

[2] Cf. Mitchell: Proc. Nat. Acad. Sci., Washington, 11, 1925); Taylor and Marshall: J. Phys. Chem., 29, 1140 (1925); Franck: Naturwiss. 47, 1063 (1924): Fowler: Proc. Camb. Phil. Soc., 22, 793 (1925); Tolman: J. Am. Chem. Soc., 47, 1524, 2652; Lewis and Smith: 1508 (1925); and others.

concentrations of the reactant and of its activated forms the velocity constant should increase with increase in the concentration of the reactant, e.g. aniline. Aniline molecules activated in the 2, 4, or 6 nuclear positions and in the two hydrogen atoms of the amino group act as reservoirs for the supply of energy to the inactive form when the inner equilibrium between all forms is disturbed. In the case of secondary bases and p substituted primary bases one of these possible centres of activation has been removed and there is thus not the same reservoir of activated molecules to draw upon. Tertiary bases and their derivatives have still fewer centres of activation and in their case any increase in the concentration of the base will produce a still smaller effect upon the velocity constant.

It is next necessary to deal with the effect of the active form of the solvent. If interchange of energy can take place between the activated solvent molecules and the inactivative reactant then for all except very high concentrations of the reactant the concentration of the active form of the solvent will be constant since the solvent concentration will be constant; this however will not be true if the active form of the solvent forms a complex molecule with the solute. The probability of an effective collision between inactive solute and activated solvent will depend therefore only on the concentration of the reactant as long as the temperature and the nature of the solvent are unaltered. This effect will therefore be of a lower order as regards concentration of the reactant than the effect of the other active forms of the reactant itself. From the experimental results it seems that this effect is either itself inversely proportioned to the concentration of the reactant or is linked with other factors which produce this result.

The interval of time between the collisions of the two reactants increases as the concentration of each reactant decreases and thus the possibility of activation by collision with activated solvent before collision with the other reactant increases; so also does the possibility of collision of an activated reactant molecule with an inactive solvent molecule. But the concentration of activated solvent molecules cannot rise above the equilibrium value for the conditions concerned, there is no loss of activated solvent molecules by reaction as there is of reactant molecules. The exchange of energy between solute and solvent is therefore practically unilateral and as the time interval between collisions of the two reactants increases i.e. as the concentration decreases, the opportunity for activation by collision with active solute molecules increases and so the velocity constant increases. This effect is observed with benzyl chloride and tertiary aromatic bases.

The effect of concentration upon the velocity constants for the reaction between benzyl chloride and the aromatic bases examined follows the following order:—primary bases (not *p*-substituted) $k = f(c^a)$, secondary bases and *p*-substituted primary bases $k = f(c^o)$, tertiary bases $k = f(c^{-b})$. The order deduced with the help of the considerations indicated above is:—primary non *p* substituted bases $k = f(c^{p+q+1})$, secondary bases and *p* substituted primary bases $k = f(c^{q+1})$, tertiary bases $k = f(c)$. If the effect of the solvent is also

considered, then, as indicated above, for tertiary bases $k = f(c^{-1})$ whence the other equations become $k = f(c^{q-1})$ and $k = f(c^{p+q-1})$, the same order as found experimentally.

The activation of the molecules of the reactants by collision with activated solvent molecules has obviously a close bearing upon the effect of the solvent upon the rate of reaction. The rate of reaction will tend to be greater in those solvents which possess the greatest concentrations of activated molecules i.e. which are themselves most reactive. The results obtained by Menschutkin[1], Table III, support this to some extent.

TABLE III

Velocity of Reaction between Ethyl Iodide and Triethylamine, Menschutkin (loc. cit.)

| Solvent | $k_1$ (comparative) | Solvent | $k_1$ (comparative) |
|---|---|---|---|
| Hexane | 1 | Phenetole | 117.7 |
| Heptane | 1.3 | Ethyl Alcohol | 203.3 |
| Benzol | 38.2 | Benzyl Alcohol | 742.2 |
| Chlorbenzol | 128 | Acetone | 337 |
| Brombenzol | 150 | Acetophenone | 718 |
| Diethyl ether | 4.2 | | |

Hawkin's results for the reaction between alkyl bromide and pyridine at 28.3° are as follows:—

toluene 0.00023, benzene 0.000305, nitrobenzene 0.0129, *p*-nitrotoluene 0.00657 acetone 0.00505, acetophenone 0.0104 alcohol 0.00251.

Benzene hydrocarbons are more reactive than aliphatic and reactions in them show a higher velocity constant. Their derivatives show similar behaviour, cf. acetone and acetophenone, ether and phenetole, ethyl alcohol and benzyl alcohol.

The probability of interchanges of energy between the activated molecules of solvent and the unactivated molecules of the reactants may not be independent of the nature of the reactants and hence the solvent which has the greatest reactivity will not necessarily be the solvent in which the reaction measured takes place with the maximum velocity. In this connection it is also necessary to repeat that the reactivity of the solvent as ordinarily measured is a property dependent on the behaviour of the solvent towards some other reactant and will vary with the reactant chosen. It is possible that if the energy of activation of the solvent were less than that of the dissolved reactants no activation of the latter could take place.

If, in a given solvent, two or more reactions take place simultaneously, requiring for their fulfilment two or more kinds of activated molecules then the solvent will favour that reaction for which the interchange of energy between activated solvent molecules and unactivated reactant molecules takes

[1] Z. phys. Chem., 6, 41 (1890).

place with the most ease. This reaction will not necessarily be that which require the least energy of activation as the ease of activation will be governed also by steric effects[1].

The solvent may also alter the velocity of a reaction by altering the energy of activation of the reacting molecules. The measured energy of activation in the case of dimethylaniline and benzyl chloride seems to approach a minimum but these results must be accepted with caution as to the energy of activation is not a quantity susceptible of measurement with great accuracy and it is difficult to decide whether the change in the measured energies of activation is real or due to experimental error. If activation is a process affecting a molecular species which is also in equilibrium with other species then the energy of activation measured will include the thermal effects of the other equilibria involved. Whatever the final causes an alteration in energy of activation due to change in concentration will be reflected in the values of the velocity constants concerned. Thus in the case of dimethyl aniline and benzyl chloride part of the effect of concentration upon velocity constant can be attributed to its effect on the energy of activation.

Further work is in progress on this subject with derivatives of benzyl chloride and with halogen derivatives of nitro-benzene.

*University College,*
*Rangoon, Burma.*
*February 24, 1926.*

[1] Cf. Bjerrum: Z. physik. Chem., **108**, 85 (1924); Brönsted: **102**, 169 (1922).

# VELOCITY OF THERMAL DECOMPOSITION OF CARBONATES*

BY B. BRUŽS[1]

The problem of the thermal decomposition of carbonates has been undertaken with two objects in view. Firstly to bring some light on the question why many of the heterogeneous equilibria between solid substances and gases can be attained only by way of decomposition, the equilibrium pressures not being regained when the reaction is reversed. Secondly the kinetics themselves promised to give interesting results regarding the influence of temperature on reaction velocities, as previous experience with some carbonates showed that the process of decomposition could often be interpreted by means of the usual homogeneous reaction equations.

The classical theory of a dynamic equilibrium for solid-gaseous systems in general and carbonates-carbon dioxide and salt-hydrates-water vapor in particular is mainly due to the early work of C. L. Berthollet[2], H. Rose[3], H. Sainte-Claire Deville, Debray[4], and Pfaundler[5].

The general conclusion of this work can be summarized as follows. At equilibrium, the velocities of decomposition and recombination are equal and, therefore, the pressure of the gaseous phase is determined by the temperature. Ample experimental proof was accumulated by the same authors to show the catalytic activity of water in the case of the thermal decomposition of carbonates.

The question has obtained its thermodynamic solution in the "exact" formula of Nernst for calculation of equilibrium constants of chemical reactions and, in a special case, the "approximation formula" of Nernst for the equilibrium constant for a carbonate

$$\log p = -Q/4.571T + 1.75 \log T + 3.2$$

enables one to determine approximate carbon dioxide pressures for any carbonate from the knowledge of the heat of the reaction

$$MeO + CO_2 = MeCO_3 + Q.$$

But, some very large discrepancies in the experimental determinations of carbon dioxide pressures and theoretical considerations (Langmuir) have cast doubts on the validity of the kinetic explanation of the equilibrium. Nernst has introduced in his work the idea of the equilibrium taking place in the gaseous phase, where all components are supposed to be present in the form of their saturated vapor. Ostwald has called attention to the improbability of such an assumption. It is difficult to imagine substances like calcium oxide having appreciable vapor pressure.

---

* Contribution from the Laboratory of Physical Chemistry, Princeton University.

[1] Charlotte Elizabeth Procter Fellow.

[2] Essaide Statique chimique, 48-53 (1803).

[3] Pogg. Ann., **82**, 545 (1851); **55**, 415 (1842).

[4] Compt. rend., **64**, 603 (1867); **79**, 890 (1874).

[5] Pogg. Ann., **131**, 55 (1867); Jubelband 182 (1874).

Another explanation which would replace the mechanisms of Berthollet and Nernst was given by Langmuir[1], who proposed the idea of a reaction taking place at an interface metal oxide-metal carbonate or salt hydrate-salt respectively.

No extensive investigations have been made of the velocities in question. The first case was studied by G. N. Lewis[2], who investigated the decomposition of silver oxide and found the reaction to obey the equation of an autocatalytic reaction, where silver plays the rôle of the catalyst. But, his final conclusion was that he really measured the velocity of the reaction $2O = O_2$ in presence of silver. Hinshelwood and Bowen[3] and Hinshelwood[4] investigated a number of substances, most of them of an explosive character and are inclined to believe in interface reactions. Some analogous results in cases of mostly autoaccelerated reactions have been obtained by Sieverts and Thebérath[5], Otto and Fry[6], and Crowther and Cutts[7]. Reaction velocities not showing acceleration have been described by Centnerszwer and Bružs[8].

## The Apparatus

The main aim of the apparatus employed is to investigate the reaction from its very beginning and secondly to conduct it at constant temperature and pressure. Fig. 1 gives a schematic idea of the apparatus.

The substance is placed in the reaction vessel A, a narrow glass tube and connected through the ground seal B to the gasholder C, an iron vessel of large size. On account of the largeness of the vessel the gas remains practically at the original pressure when not more than 100 ccm. of gas are collected in it. The gasholder is kept at constant temperature (25°) in a thermostat K. This arrangement permits an investigation of the reaction at different pressures, although most of the experiments in this investigation have been conducted at atmospheric pressure. Through the stopcock F the apparatus is filled with carbon dioxide. When the reaction takes place, the gas pressing on the surface of the mercury in C causes mercury to flow over in D. The overflowing mercury is collected in E and gives a measure of carbon dioxide evolved in the reaction. G is an iron block, the furnace, heated by nichrome wire wound around it. It has two drilled holes, just fitting the reaction vessel and the thermometer I. Besides that there is a larger hole (not shown in Fig. 1) for a larger reaction vessel. The furnace is very carefully insulated with asbestos and magnesia, so that for temperatures up to 700° it does not require more than 1.5 amps. (at 110 volts) and makes hand regulation with an ammeter and resistance very easy. The temperature in the experiments very seldom fluctuated more than ± 0.1°.

---

[1] J. Am. Chem. Soc., **38**, 222 (1916).
[2] Z. physik. Chem., **52**, 310 (1905).
[3] Phil. Mag., (6), **40**, 569 (1920); Proc. Roy. Soc., **99A**, 203 (1921).
[4] J. Chem. Soc., **119**, I, 721 (1921).
[5] Z. physik. Chem., **100**, 463 (1922).
[6] J. Am. Chem. Soc., **45**, 1134 (1923).
[7] Proc. Roy. Soc., **106A**, 215 (1924).
[8] Acta Univ. Latviensis **11**, (1924); Z. physik. Chem., **115**, 365 (1925); J. Phys. Chem., 29, 733 (1925).

## The Velocity of Decomposition of Ferrous Carbonate

From the number of carbonates investigated in this research with respect to their velocities of thermal decomposition the crystalline natural siderite can be described first on account of the simplicity of this process. The velocity of decomposition of very pure large crystals of siderite of about 0.4 gr. has been measured in the range of 491°-581°C. The decrease of the velocity of carbon dioxide evolution with time clearly showed that the process can be described by the formula of a unimolecular reaction.

For the sake of simplicity and convenience the following method of calculation has been applied. The volume of carbon dioxide evolved during fixed intervals of time (1/2 min.-20 min., depending on the temperature of the experiment) was accepted as a measure of the velocity of decomposition in the interval. The velocity of a unimolecular reaction decreases with time according to the formula:

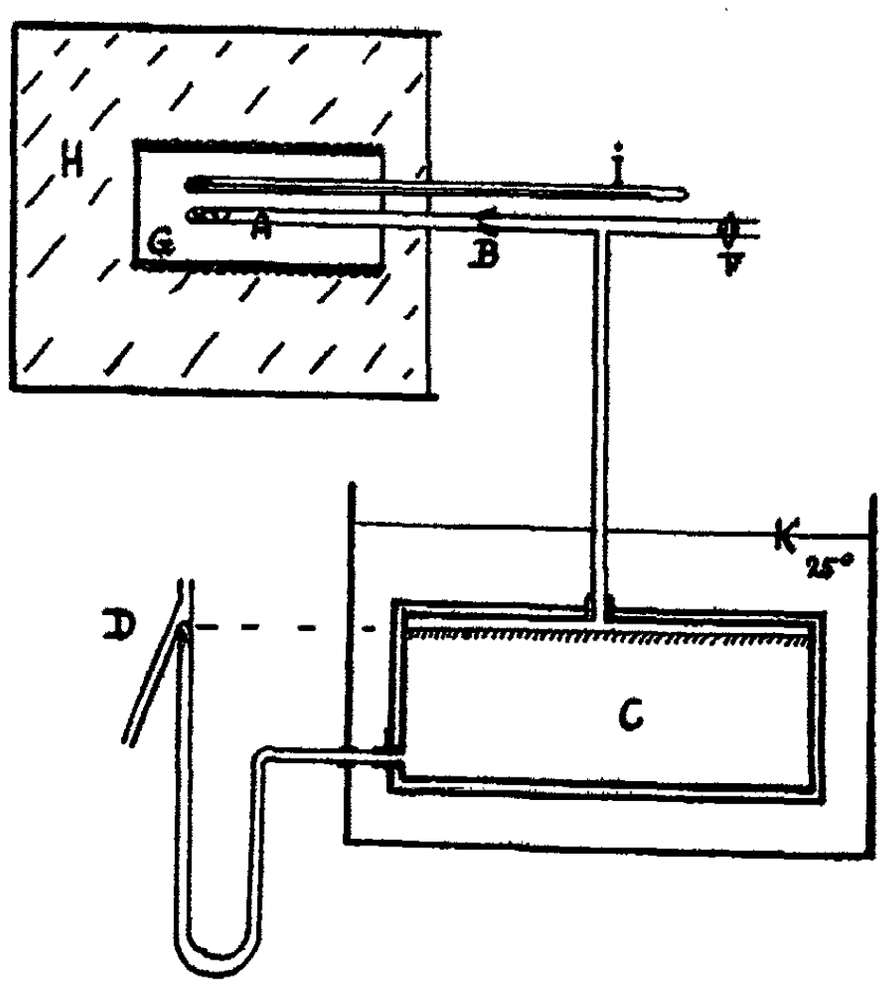



FIG. 1

$$I_t = I_o e^{-\lambda t}$$

where $I_t$ is the velocity at the moment $t$, $I_o$ the initial velocity and $\lambda$ the reaction constant.

From this equation the following relation is easily derived

$$\lambda = \frac{\ln I_{t_1} - \ln I_{t_2}}{t_2 - t_1}$$

in words: the slope of the straight line representing the plot of the logarithms of the velocities against time gives the constant of the reaction.

In fact the data of all experiments except the one experiment at the lowest temperature (491°) when plotted in the way mentioned above gave straight lines. The constants[1] of the reaction for the different temperatures obtained by this calculation are given in Table I.

TABLE I

| C° | λ | λ calc. |
|---|---|---|
| 491 | .00805 | |
| 501 | .0106 | .011 |
| 511 | .0221 | .022 |
| 521 | .0442 | .044 |
| 531 | .0851 | .085 |
| 540 | .154 | .150 |
| 541 | .191 | .180 |
| 550 | .352 | .290 |
| 553 | .301 | .350 |
| 561 | .607 | .580 |
| 566 | .667 | .780 |
| 573 | .989 | 1.18 |
| 581 | 1.472 | 1.90 |

When the logarithms of the reaction constants were plotted against the reciprocals of the absolute temperature a straight line resulted, which meant that the Arrhenius formula for the relation between reaction constants and temperature was valid for this reaction. The value of the critical increment E of the Arrhenius formula

$$E = \frac{R}{T_2^{-1} - T_1^{-1}} \cdot \ln \frac{\lambda_{T_1}}{\lambda_{T_2}}$$

has been calculated from the reaction constants at 501° and 561°. E was found to be 85,500 cals. How closely the observed values agree with the values recalculated from the Arrhenius equation is shown by the third column of the table. Table II shows the calculated percentage decomposition compared with the observed values for eight experiments in a wide range of temperature.

A marked deviation can be seen in the two latter experiments, but one must take into consideration that a deviation of 15 percent is not too high for a reaction the half-lifetime of which is 0.58 min.

Two further questions were investigated in connection with the decomposition of siderite.

As has been noted above, the experiment for the lowest temperature gave an abnormal value for the velocity constant. To settle this question 5 experiments were conducted at low temperatures with large siderite crystals (3-4 grams). In all cases the velocities had very low values and the plots of

[1] All constants are calculated with the use of natural logarithms and are given in reciprocal minutes. Time is given in minutes.

TABLE II

| 501° time | % decomposed calc. | obs. | 511° time | % decomposed calc. | obs. | 521° time | % decomposed calc. | obs. |
|---|---|---|---|---|---|---|---|---|
| 20 | 20 | 22 | 10 | 20 | 22 | 5 | 20 | 20 |
| 40 | 36 | 38 | 20 | 36 | 38 | 10 | 36 | 36 |
| 60 | 48 | 50 | 30 | 48 | 49 | 15 | 48 | 48 |
| 80 | 59 | 59 | 40 | 59 | 59 | 20 | 59 | 58 |
| 100 | 67 | 67 | 50 | 67 | 67 | 25 | 68 | 66 |
| 120 | 73 | 73 | 60 | 73 | 73 | 30 | 74 | 72 |
| 140 | 79 | 79 | 70 | 79 | 78 | 35 | 79 | |
| 160 | 83 | 83 | 80 | 83 | 82 | 40 | 84 | 82 |
| 180 | 86 | | 90 | 86 | 86 | 45 | 87 | 86 |
| | | | 100 | 89 | | 50 | 90 | 90 |

| 531° time | % decomposed calc. | obs. | 541° time | % decomposed calc. | obs. | 553° time | % decomposed calc. | obs. |
|---|---|---|---|---|---|---|---|---|
| 2 | 16 | 16 | 1 | 16 | 16 | 1 | 30 | 28 |
| 4 | 29 | 29 | 2 | 30 | 30 | 2 | 50 | 49 |
| 6 | 40 | 40 | 3 | 42 | 42 | 3 | 65 | 63 |
| 8 | 49 | 50 | 4 | 51 | 51 | 4 | 75 | 74 |
| 10 | 57 | 58 | 5 | 59 | 59 | 5 | 83 | 81 |
| 12 | 64 | 64 | 6 | 66 | 66 | 6 | 88 | 87 |
| 14 | 70 | 70 | 7 | 72 | 71 | 7 | 91 | 91 |
| 16 | 74 | 75 | 8 | 76 | 76 | 8 | 94 | 94 |
| 18 | 78 | 79 | 9 | 80 | 79 | 9 | 96 | |
| 20 | 82 | 82 | 10 | 84 | 82 | 10 | 97 | 97 |
| 22 | 85 | | 15 | 93 | 91 | 11 | 98 | 98 |
| 24 | 87 | | 20 | 97 | 94 | 12 | 99 | 99 |
| 26 | 89 | 88 | | | | | | |

| 561° time | % decomposed calc. | obs. | 573° time | % decomposed calc. | obs. |
|---|---|---|---|---|---|
| 0 | 44 | 33 | 0.5 | 45 | 36 |
| 1 | 69 | 57 | 1.0 | 69 | 63 |
| 2 | 82 | 75 | 1.5 | 83 | 79 |
| 3 | 90 | 86 | 2.0 | 91 | 86 |
| 4 | 95 | 93 | 2.5 | 95 | 92 |
| 5 | 97 | 96 | 3.0 | 97 | 95 |
| 6 | 98 | 98 | 3.5 | 98 | |
| 7 | 99 | 99 | 4.0 | 99 | 99 |

the logarithms of the velocities against time showed indeed a linear course; but, one could readily see that the velocity of carbon dioxide evolution would reach zero before the substance would be totally decomposed. Still, the slope

of the curve was calculated as by this process we eliminate the time factor. The percentage decomposition which could be achieved if the reaction were continued until the velocity had reached zero can then be readily extrapolated from the slope of the curve and the initial velocity $I_o$ as

$$I_o = \lambda N \text{ and } N = I_o/\lambda$$

If we give the value of N so obtained a meaning of "active mass" then $\lambda$ becomes the reaction constant. Table III gives these values.

TABLE III

| C° | $\lambda$ | N |
|---|---|---|
| 445 | .0035 | |
| 455 | .0064 | 9 percent |
| 465 | .0058 | 14 " |
| 485 | .0058 | 50 " |
| 495 | .0074 | 100 " |

We must draw from these experiments the conclusion that in the range of temperature between 455°-495° the velocity constant of the reaction remains practically constant and only the active mass increases with temperature. Above 495° the active mass reaches the value of 100 percent.

It is worth while noting at this place that the samples of the siderite after this partial decomposition were investigated with respect to interface formation, but, it was found that even the largest and least decomposed samples had turned black uniformly throughout the whole crystal.

The second question investigated concerned the dependence of the reaction constant upon the state of grinding. Crystals from the same batch of siderite that had been used in the previous experiments were ground and sieved through screens; a uniform fraction of powder was collected between two screens of close mesh number and used for five experiments. The average size of the crystals measured under the microscope was 0.3 mm. The curves representing the plot of the logarithms of the velocity against time again showed a straight line relationship and the reaction constants could be easily calculated. They are given in Table IV.

TABLE IV

| C° | $\lambda$ | |
|---|---|---|
| 485 | .0065 | N = 60 percent |
| 495 | .0065 | |
| 505 | .0166 | |
| 515 | .0414 | |
| 525 | .0966 | |

Here again we see the same fact that the reaction constant for temperatures below 495° is too high, namely at 485° it is as high as the reaction constant at 495° but, as in the previous case, the reaction does not tend to go to completion. The "active mass" is only 60 percent.

The constants for the four experiments carried out at temperatures at and higher than 495° lie on a straight line, when their logarithms are plotted against the reciprocal absolute temperature. The critical increment is higher than in the reaction with a single crystal, it is 110,800 cals..

It must be mentioned that the velocity of a small part of the initial stage of the reaction exceeds the values to be expected from the greater part of the reaction. This small deviation seems to be due to small amounts of very fine dust of broken crystals. This observation is in accord with the higher value for the critical increment found with the smaller crystals.

### Velocity of Decomposition of Synthetic Ferrous Carbonate

Synthetic ferrous carbonate has been prepared by the method of Sénarmont, by the action of a concentrated ferrous chloride solution on calcium carbonate at 170°. The carbonate obtained, when dried, lost, together with the water, about 20 percent of its carbon dioxide. It readily dissolved in cold acids.

Nevertheless, some experiments carried out with this preparation which did not yield any definite results, still gave an idea about the velocity of decomposition, and mainly the important fact that decomposition at 760 mm. carbon dioxide was complete at 340° as compared with a temperature of 495° for the naturally occurring mineral.

Below 340° the decomposition is not complete and the reaction velocity is of the order of .004-.006 min.$^{-1}$. Three experiments above 340 gave better results. The constants obtained were

| | |
|---|---|
| 340° | .0110 |
| 350° | .0152 |
| 360° | .0239 |

and their logarithms when plotted against the reciprocal absolute temperature gave a straight line, which permitted one to calculate the critical increment 30,700.

### The Velocity of Decomposition of Cobaltous Carbonate

Cobaltous carbonate has been prepared in a dry and crystalline state by the action of a saturated cobaltous chloride solution during twenty-four hours on calcium carbonate powder in a sealed tube at 170°C. This method of synthesis, described by Sénarmont[1] has been applied because simple drying of the common carbonate in a stream of carbon dioxide does not yield the anhydrous carbonate. The crystalline anhydrous cobaltous carbonate is reminiscent of some natural carbonates by reason of its very slow solubility in acids.

The results of a series of 5 experiments made at temperatures ranging from 427°C. to 477°C. were plotted in the following way. The scale of the abscisse (time) has been increased by 100 percent for every succeeding experiment, which is always made at 10° higher than the preceding one. The

[1] Ann. Chim. Phys., (3) 30, 138 (1850).

ordinate represents the percentage of cobaltous carbonate decomposed. Under these conditions the initial course of the curve falls together for all experiments. The further run of the curve shows marked divergencies. In other words, the temperature coefficient for the initial stage of the reaction is very close to 2 for a 10° rise and is higher than two in the final stage.

The course of the individual curves has been analysed by plotting the logarithms of the reaction velocity against time and it has been found that the curve obtained is a straight line for the initial stage of the reaction, changes quite abruptly its slope at a certain point and continues then again as a line up to the end of the reaction. The same characteristic behaviour is shown by the plot of the reaction velocity against the percentage of decomposition.

This observation and previous experience with analogous curves lead to the conclusion that the decomposition takes place in two stages and most probably according to the scheme:

$$CoCO_3 \longrightarrow CoCO_3 \,.\, CoO + CO_2$$
$$CoCO_3 \,.\, CoO \longrightarrow CoO + CO_2.$$

This theory would further account for the fact that the temperature coefficient as mentioned above is about 2 in the first stage and higher for the second half of the reaction, the cause being that the first stage represents the first and fast reaction, the rest of the curve the second and slow reaction. The second reaction begins at higher temperature and would naturally be expected to have a higher temperature coefficient as the temperature coefficient, with other conditions maintained the same, decreases with increase of temperature.

To test the assumption, the experimental data have been compared with values theoretically to be expected. The constant of the first reaction has been evaluated from the initial velocity of the reaction, where the second reaction does not yet play an appreciable rôle. This can be done by the use of the formula

$$I = N\lambda_1 \qquad \text{and} \qquad \lambda_1 = I/N,$$

where I is the velocity of the reaction in percent per minute, $\lambda_1$ the reaction constant and N the active mass, here according to our assumption 50 percent (carbon dioxide). The constant of the final reaction has been evaluated from the final slope of the curve representing the plot of the logarithms of the velocities against time, here

$$\lambda_2 = \frac{\ln I_1 - \ln I_2}{t_2 - t_1}$$

where t is the respective time. Both constants then have been substituted in the theoretical equation for the assumed reactions:

$$CO_2 = \frac{a}{2}\left(2 + \frac{2\lambda_2 - \lambda_1}{\lambda_1 - \lambda_2} e^{-\lambda_1 t} - \frac{\lambda_1}{\lambda_1 - \lambda_2} e^{-\lambda_2 t}\right)$$

where $CO_2$ means the percentage of the total amount of carbon dioxide (a) evolved at the time t from the beginning of the reaction and $\lambda_1$ and $\lambda_2$ are the reaction constants of the first and second reactions respectively. The agreement between observed and calculated values can be seen from Table V.

TABLE V

447°
$\lambda_1 = .018$ $\lambda_2 = .0023$

| time | % decomposed obs. | calc. |
|---|---|---|
| 50 | 34 | 32 |
| 100 | 47.8 | 48 |
| 150 | 57.5 | 57 |
| 200 | 64.0 | 63 |
| 250 | 68.0 | 68 |
| 300 | 71.6 | 72 |
| 350 | 74.2 | 75 |
| 400 | 76.0 | 78 |

457°
$\lambda_1 = .040$ $\lambda_2 = .0055$

| time | % decomposed obs. | calc. |
|---|---|---|
| 20 | 28.7 | 28 |
| 40 | 42.0 | 44 |
| 60 | 51.2 | 54 |
| 80 | 58.5 | 61 |
| 100 | 63.8 | 65 |
| 120 | 68.3 | 70 |
| 140 | 72.3 | 72 |
| 160 | 75.5 | 75 |

467°
$\lambda_1 = .0805$ $\lambda_2 = .0115$

| time | % decomposed obs. | calc. |
|---|---|---|
| 10 | 29.6 | 29 |
| 20 | 44.0 | 41 |
| 30 | 54.7 | 55 |
| 40 | 62.8 | 62 |
| 50 | 68.6 | 66 |
| 60 | 73.8 | 70 |
| 70 | 77.5 | 74 |
| 80 | 80.6 | 76 |
| 90 | 83.1 | 80 |
| 100 | 85.1 | 82 |
| 110 | 86.7 | 84 |
| 120 | 88.2 | 85 |
| 150 | 91.0 | 90 |
| 360 | 99.5 | 99 |

477°
$\lambda_1 = .138$ $\lambda = .023$

| time | % decomposed obs. | calc. |
|---|---|---|
| 10 | 41.8 | 42 |
| 20 | 62.1 | 60 |
| 30 | 73.9 | 69 |
| 40 | 81.3 | 76 |
| 50 | 85.1 | 81 |
| 60 | 88.0 | 85 |
| 70 | 90.1 | 88 |
| 80 | 91.6 | 90 |
| 90 | 92.9 | 92 |
| 100 | 94.0 | 94 |
| 110 | 94.8 | 95 |
| 120 | 95.5 | 96 |
| 130 | 96.1 | 97 |
| 140 | 96.5 | 98 |
| 150 | 96.9 | 98 |

These values permit one to calculate the critical increment of the reactions, as, in the observed range of temperature, the constants of both reactions show a linear relation between the logarithms of the reaction constants and the reciprocal of the absolute temperature. From

$$E = \frac{R}{T_2^{-1} - T_1^{-1}} \cdot \ln \frac{\lambda_{T_1}}{\lambda_{T_2}}$$

we find, substituting the values determined above the critical increments $E_1$ and $E_2$ for the first and second reactions

$$E_1 = 72{,}400$$
$$E_2 = 82{,}200$$

## The Velocity of Decomposition of Zincspar

A series of thirteen experiments was conducted in the range of 407°-452°C. The substance used for these experiments was very pure natural "amorphous" zincspar; the carbon dioxide evolved in the experiments was always in close agreement with theoretical values for total decomposition.

The velocity of decomposition showed a peculair behaviour: about 65 percent of the substance was decomposed at a practically constant rate; after that, the reaction markedly slowed down and abruptly finished near the end.

No mathematical expression could be found to describe this reaction neither by postulating intermediate reaction, nor assuming a heterogeneous catalysis by zinc oxide.

The only way to find the influence of temperature was to compare the constant velocities of the main part of the reaction referred in each case to 1 gr. of carbonate. The amount of substance used in the experiments was 0.5-0.8 gr. in each run. The combined data are given in Table VI. Column 3 gives the percentage decomposition up to which the reaction velocity is constant.

TABLE VI

| °C | Const. | Validity |
|---|---|---|
| 407 | .22 cm/min | 38 percent |
| 417 | .49 | 71 |
| 423 | 1.94 | 58 |
| 427 | 2.54 | 72 |
| 427 | 2.35 | 67 |
| 430 | 2.60 | 83 |
| 432 | 2.23 | 65 |
| 437 | 3.84 | 66 |
| 437 | 7.13 | 74 |
| 438 | 3.32 | 68 |
| 442 | 6.66 | 60 |
| 447 | 14.65 | 79 |
| 452 | 11.50 | 61 |

The data do not give a good agreement and the deviations of the determined values from a continuous increase of this value with temperature exceed the experimental error.

A straight line drawn through the logarithms of the velocities plotted against the reciprocal of the absolute temperature gave a value of the critical increment 95,000.

When the reaction was finished the lumps of zinc carbonate were not broken and were yellow when hot and white when cool.

### The Velocity of Decomposition of Cerussite

The thermal decomposition of lead carbonate represents the most complicated example of the reactions investigated here. This fact could be expected from carbon dioxide pressure measurements of lead carbonate described by Centnerszwer, Falk, and Awerbuch[1], which lead the authors to conclude that three intermediate compounds $3\,.\,PbO\,.\,5PbCO_3$; $PbO\,.\,PbCO_3$; $2PbO\,.\,PbCO_3$ are formed in the course of the decomposition.

A large number of experiments was conducted with two different samples of crystalline natural lead carbonate. The results checked satisfactorily for experiments conducted in the range from 320°-350°C. with beautifully developed single crystals of cerussite weighing from 0.6-0.9 grams each. In all cases 50 percent of the total amount of carbon dioxide were evolved, which fact proves the formation of the intermediate compound $PbO\,.\,PbCO_3$, described by M. Centnerszwer, Falk and Awerbuch as stable in this range of temperature. The mathematical analysis of the decomposition curves showed that the reaction obeyed the scheme of a unimolecular reaction.

TABLE VII

| °C | λ |
|---|---|
| 320 | 0.0046 |
| 325 | .0069 |
| 330 | .0110 |
| 335 | .0173 |
| 340.3 | .0308 |
| 345.3 | .0478 |
| 350 | .1007 |

The logarithms of the reaction constants plotted against the reciprocal absolute temperature lay on a straight line. The critical increment calculated from the slope was 69,600.

The reaction curve did not indicate the formation of the intermediate compound $3PbO\,.\,5PbCO_3$ mentioned above. To find an explanation for this fact some experiments were conducted with larger amounts of substance (6-8 gr.) at low temperatures. The result was analogous to the one in the case of ferrous carbonate. Below a certain temperature, in this case, below 308°C. the substance does not decompose totally to form $PbCO_3\,.\,PbO$ but seems to form a solid phase of variable composition with an "active mass" (N) increasing with temperature. The results are given in Table VIII.

TABLE VIII

| Temp. | | |
|---|---|---|
| 296°C. | .00173 | 9 percent |
| 306 | .00155 | 49 |
| 316 | .00478 | 50 |
| 326 | .00780 | 50 |

[1] Acta. Univ. Latviensis 11, 289 (1924).

The product of the first stage of decomposition of lead carbonate PbO. $PbCO_3$ is a white substance. This last compound was decomposed into a reddish-brown oxide, PbO, at considerably higher temperatures. The decomposition was analogous to the case of zinc carbonate, namely, the velocity for about 70 percent of the reaction was constant and then slowed down very appreciably. This stage of the reaction was not investigated carefully enough but Table IX will give an idea of the influence of temperature on this reaction.

TABLE IX

| Temp. °C. | Velocity $cm^3$/gr. min |
|---|---|
| 426 | .49 |
| 436 | 1.32-1.64 |
| 446 | 2.12-2.50 |
| 456 | 3.50-6.15 |

Another substance investigated by this method was synthetic mercurous carbonate, obtained by precipitation of mercurous nitrate with potassium bicarbonate. The tendency of mercurous nitrate to hydrolyse and form a basic nitrate requires a long period of preparation, during which period the initially white substance turns slightly yellow. The product is not sufficiently pure to yield good results and therefore they will only be described briefly. The description is not omitted because this reaction differs from the previously described by its autocatalytic character.

The velocity of the reaction, very slow in the beginning once started rapidly increases to a maximum and then slows down resembling very much the curves obtained by Lewis[1] for silver oxide. The curve does not yield easily to mathematical analysis. The Ostwald formula could be best tested applying it in this

$$dx/dt = (K_1 + K_2x)(a - x)$$

differential form by plotting $dx/dt : (a - x)$ against x. The plot represented a straight line up to high values of x (a being $Hg_2CO_3$ and x being $Hg_2O$ or what amounts to the same $- CO_2$). Thus values for $K_1$ (point where the straight line crosses the axis of ordinates) and $K_2$, the slope of the line could be calculated. It was found that $K_1$ is very small[2]. $K_2$ is large and represents the catalytic effect of mercurous oxide. Unfortunately this substance is unstable, which is evident from the final inclination of the straight line towards the abscissa. Thus, a complication arises on account of the gradual disappearance of the catalyst, ($Hg_2O = HgO + Hg$). The proof of this explanation was obtained by the fact that samples of the remaining oxide showed a largely decreased amount of monovalent mercury and an appearance of metallic mercury in all the cases where the curve had suffered an appreciable inclination towards the abscissa. Another evidence for the autocatalytic character of the reaction is given by the observation that mercurous carbonate

[1] loc. cit.

[2] Lewis in his paper on silver oxide as a matter of fact does not consider it at all, although it could easily explain the asymmetry of his curves.

blackened for an hour in sunshine without a measureable loss of carbon dioxide, decomposed much faster than the pure substance, but the catalytic power of traces of mercurous oxide seems to be confined only to its presence in closest contact, because mixtures of thermally decomposed mercurous carbonate with undecomposed material showed hardly any difference from the pure samples.

## Discussion of the Results

The first object of this investigation namely the factors influencing the determination of reaction pressures of carbonates has been solved insofar that it has been shown that the reaction velocities drop logarithmically towards the equilibrium point. The equilibria seem to be obtainable with any thermodynamic degree of accuracy only by increasing the sensitivity of the method so far that they can be attained from both sides. On the other hand the results can be interpreted thermodynamically only when the reactions are known. The cases of lead and cobalt carbonates show definitely that the processes are of a complex nature which must be ascertained before any pressure measurements are made.

There remains to be given a short discussion of the results of the kinetics themselves. The simplest case seems to be zinc carbonate leading to the result that a simple isothermal process of decomposition of a substance having a constant pressure $p_s$ against an outside pressure p is proportional to the pressure difference $(p_s - p)$. As this difference under experimental conditions was constant the reaction velocity was constant also. In the case of ferrous carbonate the pressure of the carbon dioxide changes during the process with change of concentration of carbon dioxide in the solid solution. The reaction constant will be proportional to the constantly diminishing pressure difference and will yield a unimolecular reaction curve in all cases where the reaction is conducted above the temperature where the lowest pressure is one atmosphere. Below this temperature the reaction will have a unimolecular form also, but will go only to a point where the solution pressure will have fallen to one atmosphere. This gives to the value of the difference between unity and "active mass" the meaning of solubility of carbon dioxide at one atmosphere at different temperatures in the solid phase. The solubility increases with decreasing temperature. Lead carbonate undergoes both typical processes described on account of the formation of the intermediate product $PbO \cdot PbCO_3$. In the first stage carbon dioxide is soluble in this intermediate product and yields unimolecular reaction curves; in the second stage $PbO \cdot PbCO_3$ decomposes like zinc carbonate directly into PbO and carbon dioxide. Cobalt carbonate is analogous to the lead salt with the difference that both stages of the reaction are so close together that they can be differentiated only by a kinetic investigation.

The "critical increments", determined from the dependence of the reaction constants on temperature, approximate the value of 80,000 cal. and

seem therefore to be characteristic of the carbonate ion in the crystal lattice[1]. In the case of synthetic ferrous carbonate the value is very much lower probably on account of the catalytic action of water. Catalysed reactions are known to have low temperature coefficients.

I wish to thank Professor G. A. Hulett and Professor H. S. Taylor for the inspiring support and interest in this investigation.

## Summary

1. A method is described of investigating reactions of decomposition of solids yielding gaseous reaction products.

2. Ferrous, lead, cobalt, zinc and mercurous carbonates have been investigated by this method with the result that these substances decompose at rates in accord with those found valid for homogeneous unimolecular reactions.

3. The mechanisms of decomposition have been derived for all the substances mentioned.

4. All these reactions have high temperature coefficients the mean value for the "critical increment" 80,000 cal., seems to be characteristic of the carbonate ion in the crystal.

*Princeton,*
*New Jersey.*

[1] An interesting coincidence may be mentioned here. According to Schaefer and Schubert (Ann. Physik., (4) **50**, 283 (1916) ) the carbonate ion in fifteen carbonates investigated by them has three characteristic bands in the infrared with maxima at 6.5, 11.5 and 14.5μ. If we calculate the "activation energy" corresponding to the three bands with the aid of the radiation theory assumption Nhν = E we get in the sum 89.000 cal., a value which is not too far from the observed one.

6-316

# CRYOSCOPIC MEASUREMENTS WITH NITROBENZENE

## Part IV. Association in nitrobenzene solution

BY FREDERICK STANLEY BROWN AND CHARLES R. BURY

The cryoscopic method has been largely used in the study of association in solution: it is doubtful, however, if the results of any previous investigators are sufficiently accurate to decide whether the law of mass action is obeyed. Few have paid sufficient attention to the tendency of solvents to pick up water, and the consequent error in the molecular weights: even with benzene the error due to this cause is larger than can be permitted in work having this object in view[1]; with more hygroscopic solvents, such as nitrobenzene, the error may be much greater. Previous investigators have almost invariably used the van't Hoff equation, which is known to be accurate only at low concentrations, while the law of mass action can only be tested adequately by measurements over a fairly wide range, extending to concentrations at which use of this formula is quite unjustifiable.

As the result of experience gained in previous researches on the use of nitrobenzene as a solvent for cryoscopy, we believe it possible to obtain the necessary accuracy. Roberts and Bury[2] showed that the water content of the solvent could be kept constant at any desired degree of saturation by keeping the solvent in contact with phosphorus pentoxide, water, or a salt hydrate pair. Brown and Bury[3] investigated the alleged change of cryoscopic constant with water content of the solvent. The results obtained led them to put forward an equation that was obeyed by normal substances with considerable accuracy up to concentrations that gave a depression of 4°C. Lastly, Brown,[4] by investigation of the dissociation of naphthalene picrate and naphthalene-trinitrotoluene, equilibria which are known from independent work to obey the law of mass action, was able to show that these methods are sufficiently accurate for the purpose in view.

The method used to keep the water content of the solvent constant lends itself admirably to the study of the influence of the degree of moisture of the solvent on the association of solutes. In view of the interesting results obtained by Baker with pure liquids we have extended our work to the investigation of this problem.

### Experimental

The usual Beckmann method was employed: the preparation of pure nitrobenzene and the use of salt hydrate pairs for keeping the water content of the solvent constant have been described by Roberts and Bury (loc. cit.).

[1] Sidgwick: J. Chem. Soc., 117, 1340 (1920).
[2] J. Chem. Soc., 123, 2037 (1923).
[3] J. Chem. Soc., 125, 2219 (1924).
[4] J. Chem. Soc., 127, 345 (1925).

In this work nitrobenzene of three different degrees of moisture has been employed; i. e., dry, fully saturated, and partially saturated in the presence of $Na_2SO_4,0-10H_2O$.

In our choice of solutes we avoided, as far as possible, substances such as ethyl alcohol, phenol, and acetic acid, which are difficult to prepare and keep free from water: we tried, without much success, to find suitable solids, rather than liquids, for reasons of practical convenience. It is desirable that solutes should be easily purified, readily soluble in nitrobenzene at its freezing point, but should not, for reasons given below, be easily soluble in water. It is difficult to find acids that fulfil these criteria. The solutes used—benzyl and iso-amyl alcohols, β-naphthol, phenyl-acetic, propionic, cinnamic and benzoic acids—were carefully purified by crystallisation or distillation. Liquid solutes were weighed out in small glass bulbs which were dropped into the solvent and broken under its surface.

Difficulties met when working with the dry solvent, in the presence of phosphorus pentoxide, have been discussed fully elsewhere:[1] all powerful dehydrating agents (except sulphuric acid which is soluble in nitro-benzene) seem to adsorb solutes containing an hydroxyl group, and in some cases are even peptised by them.[2] In our experiments with the dry solvent, therefore, no dehydrating agent was employed; the nitrobenzene was distilled in vacuo from phosphorus pentoxide directly into the freezing point tube immediately before the experiment. The apparatus was filled with dry air, a current of which was passed through it in the usual manner throughout the duration of the experiment. Work was carried out as rapidly as possible, no series of experiments lasting more than three hours. As a rule two additions of solute were made in each series, results being checked by another series in which the highest concentration reached in the first series, after two additions of solute, was reached at once in the second series, and so on. This procedure would have enabled us to detect errors due to the absorption of moisture, but these were not observed.

A possible source of error when working with the fully saturated solvent in the presence of water, is the partition of the solute between nitrobenzene and water. If the solute is readily soluble in water, appreciable quantities may be removed from the nitrobenzene solution and the measured degree of association will be too great: also the activity of the water may be altered appreciably and the assumption that the activity of the water remains constant will be invalid. To avoid this error as much as possible, we used minimal quantities of water, and chose solutes which are not readily soluble in water. With the object of detecting passage of the solvent into the water layer, we carried out a number of experiments in which the quantity of water was varied.

[1] Brown and Bury: J. Phys. Chem., 29, 1312 (1925).

[2] Alumina is an excellent dehydrating agent and adsorbs the two alcohols that we have used as solutes to a very slight extent, if at all: it has therefore been used as dehydrating agent in several series of determinations of the association of these alcohols in dry nitrobenzene. We have come to the conclusion, however, that results obtained by the method described in the text, without employing any dehydrating agent, are more reliable, and these alone are quoted.

the amounts of nitrobenzene and solute remaining constant. The error due to this cause is quite negligible except in the case of propionic acid; the results obtained with this acid in the fully saturated solvent are probably subject to a small but appreciable error due to this cause.

All freezing points recorded are the mean of at least three closely agreeing determinations, and are, we believe, usually accurate to about 0.003°C. At least two independent series were carried out with each substance. The results obtained are given in Tables I-VII. In the first column are given the concentration (C) in grams per 100 grams solvent; in the second the observed depression (D); in the third the molecular weight (M) calculated by the formula of Brown and Bury;[1] and in the fourth the degree of association (x = M/ formula weight).

Benzoic and cinnamic acids are too insoluble for the results to have much value for the purpose of this investigation: they also have the disadvantage of dissolving only very slowly; we have not studied their behaviour in the dry solvent.

TABLE I

Benzyl alcohol—formula weight 108.1.

In dry nitrobenzene:—

| C. | D. | M. | x. | K. | γ. |
|---|---|---|---|---|---|
| 1.577 | 0.930 | 114.5 | 1.059 | 4.02 | 0.879 |
| 2.694 | 1.502 | 119.9 | 1.109 | 5.11 | 0.805 |
| 4.120 | 2.152 | 126.5 | 1.170 | 6.53 | 0.730 |
| 5.762 | 2.794 | 134.6 | 1.245 | 8.23 | 0.658 |
| 7.396 | 3.352 | 142.4 | 1.318 | 11.31 | 0.612 |
| 9.028 | 3.852 | 149.9 | 1.387 | 14.90 | 0.548 |
| 11.36 | 4.468 | 160.6 | 1.486 | 22.91 | 0.491 |

In fully saturated nitrobenzene:—

| | | | | | |
|---|---|---|---|---|---|
| 0.823 | 0.485 | 113.5 | 1.051 | 6.31 | 0.889 |
| 1.238 | 0.709 | 116.1 | 1.075 | 6.73 | 0.883 |
| 1.787 | 0.995 | 119.0 | 1.101 | 6.93 | 0.832 |
| 2.488 | 1.337 | 122.5 | 1.135 | 7.33 | 0.789 |
| 3.562 | 1.800 | 128.8 | 1.192 | 8.99 | 0.730 |
| 4.250 | 2.088 | 132.0 | 1.221 | 9.63 | 0.700 |
| 5.392 | 2.490 | 139.4 | 1.290 | 12.73 | 0.652 |
| 6.415 | 2.848 | 144.1 | 1.332 | 14.21 | 0.620 |
| 8.570 | 3.467 | 156.3 | 1.445 | 23.18 | 0.563 |
| 10.33 | 3.911 | 165.6 | 1.532 | 34.14 | 0.528 |

[1] J. Chem. Soc., 125, 2219 (1924).

TABLE II

Iso-amyl alcohol—formula weight 88.1.

In dry nitrobenzene:—

| C. | D. | M. | x. | K. | γ. |
|---|---|---|---|---|---|
| 0.965 | 0.701 | 93.5 | 1.060 | 5.51 | 0.890 |
| 2.163 | 1.400 | 103.5 | 1.174 | 9.16 | 0.743 |
| 3.245 | 1.924 | 111.9 | 1.271 | 14.66 | 0.651 |
| 3.987 | 2.202 | 119.5 | 1.356 | 21.72 | 0.590 |
| 5.246 | 2.628 | 130.7 | 1.484 | 38.52 | 0.512 |
| 6.194 | 2.895 | 139.4 | 1.582 | 64.34 | 0.470 |
| 6.416 | 2.940 | 142.1 | 1.613 | 77.67 | 0.461 |
| 6.733 | 3.007 | 145.5 | 1.652 | 100.7 | 0.446 |
| 8.455 | 3.370 | 161.9 | 1.839 | 517.5 | 0.387 |
| 12.63 | 3.680 | 180.0 | 2.043 | | 0.339 |

In partially saturated nitrobenzene:—

| | | | | | |
|---|---|---|---|---|---|
| 0.521 | 0.386 | 91.0 | 1.033 | 5.05 | 0.870 |
| 1.377 | 0.911 | 99.7 | 1.132 | 10.65 | 0.816 |
| 1.602 | 1.051 | 101.5 | 1.152 | 11.16 | 0.794 |
| 2.341 | 1.426 | 108.6 | 1.232 | 15.39 | 0.708 |
| 3.480 | 1.923 | 118.7 | 1.347 | 23.57 | 0.600 |
| 4.601 | 2.303 | 130.0 | 1.475 | 41.60 | 0.526 |
| 6.117 | 2.722 | 145.1 | 1.647 | 105.8 | 0.448 |
| 6.754 | 2.843 | 153.1 | 1.737 | 210.3 | 0.420 |
| 8.245 | 3.167 | 166.7 | 1.892 | 1344. | 0.370 |
| 10.14 | 3.429 | 188.3 | 2.137 | | 0.320 |
| 11.45 | 3.615 | 201.0 | 2.282 | | 0.294 |
| 14.75 | 3.932 | 236.7 | 2.686 | | 0.245 |

In fully saturated nitrobenzene:—

| | | | | | |
|---|---|---|---|---|---|
| 1.776 | 1.129 | 104.0 | 1.180 | 13.17 | 0.771 |
| 2.091 | 1.285 | 107.2 | 1.216 | 15.25 | 0.732 |
| 3.281 | 1.797 | 119.0 | 1.350 | 25.66 | 0.607 |
| 5.152 | 2.368 | 140.4 | 1.593 | 83.81 | 0.477 |
| 6.566 | 2.712 | 155.2 | 1.762 | 270.2 | 0.412 |
| 8.305 | 3.024 | 175.1 | 1.987 | 126900. | 0.352 |
| 9.965 | 3.248 | 194.7 | 2.211 | | 0.309 |
| 11.32 | 3.421 | 209.3 | 2.375 | | 0.283 |
| 14.06 | 3.660 | 241.9 | 2.746 | | 0.241 |

TABLE III

β-Naphthol—formula weight 144.1.

| C. | D. | M. | x. | K. | γ. |
|---|---|---|---|---|---|
| In dry nitrobenzene:— | | | | | |
| 0.737 | 0.348 | 144.5 | 1.003 | 0.442 | 0.989 |
| 2.134 | 0.989 | 145.6 | 1.010 | 0.597 | 0.967 |
| 2.861 | 1.310 | 146.7 | 1.017 | 0.793 | 0.955 |
| 4.927 | 2.197 | 148.0 | 1.027 | 0.729 | 0.926 |
| 6.095 | 2.680 | 148.7 | 1.032 | 0.711 | 0.911 |
| 7.459 | 3.220 | 149.9 | 1.040 | 0.758 | 0.894 |
| In partially saturated nitrobenzene:— | | | | | |
| 1.718 | 0.792 | 145.1 | 1.007 | 0.492 | 0.971 |
| 2.465 | 1.121 | 146.3 | 1.015 | 0.849 | 0.951 |
| 4.519 | 2.000 | 147.9 | 1.026 | 0.772 | 0.920 |
| 6.440 | 2.780 | 149.5 | 1.037 | 0.809 | 0.893 |
| 8.507 | 3.580 | 151.0 | 1.048 | 0.819 | 0.868 |
| In fully saturated nitrobenzene:— | | | | | |
| 2.002 | 0.910 | 146.0 | 1.013 | 0.833 | 0.967 |
| 3.256 | 1.452 | 147.2 | 1.021 | 0.870 | 0.935 |
| 4.032 | 1.778 | 148.1 | 1.028 | 0.936 | 0.919 |
| 5.267 | 2.270 | 150.4 | 1.043 | 1.185 | 0.896 |
| 6.901 | 2.903 | 151.9 | 1.054 | 1.170 | 0.869 |
| 8.061 | 3.343 | 152.8 | 1.060 | 1.216 | 0.849 |
| 8.760 | 3.579 | 154.5 | 1.072 | 1.321 | 0.839 |

TABLE IV

Phenyl-acetic acid—formula weight 136.1.

| C. | D. | M. | x. | K. | γ. 1 |
|---|---|---|---|---|---|
| In dry nitrobenzene:— | | | | | |
| 1.126 | 0.363 | 211.6 | 1.555 | 431.5 | 0.47 |
| 3.629 | 1.069 | 228.9 | 1.682 | 351.7 | 0.290 |
| 4.289 | 1.242 | 231.7 | 1.703 | 354.7 | 0.263 |
| 5.426 | 1.557 | 232.8 | 1.710 | 304.7 | 0.246 |
| 8.288 | 2.323 | 234.8 | 1.726 | 231.3 | 0.207 |
| 10.52 | 2.913 | 235.0 | 1.727 | 187.1 | 0.185 |
| 13.41 | 3.655 | 235.5 | 1.730 | 153.1 | 0.172 |
| In fully saturated nitrobenzene:— | | | | | |
| 0.938 | 0.337 | 186.6 | 1.372 | 153.7 | 0.601 |
| 1.433 | 0.488 | 196.4 | 1.443 | 161.6 | 0.528 |
| 3.600 | 1.107 | 214.9 | 1.579 | 163.1 | 0.364 |
| 4.133 | 1.264 | 215.8 | 1.584 | 150.5 | 0.345 |
| 4.645 | 1.407 | 216.9 | 1.594 | 141.0 | 0.329 |
| 7.863 | 2.272 | 223.9 | 1.645 | 124.9 | 0.270 |
| 9.219 | 2.617 | 226.2 | 1.663 | 122.3 | 0.250 |
| 11.62 | 3.242 | 227.7 | 1.673 | 107.4 | 0.229 |
| 13.00 | 3.577 | 229.3 | 1.685 | 106.3 | 0.219 |

TABLE V

Propionic acid—formula weight 74.1.

In dry nitrobenzene:—

| C. | D. | M. | x. | K. | γ. |
|---|---|---|---|---|---|
| 0.380 | 0.238 | 109.2 | 1.474 | 400.6 | 0.459 |
| 0.952 | 0.536 | 121.0 | 1.632 | 487.7 | 0.303 |
| 1.837 | 0.960 | 129.1 | 1.743 | 648.0 | 0.221 |
| 2.885 | 1.439 | 134.2 | 1.811 | 886.2 | 0.178 |
| 4.172 | 2.033 | 135.8 | 1.834 | 821.2 | 0.151 |
| 6.073 | 2.885 | 137.1 | 1.850 | 733.5 | 0.128 |
| 6.266 | 2.952 | 138.1 | 1.864 | 881.0 | 0.126 |
| 6.713 | 3.132 | 139.0 | 1.875 | 1018 | 0.122 |
| 9.508 | 4.279 | 140.9 | 1.902 | 1905 | 0.106 |

In partially saturated nitrobenzene:—

| | | | | | |
|---|---|---|---|---|---|
| 0.788 | 0.458 | 116.2 | 1.570 | 645.4 | 0.347 |
| 1.171 | 0.643 | 123.0 | 1.661 | 743.3 | 0.292 |
| 1.495 | 0.806 | 125.1 | 1.689 | 717.6 | 0.262 |
| 3.273 | 1.625 | 133.8 | 1.805 | 915.8 | 0.184 |
| 6.070 | 2.837 | 138.8 | 1.873 | 1227 | 0.137 |
| 8.026 | 3.620 | 142.2 | 1.919 | 2351 | 0.120 |

In fully saturated nitrobenzene:—

| | | | | | |
|---|---|---|---|---|---|
| 0.793 | 0.450 | 117.8 | 1.590 | 208.7 | 0.396 |
| 1.396 | 0.762 | 122.0 | 1.646 | 164.6 | 0.304 |
| 3.031 | 1.532 | 129.7 | 1.751 | 143.5 | 0.217 |
| 4.973 | 2.352 | 136.5 | 1.842 | 788.4 | 0.172 |
| 6.958 | 3.162 | 139.8 | 1.887 | 1208 | 0.147 |
| 8.594 | 3.760 | 143.6 | 1.937 | 3585 | 0.133 |

TABLE VI

Benzoic acid—formula weight 122.1.

In partially saturated nitrobenzene:—

| C. | D. | M. | x. |
|---|---|---|---|
| 1.007 | 0.362 | 187.9 | 1.539 |
| 1.885 | 0.630 | 200.8 | 1.645 |
| 2.445 | 0.796 | 205.8 | 1.686 |
| 3.119 | 1.009 | 206.2 | 1.689 |
| 3.850 | 1.221 | 209.5 | 1.716 |
| 4.838 | 1.499 | 213.0 | 1.745 |

In wet nitrobenzene:—

| | | | |
|---|---|---|---|
| 0.325 | 0.138 | 158.7 | 1.300 |
| 0.741 | 0.280 | 177.2 | 1.452 |
| 0.972 | 0.360 | 180.8 | 1.481 |
| 1.826 | 0.628 | 193.9 | 1.588 |
| 3.111 | 1.019 | 202.2 | 1.657 |
| 3.890 | 1.248 | 205.4 | 1.682 |

TABLE VII

Cinnamic acid—formula weight 148.1.

In partially saturated nitrobenzene:—

| C. | D. | M. | x. |
|---|---|---|---|
| 0.657 | 0.197 | 226.5 | 1.529 |
| 0.747 | 0.220 | 229.9 | 1.552 |
| 0.862 | 0.246 | 236.7 | 1.598 |
| 1.803 | 0.477 | 253.9 | 1.714 |
| 2.159 | 0.568 | 255.7 | 1.726 |
| 2.785 | 0.710 | 262.6 | 1.774 |
| 2.995 | 0.760 | 264.0 | 1.782 |

In fully saturated nitrobenzene:—

| | | | |
|---|---|---|---|
| 0.578 | 0.170 | 208.7 | 1.409 |
| 0.774 | 0.236 | 220.0 | 1.486 |
| 0.917 | 0.376 | 222.8 | 1.502 |
| 1.620 | 0.453 | 239.2 | 1.614 |
| 1.643 | 0.459 | 239.4 | 1.616 |
| 1.955 | 0.535 | 243.9 | 1.646 |
| 2.175 | 0.582 | 249.7 | 1.686 |
| 2.525 | 0.668 | 251.8 | 1.700 |
| 2.754 | 0.712 | 258.6 | 1.746 |
| 2.920 | 0.750 | 259.1 | 1.750 |
| 3.100 | 0.775 | 266.6 | 1.797 |

The results of Beckmann and Augustin[1] for cinnamic acid are in close agreement with ours; apparently the degree of moisture of their solvent was very close to our partially saturated solvent in the presence of $Na_2SO_4$, $0-10H_2O$: their figures for benzoic acid differ considerably from ours. Ampola and Carlinfanti[2] have measured the association of benzyl alcohol: their results are in as close agreement with ours as could be expected from the accuracy of their work. Boeseken and van der Eerden[3] have studied the association in nitrobenzene of cinnamic, benzoic, phenylacetic, and propionic acids, and ofamyl alcohol (a mixture of isomers): their results are so inconsistent that nocomparison is possible.

## Conclusions

Auwers[4] came to the conclusion that associated substances could be divided into two classes, each of which was characterised by a definite type of con-

[1] Z. physik. Chem., 60, 385 (1907).
[2] Gazz., 26II, 76 (1896).
[3] Rec. Trav. chim., 33, 301 (1914).
[4] Z. physik. Chem., 30, 300 (1899).

centration-association curve: this same division holds in nitrobenzene solution for the substances that we have examined, and would appear, from a study of literature, to be perfectly general. Our work shows that the two classes are also differentiated by the effect of moisture on their degree of association. The distinction between these two classes is illustrated in Fig. 1, in which the degree of association of one substance of each class in the wet and in the dry solvent is plotted against the concentration of the solution, expressed as mols per hundred grams of solvent.

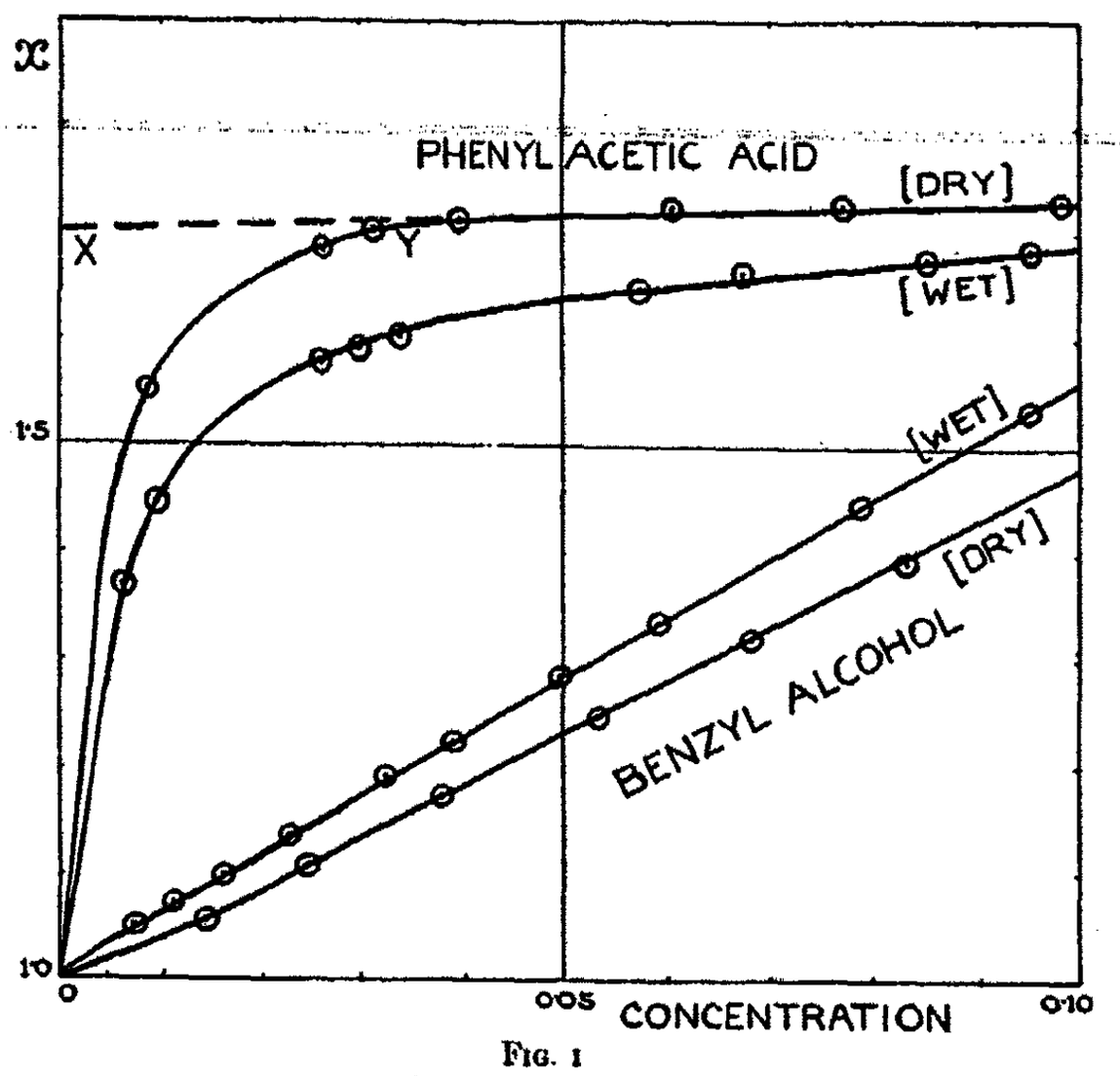



FIG. 1

With the first class (class A), of which alcohols and phenols are typical examples, the degree of association increases steadily with concentration, and does not appear to reach a limit. These substances are more associated in the wet solvent.

With the second class (class B), of which acids are typical examples, the degree of association increases rapidly with concentration up to a point, beyond which it only increases very slowly: i. e., the degree of association seems to have a limiting value. With the two acids for which it has been found possible to measure the association to sufficiently high concentrations, this limit is approximately, but not exactly, 2. Substances of this class are more associated in the dry solvent, at any rate in dilute solution.

With one substance of this class (propionic acid) we have reached a point where the wet and dry curves intersect. It is probable from the direction of the curves that all the other substances of this class would behave in a similar manner at sufficiently high concentrations: in the figure the wet and dry curves of phenyl-acetic acid are obviously approaching each other at high concentrations.

Several observers, working with substances of class B, have overlooked the steep part of the curve in dilute solution, and have suggested that the association-concentration curve in dilute solution is of the type shown by the dotted line XY in Fig. 1—that is to say, the solute has an abnormal molecular weight even at infinite dilution (See, for example, Beckmann and Augustin (loc. cit.) on benzoic acid in nitrobenzene, Hentschel[1] on acetic acid in benzene. The question is discussed by Turner, "Molecular Association," p. 35 (1915)).

The second conclusion to be drawn from this work is that none of the solutes examined obey the law of mass action, with the possible exception of $\beta$-naphthol, which is so slightly associated, even at the highest concentrations, that it is hardly fair to draw any conclusions from it. That substances of class A do not obey the law is obvious from the form of the association-concentration curve. If association to double molecules is assumed, it is possible to calculate the mol fractions of single and double molecules ($N_s$ and $N_d$) from the values of x given, and thence the equilibrium constant ($K = N_d/N_s^2$), the values for which are given in the fifth column of Tables I-V. These are not constant in any one series, and no better agreement is obtained by assuming the formation of triple or more complex molecules.

The fact that the law of mass action is not obeyed forces one to the conclusion that the assumption of association is not a complete explanation of the abnormality of these substances; it is also necessary to assume that for some unknown reason either the single molecules, the complex molecules, or both, do not form ideal solutions in nitrobenzene, that is to say, their active masses are not proportional to their concentrations expressed as mol fractions. If this is the case, it is not valid, except at infinite dilution, to deduce the molecular weights or degrees of association of associated substances from freezing points or any other related properties of their solutions: at best these quantities are a convenient measure of the abnormality of the solution.

Since association is not a complete explanation of the abnormal behaviour of these substances, and since the degree of association would appear to be an unmeasurable quantity, it is desirable to keep in mind the possibility that association does not occur at all. Whilst most organic substances containing an hydroxyl group are markedly abnormal from every point of view, there seems to be no definite evidence of the existence of complex molecules. Even the abnormal molecular weights of acids in the gaseous state have been shown to be largely due to an experimental error—neglect of an adsorbed layer of

[1] Z. physik. Chem., 2, 306 (1888).

acid on glass surfaces.[1] Tyrer's criticism of the method of deducing degrees of association from the temperature coefficient of molecular surface energy[2] seems unanswerable, and it is probable that abnormal values of this constant (and, indeed, most of the abnormal properties of these compounds) are due, not to association, but to their polarity,[3] or intramolecular ionisation as it was originally called by Thomson.[4] Baker's observations of the properties of certain dry liquids,[5] most of which were typically normal compounds, merely proves that these liquids are mixtures, but not necessarily associated, as is usually assumed. There are, for example, grounds for belief that benzene is a mixture of tautomeric forms of the same molecular weight.[6] The results obtained by Baker and McBain[7] for the adsorption of toluene and acetic acid on charcoal, which they attribute to the existence of acetic acid as double molecules, can be explained equally well by the assumption that a molecule of toluene occupies twice as much space as does one of acetic acid on the surface of charcoal. The only satisfactory chemical[8] evidence of association is for substances with uneven numbers of electrons in the molecule, such as $NO_2$, $(C_6H_5)_3C$, and I.

## Calculation of Activities

As has been pointed out above, the degree of association is, at best, a convenient measure of abnormality—it is, moreover, an unsatisfactory measure: since "associated" substances do not form ideal solutions, the degree of association will depend on the experimental means employed to determine it. (This, it will be noticed, is characteristic of the degree of association.) A much more suitable measure of the abnormality is the activity, since this should be independent of the experimental means used to determine it, provided that they have the necessary accuracy. We have therefore calculated activity coefficients from our freezing point data.

These calculations of activities are offered with reserve, as preliminary results, for the thermodynamic data for nitrobenzene are not free from uncertainty: also, calculation of activities of solutes involves extrapolation to infinite dilution, and is therefore liable to serious error if accurate data for dilute solutions are lacking: the Beckmann method is known to be unsuitable for accurate work in dilute solutions, and in our experimental work we have paid little attention to this region: when more accurate data are available, it

[1] Drucker and Ullmann: Z. physik. Chem., 74, 567 (1910).
[2] Z. physik. Chem., 80, 50 (1912).
[3] Hildebrand: "Solubility" American Chemical Society Monograph Series, (1924).
[4] Phil. Mag., (6) 27, 757 (1914).
[5] J. Chem. Soc., 121, 568 (1922).
[6] Ingold: J. Chem. Soc., 121, 1133 (1922).
[7] J. Am. Chem. Soc., 46, 2718 (1924).
[8] There is strong evidence from band spectra that some elements, such as helium, mercury, and sodium, do form complex molecules ($He_2$, $Hg_2$, $Na_2$) in the gaseous state, though these substances are among the most normal gases known to chemists. There is, as yet, no evidence as to whether these double molecules carry an electric charge or not, or whether their existence is probable under normal conditions.

may be necessary to multiply our results for any one series throughout by a constant. This uncertainty applies more particularly, to substances of class B, and to results for the moist solvent. We are at present engaged in trying to confirm some of these activities by an independent method.

The method of Lewis and Randall[1] was employed: the activity of the solvent ($\alpha_1$) is connected with the freezing point depression ($\theta$, which for the dry solvent is the same as D in our tables) by their equation XXIII-16. Taking the latent heat of fusion of nitrobenzene to be 22.46 cal.,[2] a value which is in excellent agreement with our molecular weight determinations of normal substances,[3] and taking the difference of the specific heats of solid and liquid to be 0.02 cal.,[4] this equation becomes:—

$$d \ln \alpha_1 = d\theta\,(-0.01785 - 0.000112\,\theta). \qquad (1)$$

If $m$ is the number of mols solute, calculated from the formula weight, per mol of solvent, their equation XXII-19 becomes:—

$$d \ln \alpha_2 = \frac{-d \ln \alpha_1}{m}: \qquad (2)$$

where $\alpha_2$ is the activity of the solute. Combination of these two equations leads to the equation:—

$$\ln \frac{\alpha_2}{m} = \int_m^{\circ} -j\, d \ln m - j + \int_m^{\circ} 0.000112\, \frac{\theta\, d\theta}{m} + K, \qquad (3)$$

$$\text{where } j = 1 - \frac{0.01785\,\theta.}{m}$$

The two integrals can be evaluated graphically; K, the integration constant, is zero (with the dry solvent).

When dealing with the moist solvent, it is convenient to regard the depression of freezing point as taking place in two stages: first, by the addition of water, until the depression is $D_w$: in the second stage the activity of the water is kept constant, since the solvent is in contact with free water or a salt hydrate pair, and the freezing point is further depressed by an amount (D) through the addition of C grams of solute per 100 grams of nitrobenzene. Equation (1) is valid, provided that $\theta$ is put equal to $D+D_w$: for partially and fully saturated nitrobenzene the values of $D_w$ are 0.323° and 0.511° respectively.[5] So long as the activity of the water is kept constant, equation (2) is true. Equation (3) is therefore valid, but the integration constant is no longer zero, since j is infinite when m is equal to zero. The only way of overcoming this difficulty that we can suggest, is to choose an arbitrary value of K such that the value of $\ln \alpha_2/m$ at infinite dilution, obtained by extrapolation, is zero.

---

[1] "Thermodynamics" (1923).
[2] Meyer: Z. physik. Chem., **72**, 225 (1910).
[3] J. Chem. Soc., **123**, 2037 (1923); **125**, 2219 (1924).
[4] Tammann: "Kristallisieren und Schmelzen", p. 228 (1903).
[5] J. Chem. Soc., **123**, 2037 (1923).

The values of $\alpha_2/m$ obtained in this way, for the wet and dry solvents, have been multiplied by $(m+1)$, giving the activity coefficient ($\gamma = \alpha_2/N_2$, where $N_2$ is the mol fraction of solute): values of this are given in the sixth columns of Tables I-V. Values at round concentrations, obtained by interpolation, are given in Table VIII, for solutions in dry and in fully saturated nitrobenzene. Activities for solvents in the dry solvent should be comparable with those calculated from vapor pressure measurements; those in the wet solvent with activities from distribution experiments.

TABLE VIII

Activity coefficients at round concentrations.

| Mol fraction. | | .01 | .02 | .03 | .05 | .07 | .10 | .13 |
|---|---|---|---|---|---|---|---|---|
| Substance. | | Activity coefficient. | | | | | | |
| Benzyl alcohol | (dry) | .93 | .87 | .81 | .71 | .63 | .53 | |
| | (wet) | .91 | .83 | .77 | .68 | .59 | .49 | |
| Iso-amyl alcohol | (dry) | .91 | .83 | .74 | .61 | .51 | .40 | .33 |
| | (wet) | .90 | .81 | .72 | .57 | .46 | .36 | .29 |
| *b*-naphthol | (dry) | .98 | .96 | .94 | .90 | .87 | | |
| | (wet) | .97 | .95 | .92 | .87 | .82 | | |
| Phenyl-acetic acid | (dry) | .47 | .36 | .29 | .24 | .20 | .18 | |
| | (wet) | .57 | .44 | .37 | .30 | .26 | .22 | |
| Propionic acid | (dry) | .36 | .27 | .22 | .17 | .15 | .12 | .11 |
| | (wet) | .49 | .32 | .27 | .21 | .18 | .15 | .13 |

## Summary

1. The depression of the freezing point of dry, wet, and partially saturated nitrobenzene by benzyl and iso-amyl alcohols, β-naphthol, and phenyl-acetic, propionic, benzoic, and cinnamic acids have been measured.

2. "Associated" solutes can be divided into two distinct classes: alcohols and phenols are apparently more associated in the wet solvent, and their degree of association seems to increase without limit as the concentration is increased: organic acids are apparently more associated in the dry solvent, and the degree of association approaches a limit.

3. The change in the degree of association with concentration does not obey the law of mass action. The consequences of this fact are discussed.

4. Preliminary calculations of the activities in dry and in wet nitrobenzene have been made.

---

We are grateful to Mr. L. J. Hudleston for advice on some points in thermodynamics. One of us (F. S. B.) desires to acknowledge his indebtedness to the Board of Scientific and Industrial Research for a maintainance grant (1923-1925), and to this College for the award of a Garrod Thomas research Scholarship (1925-1926).

*Edward Davies Chemical Laboratories,*
*University College of Wales,*
*Aberystwyth,*
*Wales.*

*Dec. 21 (1925).*

# THE SCATTERING OF LIGHT BY AQUEOUS SODIUM SILICATE SOLUTIONS

BY P. B. GANGULY

The object of the following investigation was to compare the light-scattering powers of a series of aqueous solutions of "sodium silicate", containing different concentrations and different ratios of $SiO_2$ to $Na_2O$, in the hope that such a comparison would provide some evidence concerning the presence in the solutions of colloidal complexes or micelles. When a beam of light is passed through the solution, the colloid particles will scatter light in addition to that scattered by the molecules and ions, and this scattering effect will be much more intense. Another object of the present investigation was to ascertain whether there is a marked increase of light scattering when solutions of equivalent $Na_2O$ or $SiO_2$ concentration, but containing increasing quantities of $SiO_2$ are compared.

For particles of low light absorption the intensity, I, of the scattered light is given according to Lord Rayleigh by the expression $I = Knr^6/\lambda^4$ where $k$ is a constant depending on the intensity of the incident beam, the refractive indices of the liquid and the disperse phase and the angle of observation of the scattered beam, $n$ the number of particles per unit volume, $r$ their radius and $\lambda$ the wave-length of the incident light. If $c$ be the concentration (mass per unit volume) and $\rho$ the density of the particles of the disperse phase, $c = 4/3\pi r^3 n\rho$, and therefore $I = kcv/\rho\lambda^4$, where $v$ = volume of a particle. Thus the intensity of the scattered light is directly proportional to the concentration of the disperse particles and to the volume of each particle. A similar expression for substances with a higher light absorption has been given by Mie[1].

The applicability of the Rayleigh formula to a colloidal solution was tested by Mecklenburg[2] who was working with Odén's sulphur sols found that only smaller particles, of sizes between 5 and 93 $\mu\mu$, scattered light in accordance with the above formula. More recently Bechhold and Hebler[3] examined the light scattered from $BaSO_4$ particles in a Klienman nephelometer and found that the Rayleigh equation was applicable to particles of size up to 800 $\mu\mu$ but not beyond.

In the present work the relative intensities of the scattered light were not quantitatively determined, the various solutions being graded by comparison against a standard turbid medium in the instrument devised by Kingslake[4]. This consists of two tubes which are carried by metal sheaths mounted in vertical slides, a parallel beam of light being passed through the tubes, one of which contains the solution under examination and the other some suitable

[1] Ann. Physik, 25, 377 (1908).
[2] Kolloid-Z., 16, 97 (1915).
[3] Kolloid-Z., 31, 70 (1922).
[4] Trans. Optical Soc., (2) 26, 53 (1924-25).

opalescent medium as a standard. With the help of a Nutting prism, the lights scattered from the two tubes are brought into juxtaposition, and by sliding the standard tube up and down the fields can be matched in brightness. The standard opalescent medium used in the present experiments was a 2 per cent gelatine gel containing finely disperse barium sulphate (0.05 gram per 100 cc.). By employing very pure gelatine and introducing a little xylene on the top of the tube (kept securely stoppered) the standard can be preserved from change. Proceeding in this way, the light scattered from any given silicate solution can be matched in brightness by the light scattered from some particular thin "slice" of the standard medium. The latter was calibrated by comparing it against aqueous alumina sols of different concentrations, these sols being prepared by Graham's method[1]. The water used for diluting the

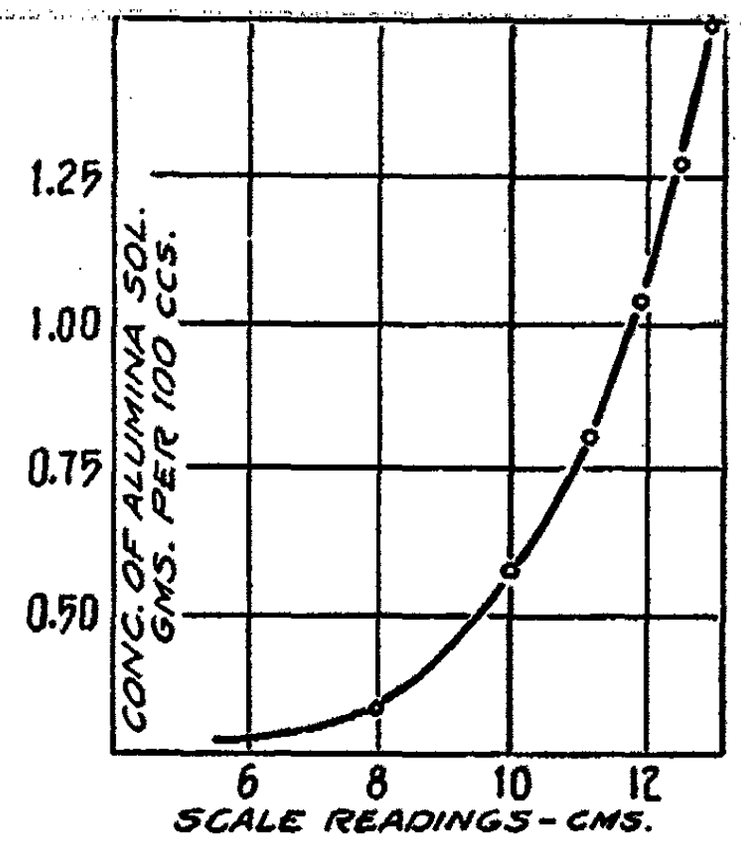



FIG. 1

original alumina sol and for all subsequent purposes was rendered as free from dust as possible by filtration through a Zsigmondy membrane filter. Examination in an ultramicroscope showed that such water was fairly free from suspended particles. The calibration curve is shown in Fig. 1 in which the scale reading of the standard is plotted against the concentration of the alumina sol (in grms. alumina per 100 cc.).

Eight technical silicate solutions varying in the molar ratio $SiO_2/Na_2O$ from 2.0 to 4.2 were obtained from Brunner, Mond & Co. In order to free these solutions from suspended coarse particles, they were allowed to stand many months in stoppered bottles, after which the supernatant solutions were removed and further freed from such suspensions by centrifuging and by filtration through Zsigmondy "analytical" membrane filters. By suitable dilution with dust-free water these eight solutions were compared at a constant $SiO_2$ concentration of 2.5 molar. The results are shown in Table I.

[1] Phil. Trans., 151, 183 (1861).

TABLE I

| Technical Silicate Solution | Molar Ratio $SiO_2/Na_2O$ | Scale reading of standard | Corresponding concentration of equivalent alumina sol. (grms. per 100 cc.) |
|---|---|---|---|
| A | 4.2 | 12.9 | 1.35 |
| B | 3.95 | 12.4 | 1.12 |
| C | 3.8 | 11.9 | 0.93 |
| D | 3.3 | 11.3 | 0.75 |
| E | 3.0 | 8.3 | 0.27 |
| F | 2.9 | 8.6 | 0.294 |
| C | 2.5 | 9.2 | 0.36 |
| H | 2.0 | 8.5 | 0.285 |

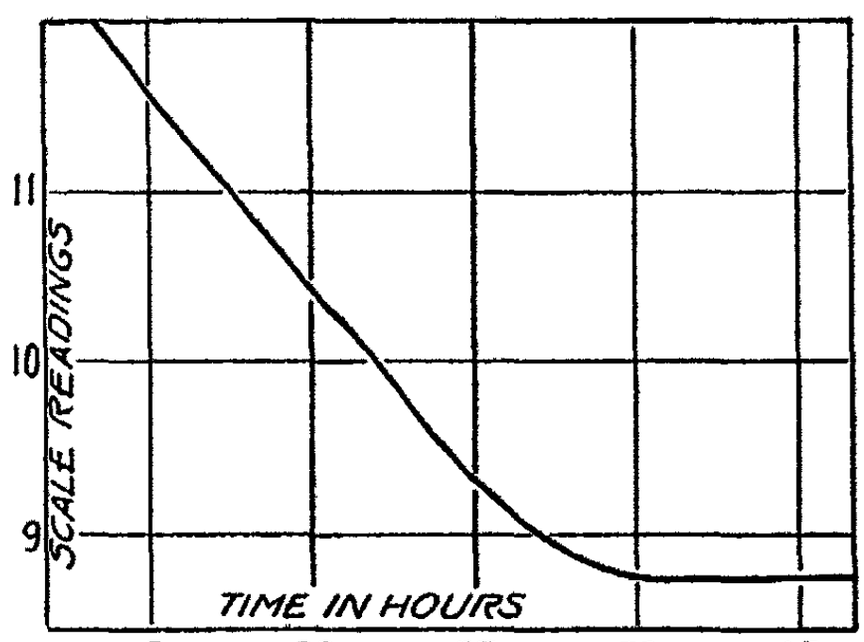



FIG. 2

It will be seen that between the ratios 2.0 and 3.0 there is not much change in scattering power, and no regular increase. Between ratios 3.0 and 3.3 there is a rapid increase in scattering power, and between 3.3 and 4.2 a steady increase with increase of ratio of $SiO_2$ to $Na_2O$. The corresponding concentrations of the alumina sols possessing equal scattering powers show that the observed increases in scattering power correspond in all probability to increasing contents of colloidal particles or micelles in the silicate solutions or to increasing size of those already present. Probably both effects occur.

As the technical solutions may vary in mode of preparation, it was considered likely that more comparable results would be obtained by starting with the technical solution of highest ratio (A) and preparing, by addition to it of suitable quantities of water and alkali, a series of solutions of varying ratio of $SiO_2$ to $Na_2O$. Two such series were prepared, all the solutions being 2.5 molar with respect to $SiO_2$ in one series and 2 molar with respect to $Na_2O$ in the other.

In order to investigate the time required by such solutions to reach a state of equilibrium, 35.04 grms. of the 4.2 ratio silicate solution were mixed with 2.608 grm. of NaOH and sufficient water to make up the volume to 50 cc. The resulting solution is 2.5 molar with respect to $SiO_2$ and the ratio of silica to alkali in it is 2. This solution was examined in the nephelometer from time to time, the results being shown in Fig. 2. This curve exhibits clearly the very interesting and marked decrease of scattering power with time, indicating that colloidal complexes or micelles are being gradually converted into simpler colloidal units, or partly into simple molecules and ions. It will be seen from Fig. 2 that equilibrium was attained in fifty hours. All solutions used in these experiments were therefore left for three days before being examined in the nephelometer. The NaOH solutions were prepared from metallic sodium, and allowed to stand in closed vessels for several weeks, after which the top layer was siphoned off for use. The results are shown in Tables II and III.

TABLE II

Silicate Solutions 2.5–molar with respect to $SiO_2$

| Molar Ratio $SiO_2/Na_2O$ | Scale Reading | Concentration of corresponding $Al_2O_3$ sol. |
|---|---|---|
| 4.2 | 12.9 | 1.34 |
| 4.0 | 12.5 | 1.14 |
| 3.8 | 12.2 | 1.025 |
| 3.5 | 11.3 | 0.75 |
| 3.0 | 9.7 | 0.42 |
| 2.7 | 9.3 | 0.375 |
| 2.5 | 9.1 | 0.35 |
| 2.2 | 8.8 | 0.31 |
| 2.0 | 8.6 | 0.294 |
| 1.7 | 8.1 | 0.25 |
| 1.5 | 7.6 | 0.225 |
| 1.0 | 7.0 | 0.187 |

TABLE III

Silicate Solutions 2–molar with respect to $Na_2O$

| Molar Ratio $SiO_2/Na_2O$ | Scale Reading | Concentration of corresponding $Al_2O_3$ sol. |
|---|---|---|
| 4.2 | 13.2 | 1.52 |
| 4.0 | 13.0 | 1.4 |
| 3.8 | 12.6 | 1.19 |
| 3.5 | 11.8 | 0.9 |
| 3.3 | 10.8 | 0.65 |
| 3.0 | 9.9 | 0.45 |
| 2.5 | 9.1 | 0.35 |
| 2.0 | 8.1 | 0.25 |
| 1.5 | 7.0 | 0.19 |
| 1.0 | 6.1 | 0.15 |

All the sodium silicate solutions scatter light very considerably, the scattering power being altogether of a different order from that of ordinary molecular solutions. Thus even very concentrated solutions of sodium hydroxide, when properly freed from suspended particles, give scale readings on the standard lying between 2 and 4, whilst for the silicate solutions the readings lie between 8 and 13. In this connection it must be recollected that the scattering power increases rapidly with the scale reading of the standard, as may be seen from Fig. 1.

The results given in Tables II and III are shown graphically in Fig. 3.

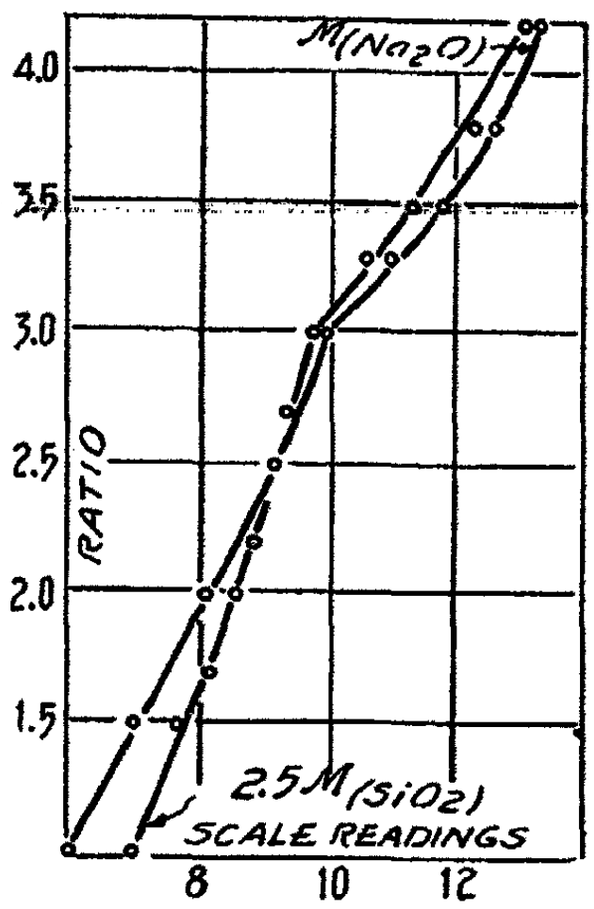



FIG. 3

Both curves show apparent breaks at the 3 ratio solutions, the scattering power at this point beginning quite sharply to increase more rapidly with increase of the molar ratio of $SiO_2$ to $Na_2O$. A similar result emerged from the comparison of the scattering powers of the technical solutions. There is therefore very good evidence that after the ratio 3 is passed the number or the size of the colloid particles or micelles begins sharply to increase more rapidly with increase of the ratio.

The various technical silicate solutions have been examined in a slit ultramicroscope and the particles counted. It has already been stated that the water used for dilution purposes though filtered through a membrane filter was not optically void. When allowed to stream through the apparatus it showed a light cone, but when the flow was stopped only a few particles could be seen in the field of vision. Table IV gives the average counts for the technical silicate solutions, all the solutions being $\frac{1}{8}$-molar with respect to $SiO_2$.

TABLE IV

| Solution | Molar Ratio $SiO_2/Na_2O$ | Average number of visible particles per cc. |
|---|---|---|
| A | 4.2 | $3.4 \times 10^9$ |
| B | 3.95 | $1.9 \times 10^9$ |
| C | 3.8 | $1.8 \times 10^9$ |
| D | 3.3 | $1.5 \times 10^9$ |
| E | 3.0 | $1.17 \times 10^8$ |
| F | 2.9 | $1.28 \times 10^8$ |
| G | 2.5 | $1.34 \times 10^8$ |
| H | 2.0 | $1.05 \times 10^8$ |

If the particle concentration be plotted against ratio, as given in Fig. 4, the resulting curve shows that there is a very sudden and rapid change in the rate of increase of particle concentration with ratio as the ratio 3 is exceeded. This result is in agreement with the measurements on light scattering power.

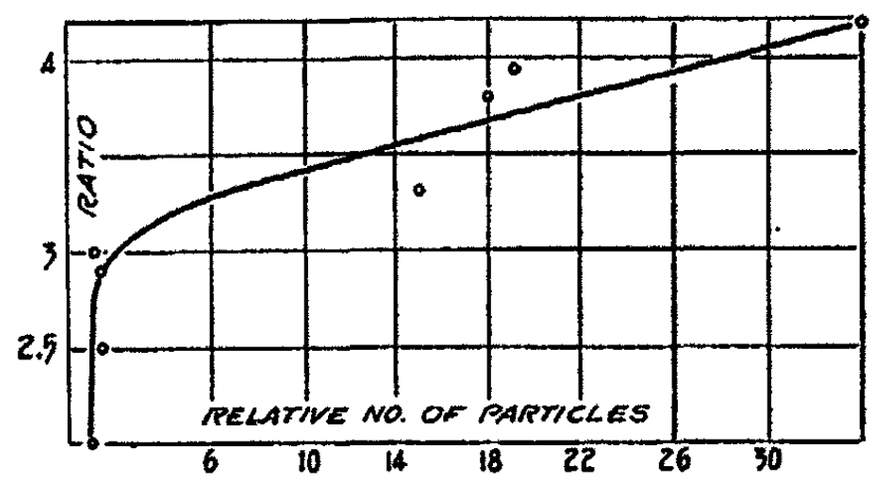



FIG. 4

## Summary

1. Aqueous soldium silicate solutions of varying ratio of silica to alkali have been examined as to their relative scattering power for white light. The scattering power is very much greater than that of ordinary molecular solutions, and the rate of change of this property with increase of ratio undergoes a sudden increase after the ratio 3 is exceeded.

2. The silicate solutions have been examined in a slit ultra-microscope and the average number of visible particles per cc. determined. The results show that when the ratio 3 is exceeded there occurs a very rapid increase in the number of particles per cc.

3. It is inferred that the sodium silicate solutions contain colloidal aggregates or micelles, that these increase in concentration or size (or both) as the ratio of silica to alkali increases, and that the amount of colloidal matter increases rapidly with increase of this ratio after the ratio 3 is exceeded.

In conclusion the author wishes to express his thanks to Professor F. G. Donnan, for his many valuable suggestions and for his kind interest in this work.

*The William Ramsay Laboratories of*
*Physical and Inorganic Chemistry,*
*University College,*
*London.*
*Feb. 9, 1926.*

30-83

# A LABORATORY LATEX[1]

BY HSI-CHING CHEN

The raw material which forms the basis of the rubber industry is a gum imported from the tropical regions of Asia, Africa, and America. It is obtained in the form of an aqueous emulsion or latex secreted in the cambium of certain trees and creepers. From this latex the rubber is obtained as a tenacious, springy, self-adhesive mass by methods of coagulation which vary somewhat widely with botanical origin, local custom, and other factors. An average analysis of rubber latex shows it to contain the rubber hydrocarbons as it's chief constituents to the extent of 25-40% rubber with varying amounts of resins, sugars, proteins, and mineral salts, the balance being water. In plantation rubber from Ceylon the rubber content is usually put at about 40% and the water content at about 55%. The globules in the emulsion are said to be about $3\mu$ in diameter for *Ficus elastica*, $2\mu$ for *Hevea brasiliensis* and less than $1\mu$ for *Funtumia elastica*.

While there is no reason to suppose that the rubber latex differs in principle from other emulsions, there is a wide-spread belief that the rubber latex is in a class by itself because it is apparently the only emulsion with which rubber chemists have ever worked. It seemed desirable therefore to see whether one could make a substitute latex which could be studied easily in the laboratory and which would duplicate many or perhaps most of the reactions of the real latex. Evidently the first requisite for a laboratory latex is that the emulsified material should be liquid but should solidify when the emulsion cracks. This was easy to do, though the method is not that adopted by nature in the rubber latex. Cazeneuve[2] has shown that acetaldehyde liquefies camphor and that the resulting liquid floats on water. By emulsifying the mixture of camphor and acetaldehyde, we can get an emulsion. When the emulsion cracks, the acetaldehyde will evaporate leaving solid camphor behind.

The acetaldehyde used in these experiments was made from paraldehyde by distillation from concentrated sulphuric acid. Only freshly prepared samples were used. Since the camphor could not be ground, one gram of it was cut into small pieces and placed in a test-tube into which was run 4cc $H_2O$ and 2cc aldehyde. Two liquid layers are formed with the camphor solution floating on top. About 0.02 grams of sodium oleate were added and the whole shaken intermittently[3] until an emulsion was formed.

---

[1] Based on a thesis for the M.Sc. degree in Chemistry presented to the Faculty of the Graduate School of Cornell University in May, 1922.

[2] Bull. (2) **36**, 650 (1881).

[3] Briggs: J. Phys. Chem. **24**, 120 (1920).

The methods of coagulation of the rubber may be classified[1] as follows:—

1. Smoking: by injecting steam and acid smoke. Smoking with Urucury nuts in the lower Amazon regions and with hard woods above Manaos. The smoke is said to contain acetone, acetic acid, creosote, and tarry matters.

2. Evaporation. The latex dries to 'scrap' if allowed to run down the bark. It may be poured into saucer-shaped stumps in which case the wood soaks up the water or the water evaporates into the air.

3. Boiling. This method of coagulation can be used for Castilloa, Ficus, and Funtumia latices but does not work satisfactorily with Hevea.

4. Dilution. This causes coagulation with Castilloa, Landolphia, and Funtumia but not with Hevea.

5. Addition of acids, salts, alcohol, acetone, etc. Over 90% of the plantation rubber latex is coagulated with acetic acid in some form. Alcohol and acetone give an admirable coagulation but are too expensive. Hübener points out that alcohol works only in presence of salts which is exactly what one would expect from what one knows about negatively charged sols[2]. Whitby[3] states that dialyzed latex is not precipitated by methyl, ethyl, or amyl alcohol but is by acetone.

6. Beating, churning, and centrifuging. Beating worked with Manihot rubber. Beadle and Stevens[4] state that churning or shaking has no effect on normal Hevea latex. "If, however, sufficient of a coagulant be added to produce creaming and flocculation on standing, the effect is hastened and the flocks are more dense if the liquid be shaken vigorously. It is natural to suppose that with shaking or churning we have merely the mechanical effect of bringing the aggregates into frequent contact with each other, causing them to adhere and join up, forming larger and more compact aggregates." Centrifuging[5] works well with Castilloa ($3\mu$), not very well with Hevea ($2\mu$), and not at all with Funtumia ($\langle 1\mu$), which is exactly what one would expect so far as creaming is concerned.

In order to duplicate to some extent the South American method of smoking, acetic acid and steam were distilled into the emulsion. Cracking and solidification occurred. Of course this is really coagulating with hot acetic acid; but people have always made the distinction.

If the laboratory latex is allowed to evaporate, the emulsion cracks and solid, white camphor is obtained as the acetaldehyde passes off. Slight warming speeds up the cracking considerably. When the laboratory latex is boiled, the emulsion breaks down. The differences observed with different natural latices are undoubtedly due to variations in the amount and nature of the

[1] Clouth: "Rubber, Gutta Percha and Balata," 66 (1903); Spence: "Lectures on India Rubber," 25 (1909): Schidrowitz: "Rubber," 127 (1911); Hübener: Kolloid-Z. 16, 5 (1915).

[2] Bancroft: Rec. Trav. chim. (4) 3, 733 (1923); Bancroft and Gurchot: J. Phys. Chem. 28, 1279 (1924); Gurchot: 30, 83 (1926).

[3] "Plantation Rubber and the Testing of Rubber," 34 (1920).

[4] Eighth Congress Applied Chemistry, 9, 37 (1912).

[5] Beadle and Stevens: Kolloid-Z. 13, 210 (1914).

protecting colloid. When the laboratory latex is diluted with about 10 cc of water, the emulsion is destroyed. Freezing[1] also gives camphor. With more emulsifying agent the emulsion would not break down on dilution or on freezing and would then behave like the Hevea latex.

It seemed unnecessary to make cataphoresis experiments because the liquid drops would certainly go to the anode in a soap solution. Centrifuging seemed also to be a mere waste of time. It is evident that the laboratory latex duplicates the real one in many respects. One could give additional stability against heating and evaporation by using a less volatile liquid than acetaldehyde; but it would take correspondingly longer before the camphor solidified. Some people may be horrified by the use of soap; but it is perfectly possible to substitute any other protecting colloid so long as it does not reverse the emulsification. It would also be an easy matter if one wished to duplicate or simulate the bacterial action which occurs in the natural latex.

## Summary

Practically all the reactions of a rubber latex may be duplicated with an emulsion made up of one part camphor, four parts water, 0.02 parts sodium oleate and 1.5 parts acetaldehyde. On coagulation the camphor is obtained as a white solid. The following methods of coagulating rubber have been duplicated with the laboratory latex: smoking, evaporation, boiling, dilution, and addition of acetic acid, oxalic acid, tannic acid, tartaric acid, formic acid, citric acid, hydrochloric acid, sulphuric acid, hydrofluoric acid, alum, and alcohol. No coagulation was obtained with acetone or phenol; but this could perhaps have been secured if another emulsifying agent had been used.

I wish to extend my thanks to the various members of the staff of the Department of Chemistry for help which I have received and I wish particularly to thank Professor W. D. Bancroft, who suggested the investigation and whose kindly interest has assisted me over many difficulties.

*Cornell University.*

[1] Zsigmondy-Spear: "The Chemistry of Colloids," 8 (1917).

## NEW BOOKS

**A Dictionary of Applied Chemistry.** *By Sir Edward Thorpe. Vol. VI. Revised and enlarged edition. 24 × 16 cm: pp. viii+791. London and New York, 1926. Price: $20.00.* This is the next to the last volume of the series and has been put through the press by H. Forster Morley. Among the interesting topics are: saccharin, safflower, sand, sandstone, saponification, sealing wax, selenium, sewage, shellac, silicon, silica, silk, silver, smoke, soap, sodium, soils, solder, solubility, soluble or water glass, solution, soya bean, specific gravity, spectroscopy, starch, steam, stearin, strontium, sublimation, sugar, sulphide dyes, sulphur, sulphuric acid, synthetic drugs, tallow, tannins, tantalum, tartaric acid, tea, tellurium, terpenes, and tetralin.

"The prevailing view that, except for its action on the organs of taste in the mouth, saccharin is an inert substance having no action on organs and tissues, is not tenable. Acting in the mouth, it decreases appetite, gastric secretion, and peptic digestion. Acting in the small intestine, it decreases absorption; on the erythrocytes, it decreases haemolysis. These actions cannot be explained by the osmotic factor. Saccharin in the blood, in proportion to its concentration, passes into the lymph, cerebrospinal fluid, saliva, tears, and mammary secretion," p. 3.

Safflower must be almost the only substance which is purified by dyeing cloth with it and then extracting the dye from the cloth, p. 7. "To obtain carthamin, safflower is well washed with slightly acidified water to remove the yellow colouring, then it is steeped for some time in a cold dilute solution of sodium carbonate. If the alkaline solution be now acidified with acetic or tartaric acid the carthamin is precipitated in so finely divided a condition that it cannot be collected successfully. This difficulty is obviated, however, by making use of the fact that carthamin is readily attracted and removed from its acidified solution by cellulose. Hence bleached cotton is immersed and moved about in the alkaline solution which is at the same time acidified gradually with tartaric or citric acid.

"In this manner the carthamin is precipitated slowly and is attracted at once by the cotton which thus becomes dyed red. After washing the dyed cotton with slightly acidified water, the colouring matter is dissolved off by means of a dilute solution of sodium carbonate, from which the carthamin is thrown down, on the addition of tartaric acid, as a bright-red precipitate, which is now in a purer and more granular form."

Under saponification, p. 41, the use of one percent of lime is cited as a case of catalysis whereas there is undoubtedly a formation of a water-in-oil emulsion. "Shakudo is an alloy consisting essentially of copper and gold, which is used in Japan for the manufacture of objects of art, and is colored by treatment with aqueous solutions containing copper sulphate and acetate. The coloration is due to the production of a layer of cupric oxide, the tint being determined by the thickness of the layer," p. 79. "Schaum and Lang state that for transmitted light the diameters of the particles of colloidal silver associated with the following colours are: yellowish-orange 60$\mu$; orange-red 90$\mu$; purple 120$\mu$; violet 150$\mu$; and bluish-green 180$\mu$," p. 120.

"The character of smoke varies with its source, and in most cases the nose is able to detect the character of the burning material from the smell of the condensing vapours in the smoke, so that tobacco smoke, coal smoke, wood smoke, the smoke from green vegetable matter, rags, animal matter, or gunpowder have such distinctive characteristics that the sense of smell differentiates at once between them.

"The form of smoke which is, perhaps, the most injurious, and to which we are most, accustomed, is that produced by the use of bituminous coal as a fuel for manufacturing and domestic use, and which, with the growth of the population of the country and the prodigal methods of using the fuel, has created in our large towns atmospheric conditions that are little short of a national scandal.

"When in the thirteenth century bituminous coal was first used for fuel purposes, the smoke to which it gave rise roused such indignation that a decree was passed in 1306 forbidding its use; but fuel had to be found, and the supply of timber proving insufficient, attempts were made once more to introduce it, but again public opinion led to its banishment during the reign of Queen Elizabeth. The third attempt, however to bring it into use proved successful, and slowly the consumption increased, until the last century saw coal established firmly, not only as a fuel for domestic consumption, but also as a great source of power; and it was the possession of great stores of the fuel that gave England her commercial supremacy," p. 138.

"The double melting-point of tristearin is attributed to the existence of two modifications the more stable of which melts about 71.6°-72.2°, and the instable form about 55°, the latter being reconverted into the stable form on heating it at a higher temperature or allowing it to remain. In spite of the speed of solidification, the solidification point of tristearin is usually given as that of the instable form (about 55°). . . . On seeding liquid tristearin with the stable modification above 60°, solidification takes place without the formation of the instable form, but the latter is apparently always produced after seeding, even with the stable form, at temperatures below 56°," p. 400. Apparently twenty-five years is not sufficient for organic chemists to master the theory of two modifications occurring in the melt.

"Owing to our lack of knowledge concerning the physiology of sleep and possible chemical processes that take place, we are equally ignorant of the exact manner in which sleep is produced by hypnotics. In effect, we must distinguish between narcotics (represented by opium), which produce unconsciousness by intoxication, and the true hypnotics (represented by chloral), in which the sleep is apparently normal. In view of the fact that the sleep produced by the opium class is often attended with undesirable by-effects, and that during their prolonged administration the element of habituation must always be considered, they have been reserved for cases of insomnia due to severe pain, and have been largely replaced in other forms of sleeplessness by the synthetic hypnotics. While this latter class approach the normal conditions, yet the ideal hypnotic remains to be discovered. This must act upon the nerve centres, followed later by the most automatic and stable centres, avoiding any profound influence on the respiratory or circulatory centres. Elimination must be rapid and complete, leaving no trace of cumulative or secondary action such as digestive disturbances, headache, etc. The hypnotic effect of the aliphatic hydrocarbons, developed through the introduction of hydroxyl groups (alcohols), is well known. That the hydroxyl serves no further purpose than that of an anchoring group is proved by the inert properties of the polyhydric alcohols. That the ethyl group produces a profound hypnotic effect, as in alcohol, is further demonstrated by the decomposition of chloral in the blood to trichlorethyl alcohol, and the necessary presence of alkyl groups in the most important classes of hypnotics. The introduction of the ethoxyl group into caffeine imparts a narcotic effect. It can be said in general that the alkyl groups, more especially the ethyl, possess a distinct sedative action upon the nervous system. The methyl group generally eliminates or diminishes hypnotic action when associated with an ethyl or propyl group; the propyl radicle with other higher radicles increases the intensity and also toxicity, while their corresponding *iso* groups generally diminish it. Sulphur replacing oxygen contributes to toxicity. The alkyl radicles do not carry hypnotic or sedative action under all conditions; it is only the association of certain groups or nuclei or their structural environment that determines this action. The presence of a sulphonic or carboxyl group inhibits physiological action, and diminishes toxicity. Another factor is insolubility, that is, failure to break down in the system; thus tetronal, which, theoretically, should possess a more profound hypnotic action than trional, is practically inert. A further insight is gained on studying the groups," p. 618.

"Antiseptics are chemicals which have the power, in small quantities, to prevent infection or to arrest the multiplication of bacteria, and should be free from harmful action upon the human organism. Disinfectants destroy bacterial life and the noxious properties

of putrefactive or fermentative products. Usually, small quantities of these chemicals are antiseptic, and large amounts disinfectant, in their effects.

"The great variety of bacterial life, the kind, state, extent, composition, quantity, and condition of the associated matter, together with the difficulty of fixing, inhibiting and sterillising of disinfectants makes the subject of standardisation of disinfectants perplexing and difficult. An ideal disinfectant must be able to destroy bacteria, be harmless to the human organism, penetrative, free from local irritation, toxic action and disagreeable odour. Very few, if any, of the disinfectants are adapted for universal use because of the great variety of conditions presented, hence each product is adapted for some special field of work.

"Intestinal antisepsis is not attainable, because if the antiseptic were sufficiently powerful to destroy bacteria it must necessarily exhibit a toxic action on the human system. However, in certain lines, this class of antiseptics serves admirably in inhibiting the development of milder types of bacteria and neutralising the action of toxins in infections of the respiratory and urinary tracts. Combinations of bismuth and various antiseptics have become popular in treatment of intestinal disturbances due to fermentative changes or infection. To these must be added various compounds of beta-naphthol," p. 624.

*Wilder D. Bancroft*

**Explosifs, Poudres, Gaz de Combat.** *By Paul Pascal. 25 × 16 cm; pp. viii+296. Paris: J. Hermann, 1925. Price: 35 francs.* This book is based on lectures given at Lille, and the author implies that, for military reasons, he has not told all that he knows. The book is divided into four parts: explosion and detonation; manufacture of explosives; explosive mixtures and propellants; war gases.

There are some rather interesting paragraphs, p. 7, on the situation after the war started. "We had to evacuate the powder factory at Esquerdes near St. Omer when the drive for the Channel began, and had to start over again in the factories of the Southwest. The loss of our coke ovens in the North increased the shortage of hydrocarbons. It was necessary to import benzene and to extract the aromatic hydrocarbons from Borneo petroleum. Our black-powder factories were used to manufacture schneiderite and everywhere new factories were built which utilized the ammonium nitrate from Norway to supplement the stocks of melinite received from America. It was because of this production that it was necessary to install factories for the production of synthetic ammonia at Angoulême, Bassens, Borgues, and elsewhere.

The field of explosives was the one in which the really chemical effort was most serious. It was necessary to use new or more effective methods; the manufacture of synthetic phenol increased from six hundred to three hundred and seventy thousand kilograms per day and we had to rely on outside for only a negligible amount of this compound. The output of the French factories, supplemented by those of the confiscated German dye works, enabled us to meet the most urgent needs. Toulouse even supplied Italy when she first came in; we supplied the Balkans throughout the whole war and the Americans in 1917-1918."

It is possible to eliminate almost completely the flare-backs and to decrease the flash from the gun by adding alkaline salts to the charge, p. 82. To prevent the propagation of explosion flames in mines, planks are placed overhead on which finely divided cinders are piled. The explosion shakes down the dust, p. 88.

By fractional precipitation of nitro-cotton from acetone by means of toluene, it is possible to separate a two percent sol having a viscosity of 0.1 into two portions, one having a viscosity of 0.6 and the other of 0.007, p. 103. "Cotton is an expensive form of cellulose and also an exotic material and is hard to secure when there is a submarine war on. We have hoped to decrease these difficulties by growing it in our African colonies; but wood constitutes the real source of directly available cellulose," p. 130.

Liquid air explosives consist essentially of a combustible compound soaked in liquid air or, better still, in liquid oxygen. The combustible matter must be in a sufficiently fine powder to constitute an adsorbent mass and it is desirable that the grains themselves be porous. When the adsorbing power is so low that the substance will not hold the weight of oxygen necessary for complete combustion, it is necessary to incorporate an inert adsorbent

such as distomaceous earth. A solid adsorbent must be used if the combustible substance is liquid or pasty at the temperature of liquid oxygen, p. 190.

In order to cut down the danger of explosion when grinding the materials for black powder, it is customary to make up two binary mixtures, one of carbon and sulphur, and the other of carbon and potassium nitrate, p. 201. Straight chlorate explosives are too dangerous to make but they are more safe if mixed with a plastic combustible material such as tar, p. 218. The nitrocellulose powders are stabilized with aniline in Italy, with diphenylamine in Russia and Germany, and with amyl alcohol in France.

*Wilder D. Bancroft*

**Die Grundlagen der Dispersoidchemie.** *By Andor Fodor. 23 × 16 cm; pp. viii+280 Dresden and Leipzig: Theodor Steinkopff, 1925. Price: 12 marks paper; 14 marks bound.* The author is director of the Institute for Biochemistry and Colloid Chemistry at the Jewish University in Jerusalem and this book is based on lectures that he gave there. The chapters are entitled: the nature of dispersed systems; the action of solutes on dispersion; the formation of dispersed systems; some fundamental laws of dispersoid chemistry; the dispersion processes; the condensation processes; clay as a coarsely dispersed system; proteins as strongly solvated colloids; chemical reactions occurring in colloidal systems, with special reference to fermentation.

This is not a good book. The author has no very definite point of view. He lays great stress on solvation and dehydration as important factors in colloidal equilibrium—which they undoubtedly are—but he is rather hazy as to what they are and how they act. He believes in the existence of three hydrates of sulphuric acid in solution, p. 6, and he accepts Remy's view that sodium ion does not contain over sixty-six molecules of water attached, p. 7. Of the anions in the Hofmeister series he considers that sulphocyanate ion is the least hydrated, p. 42; but he does not explain why potassium iodide should liquefy gelatine more readily than water does. The following paragraph on p. 80 is not very clear even if one makes all sorts of allowances for faulty translation. "We consider solvation before all others as a process which balances the surface energy and it is therefore always correlated with the dispersion process. As we shall explain later in more detail, solvation is quite as important in balancing the surface energy as the other adsorption phenomena." What he probably means is that water often has a strong peptizing action, which nobody can deny.

The author recognizes, p. 11, that a colloidal solution is not a homogeneous phase in the Gibbsian sense because it differs from a salt solution in not being fully defined by the temperature, pressure, and concentration. On the other hand he believes in the experimental continuity of colloidal and true solutions, p. 81.

The author considers the neutralization of an electrical charge on a particle, p. 62, as involving a chemical reaction which causes the absolute disappearance of that ion, instead of merely the displacement of the ion or the adsorption of an equivalent amount of an ion having the opposite charge. Consequently he has a terrible time in understanding the very different concentrations at which ions of different valence precipitate arsenious sulphide. The same difficulty comes up in another form with clay, p. 96. Ammonia and sodium hydroxide do not behave exactly alike with clay and yet the author says that they have the same discharge value when in equivalent concentrations. This ignores entirely any effect due to the adsorption of sodium ion.

The author also believes in Wilhelm Ostwald's explanation of rhythmic banding, that it is chiefly a question of supersaturation, p. 245. This cannot be true, in view of the fact that one can get rhythmic banding even when there are some crystals in the clear spaces.

*Wilder D. Bancroft*

**Ueber Wärmeleitung und andere ausgleichende Vorgänge.** *By Emil Warburg, 22 × 15 cm; pp. x +106. Berlin: Julius Springer, 1924, Price: $1.40.* The subject is treated under the general heads; conception and properties of equalizing processes; general theory of heat conduction; stationary heat flow; states changing with the time; viscosity. It is rather interesting to notice what apparently different phenomena may be grouped under the same heading, p. 32.

"A substance should become covered with dew if, on a clear night, it is cooled by radiation below the dew-point; but according to Skinner the thin threads of a spider's web do not become covered with dew [because they keep very close to the temperature of the surrounding atmosphere]. The thin threads of the Welsbach mantle keep very close to the temperature of the flame in spite of the radiation. The same thing is true of a very thin platinum wire and consequently one can determine flame temperatures with considerable accuracy by measuring thermoelectrically or radiometrically the temperature of such a platinum wire when in the flame. In a similar way Wood determined the temperature of the glow in a Geissler tube by means of a platinum iridium wire with a diameter of 35μ, making use of the change in resistance." *Wilder D. Bancroft*

**Applied Chemistry.** *By Ira D. Garard. 19 × 14 cm; pp. vii+496. New York: The Macmillan Company, 1924. Price: $3.25.* In the preface the author says: "The purpose of this book is mainly to provide a text-book for college students who have taken a course in general chemistry and who are further interested in the application of chemistry and the manner in which it functions in modern life. . . . In addition to its use as a text, it is hoped that the book will prove useful to readers who are interested in chemistry because of its relation to their fields in science, art, or industry. . . . The plan of the book aims to systematize so far as possible the practical information of chemistry rather than to merely state the facts."

The book is divided into twenty-two chapters and an appendix which contains fifty-two carefully chosen and interesting laboratory experiments. The chapter headings include: general introduction; solutions; water; the atmosphere; combustion and oxidation; forms of energy and their chemical applications; natural and synthetic organic substances; enzymes and microörganisms; oils, fats, and waxes; carbohydrates; edible proteins; food and nutrition; preparation of foods; colloids; cleansing agents and toilet articles; textiles; dyeing and bleaching; leather and tanning; rubber and plastics; paints, varnishes, and inks; metals and alloys; glass and ceramics; fuels.

The book contains a vast amount of interesting and useful information, clearly and systematically presented. There is no reason why it may not be read with profit by the layman whose knowledge of the chemical principles is limited to the merest fundamentals, for the treatment employed throughout is of the simplest sort.

The reviewer was interested in the author's definition on p. 1 of the term "applied chemistry", which forms the title of the present work. "Applied chemistry need not be so rigidly defined as are most of the other branches. It is more general than industrial chemistry since it is not concerned with manufacturing processes alone. It might be defined as that branch of chemistry which deals with the economic welfare of man." This comes close to being a definition of pandemic chemistry.

The reviewer was particularly interested in the section on dust explosions, and especially in the part on burning aluminum dust, where water and carbon tetrachloride actually encourage the fire (p. 82); also in spontaneous combustion (p. 85) where it is said that the heat generated in a pile of hay is caused by enzyme respiration. The chapter on cleansing agents is good, and the point that soap possesses a strong germicidal action (p. 162) is well brought forward. The table of full values (p. 426) containing the cost per 1000 B.T.U. is especially instructive.

The reviewer, quite naturally, does not agree with the author's point of view in some cases, especially when it is stated that the solution pressure of zinc is its tendency to replace hydrogen ions from solution (p. 91), and that the solution pressure of copper is negative (p. 92). He is also disappointed to find that dyeing with basic dyes is ascribed to chemical union between the dyestuff and the protein fibres, and he does not altogether relish the statement (p. 318) that the theory of direct cotton dyeing is mostly conjecture.

The book fulfils most admirably the purpose for which it was written and the author should be commended for gathering together, in a fairly digestible form, such a fund of every-day chemistry.

*T. R. Briggs*

721

# PROPERTIES OF AMMONIUM NITRATE

## I. A Metastable Inversion in Ammonium Nitrate[1]

BY N. L. BOWEN

### Introduction

Ammonium nitrate has long been known to occur in a number of different crystalline forms and its several inversion points have been the subject of much study. Early and Lowry have investigated in a very careful manner all the changes taking place above room temperature and at the ordinary pressure. They found inversions[2] to occur at 32.1°, 84.2°, and 125.2°. Their results confirm earlier work, but the actual values given are the most dependable yet found. The stable transformations of ammonium nitrate are expressed in tabular form in Table I where the designations of these forms are given according to the methods of the crystallographer and the physicist.

TABLE I

Stability ranges of the modifications of ammonium nitrate at atmospheric pressure.

| Modification | Range of stability °C |
|---|---|
| Liquid | 169.6 to —— |
| Isometric (I) | 125.2 to 169.6 |
| Tetragonal (II) | 84.2 to 125.2 |
| Orthorhombic ? (III) | 32.1 to 84.2 |
| Orthorhombic (IV) | −16 to 32.1 |
| Tetragonal (V) | —— to −16 |

### Experimental Method

The writer has recently studied these transformations of ammonium nitrate by a method which permits direct observation of the changes and, at the same time, control and measurement of the temperature. A small quantity of the nitrate, previously dried, is melted on an ordinary microscopic slide and, while liquid, is covered with a cover-slip which is pressed down lightly so that upon cooling one obtains a thin film of the nitrate analogous to the thin section of the mineralogist. This is substantially the method used by Wallerant of preparing slides of nitrate for a similar purpose[3]. In the present study the slide was then placed on a wire support in a small oil bath which was mounted on the stage of a petrographic microscope and which was electrically heated by means of a coil of nichrome wire immersed in the oil.

[1] Investigations carried on with the co-operation of Peerless Explosives Company, to whom we take this opportunity of expressing our thanks.

[2] The properties of ammonium nitrate. Part I. The freezing point and transition-temperatures. J. Chem. Soc., 115, 1387 (1919).

[3] Sur le polymorphisme et l'isomorphisme des azotes alcalins. Bull. Soc. Min. Fr., 28, 311 (1905).

The container for the oil was a glass crystallizing dish with flat bottom and the slide could thus be observed by transmitted light as it is ordinarily in the absence of the bath. The temperature was controlled by varying a resistance in series with the nichrome heating coil and was measured by means of a potentiometer and thermoelement of copper-constantan which dipped into the oil and whose junction rested on the mount, being separated from the charge only by the thin cover-slip.

## Experimental Results

*General observations.* With this arrangement it was possible to observe all the stable transformations of ammonium nitrate above room temperature in a very satisfactory manner. The temperatures of the changes correspond with those given by Early and Lowry within the limits of error, especially when the change was in the direction induced by rising temperature. With falling temperature there was often much lag and it was necessary to make the cooling rate very small in order to obtain a value corresponding approximately with that obtained in the reverse direction.

The various forms of ammonium nitrate exhibit sufficient difference of optical properties that they may be distinguished from each other readily as thus viewed under the microscope. The orthorhombic form, stable at ordinary temperature, has refractive indices $\gamma = 1.64-$, $\beta = 1.61$, $\alpha = 1.41+$, and $2V$ is about $35°$. The birefringence is thus extremely high, considerably higher than that of calcite[1].

The orthorhombic (?) or monoclinic form stable between $32°$ and $84°$ has a distinctly lower birefringence, though it would still be described as very high. It is further distinguished by an optic axial angle ($2V$) of nearly $90°$.

The tetragonal form stable between $84°$ and $125°$ is uniaxial and positive. The birefringence is again distinctly lower, but would still be described as high.

The isometric form is, of course, isotropic.

On account of these differences in optical properties the transformations are readily observed between crossed nicols under the microscope and the various forms identified even when they persist in a temperature region where they are not stable.

*The metastable inversion.* In addition to, and, in some measure, in place of the stable transformations that have already received so much study, another transformation was observed which was usually more dependable and prompt than the stable transformations. This was the metastable inversion, orthorhombic (IV) $\rightleftharpoons$ tetragonal (II) which occurs at approximately 50°C.

When the molten film of nitrate is cooled it crystallizes, usually with considerable undercooling, to the isometric form which is transformed to the tetragonal form upon further cooling. The actual inversion point may be overstepped as much as 18°. The tetragonal form may then be cooled through the temperature of $84°$ without showing any change and in practically all

[1] The index $\alpha$ as given by Thomas and Hallimond at 1.45 (Trans. Faraday Soc., 20, 56 (1924)) is much too high, indeed the match with amyl valerate of index 1.411 is sensibly perfect.

cases may be cooled to a temperature somewhat below 50° before the appearance of a new form which is not the orthorhombic ? (III) form stable at this temperature, but the orthorhombic (IV) form stable below 32°. Even with very rapid cooling I have not observed the temperature to fall below 44° without the appearance of the new form, and when the rate of cooling is about one degree per minute the transformation always takes place promptly at 47°-49°. If the orthorhombic (IV) form thus obtained is now reheated, transformation to the tetragonal (II) form takes place at a temperature a little above 50°. Even with a rapid rate of heating I have not observed the orthorhombic (IV) form to persist above 54°, and with a rate of one degree per minute the change takes place promptly at 51°-52.5°. This metastable transformation is thus readily reversible and rather less readily overstepped than the stable transformations when both directions are considered.

One may sometimes heat the nitrate back and forth through the inversion point a score or more of times with repeated inversions in both directions and thus retain the one or the other of the forms in its metastable region for a total of several hours without the appearance of the stable, orthorhombic ? (III) form. If the temperature is carried below 32° no change occurs at that point, since the nitrate is already in the orthorhombic form stable below that temperature, and likewise if it is carried above 84° no change occurs at that point, since it is already in the form stable above that temperature. Moreover, when the temperature is thus carried upward or downward into the regions of stable existence of the respective forms no change is apparent in the tendency of these forms to persist in the metastable region and to exhibit the metastable inversion at 50° when the temperature is brought back to that value.

Eventually, however, any given charge of nitrate appears to change its mind and decide to assume the stable modification. I have observed this to take place in only one way and that immediately after the metastable transformation in the cooling direction. The tetragonal form is observed to change to the orthorhombic in the usual way and then immediately the stable orthorhombic ? (III) form puts in an appearance. It starts at one or two centers from which it spreads with a circular front and ordinarily begins to form before the metastable transformation is complete in all parts of the charge, so that the two changes can frequently be seen passing across the field of the microscope at the same time, the metastable inversion somewhat in advance of the change to the stable form. It thus affords an excellent example of Ostwald's law of successive reactions.

If the charge is now cooled below 32°, transformation to the orthorhombic (IV) form occurs at that temperature, and if it is heated above 34°, inversion to the tetragonal (II) form occurs, but the metastable transformation at 50° is now no longer obtained. By carrying the charge above 125° and thus changing it into the isometric (I) form the metastable inversion can frequently be induced to reappear when the charge is again cooled and by remelting the charge its reappearance is practically assured.

## Earlier Work indicating the Existence of the Metastable Inversion

Certain aspects of the observations here recorded have been noted by others. Thus Early and Lowry note that undercooling readily occurs at the 84° inversion point and state that "in many cases the salt was cooled to 32° without any indication that this change of crystalline form had taken place".[1] While there is nothing inherently improbable in such a degree of undercooling, it was never observed in the present work, the metastable transformation always occurring at a temperature well above 32°.

Wallerant noted that ammonium nitrate could be cooled through the 84° inversion point without inversion and that the tetragonal (II) form might change directly to the orthorhombic (IV) form[2]. He did not, however, note

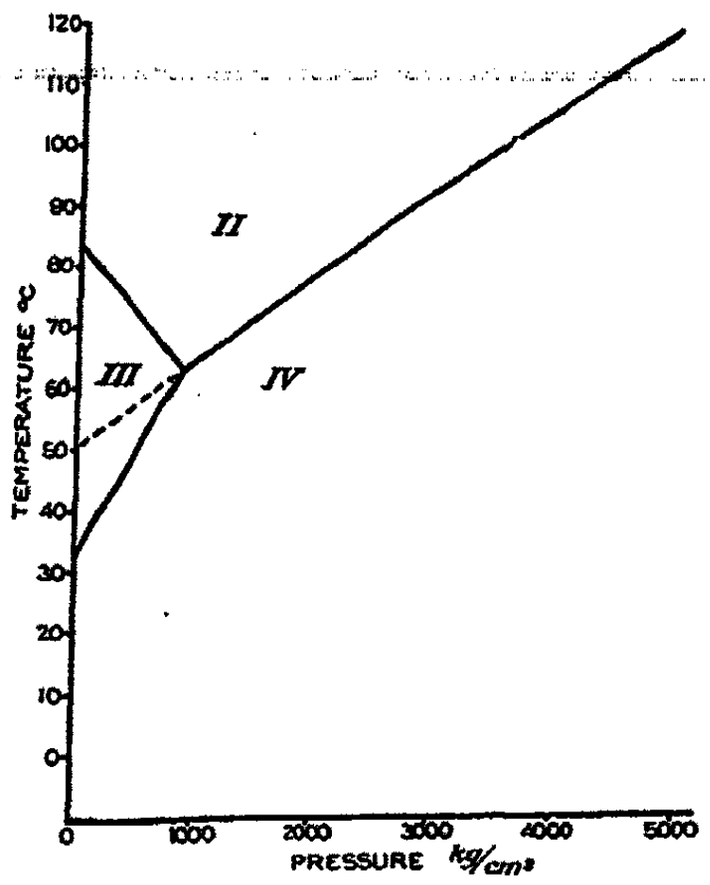



FIG. 1

Curve of variation of the orthorhombic (IV) ⇄ tetragonal (II) inversion of ammonium nitrate (after Bridgman) showing its metastable extension (broken curve) and indicating an inversion point of 50.5° at atmospheric pressure.

that the change took place at any particular temperature. Behn, studying the inversions dilatometrically, noted that the tetragonal modification could easily be cooled to a temperature of 45°, and definitely suggested that this temperature was determined by the II-IV inversion, though the final result was always the form III. He calls attention to the fact that Tammann had studied the II-IV inversion at high pressures, where it becomes a stable inversion, and that extrapolation of his curve to atmospheric pressure would indicate an inversion point of 45°.[3]

---

[1] Op. cit., p. 1392.
[2] Op. cit., p. 319.
[3] Proc. Roy. Soc., 80, 449 (1908).

There have thus been a number of indications of the existence of this transformation with falling temperature, but it has not been observed that it was definitely reversible and could be obtained with rising temperature as well.

Concerning the actual temperature of the inversion it is to be noted that the temperature of 45° where inversion was noted by Behn is definitely too low. While with rapid cooling it may fall to that temperature, with slower cooling it takes place at a temperature of from 47°-49° and with slow heating it occurs at 51°-52.5°. Having regard for the fact that all the inversions of ammonium nitrate are more easily overstepped in the cooling direction than in the opposite direction, we may place the inversion point at 50° with the suggestion that it is a little higher rather than lower, but the accuracy of the determinations does not warrant any more definite figure.

If we turn to Bridgman's determinations of the transformations of ammonium nitrate under pressure we find that he has studied the II-IV transformation throughout its stable range of some 8000 atmospheres[1]. A relatively short extrapolation of his values into the metastable region at low pressures indicates a value of 50.5° for the transformation at atmospheric pressure. This value is in good agreement with that observed in the present study. Bridgman's results on ammonium nitrate are here reproduced in Fig. 1, with the metastable extension of the II-IV curve added. Perhaps the temperature 50.5°, as determined by extrapolation from Bridgman's results, would be a more satisfactory value for recording as a constant of ammonium nitrate than any that could be determined directly in the metastable region.

## Summary

Besides the several well-known transformations of crystalline ammonium nitrate it is found that a reversible transformation takes place at approximately 50°C. The method of studying the inversion is that of direct observation under the petrographic microscope by which means the various forms can be identified in virtue of differences of optical properties. The inversion at 50°C is found to correspond with the change, orthorhombic (IV) $\rightleftharpoons$ tetragonal (II). At this temperature both forms are metastable, nevertheless the transformation is, in many respects, more prompt and dependable than most of the stable inversions. Extrapolation of Bridgman's values for the II $\rightleftharpoons$ IV inversion at high pressures, where it is a stable transformation, indicates a value of 50.5° for the temperature of this change at atmospheric pressure. This temperature is in good agreement with that here directly determined.

[1] P. W. Bridgman: "Polymorphic Changes under Pressure of the Univalent Nitrates". Proc. Am. Acad. Arts Sci., **51**, 605 (1916).

726

# PROPERTIES OF AMMONIUM NITRATE

## II. The System: Ammonium Nitrate-Ammonium Chloride[1]

BY N. L. BOWEN

### Introduction

There has recently appeared a series of papers on the properties of ammonium nitrate, the result of investigations instituted by Professor Lowry but carried on latterly by Professor Perman. One of these has already been referred to in Part I of the present series. Another deals with the reciprocal salt-pair, ammonium nitrate and sodium chloride[2]. The binary system: $NH_4NO_3$-$NH_4Cl$ is included within this salt-pair system and was accordingly investigated by Perman. He concludes that "no isomorphous mixtures or double salts are formed".[3] The present investigation confirms his conclusion regarding double salts but shows that with respect to isomorphous mixtures his conclusion is subject to revision.

The ordinary method of investigating such a system is to subject mixtures to thermal analysis in the form of heating or cooling curves. When the results from a number of mixtures are assembled it is frequently possible to deduce a complete equilibrium diagram, but not infrequently there may still be some ambiguity. The present investigation arose from the fact that a marked break was obtained at 109°C on the heating curve of a mixture of ammonium nitrate with 3 per cent ammonium chloride. Since no break was obtained at 125° it was considered probable that the break was due to the tetragonal (II) ⟶ isometric (I) inversion of the nitrate as changed by the presence of $NH_4Cl$, a fact which necessitates solid solution. It was felt, however, that multiplication of heating curves would probably still leave ambiguity and that a method of direct observation of the changes should be adopted.

Accordingly various mixtures were studied in an oil bath under the microscope, the arrangement of which has already been described in Part I. Thus was permitted, at measured temperatures, the direct observation of inversions, formation and unmixing of solid solutions, beginning of melting and completion of melting, in fact all the changes necessary for the construction of a complete equilibrium diagram. For the study of those changes that may take place slowly such as the mixing and unmixing of solid solutions, it was possible to keep the temperature of the oil bath constant within about one degree for several hours by using a storage battery as a source of current.

The investigation as a whole constitutes an excellent example of one manner in which the petrographic microscope may be used as an aid to the study of chemical equilibrium. On account of the fact that all of the changes

[1] Investigations carried on with the co-operation of Peerless Explosives Company, to whom we take this opportunity of expressing our thanks.

[2] E. P. Perman: J. Chem. Soc., 121, 2473 (1922).

[3] Op. cit., p. 2480.

involved can be viewed actually in progress, the question of alternative interpretations scarcely enters. This is not always true in equilibrium diagrams, especially of systems where solid solution occurs, as evidence of which fact might be cited the several forms of the iron-carbon diagram that are current. The range of variety of the phenomena exhibited and directly observable, the relative ease of attainment of equilibrium, the accessibility of the temperatures involved and the consequent simplicity of apparatus required render the present system a very advantageous one to assign to students for

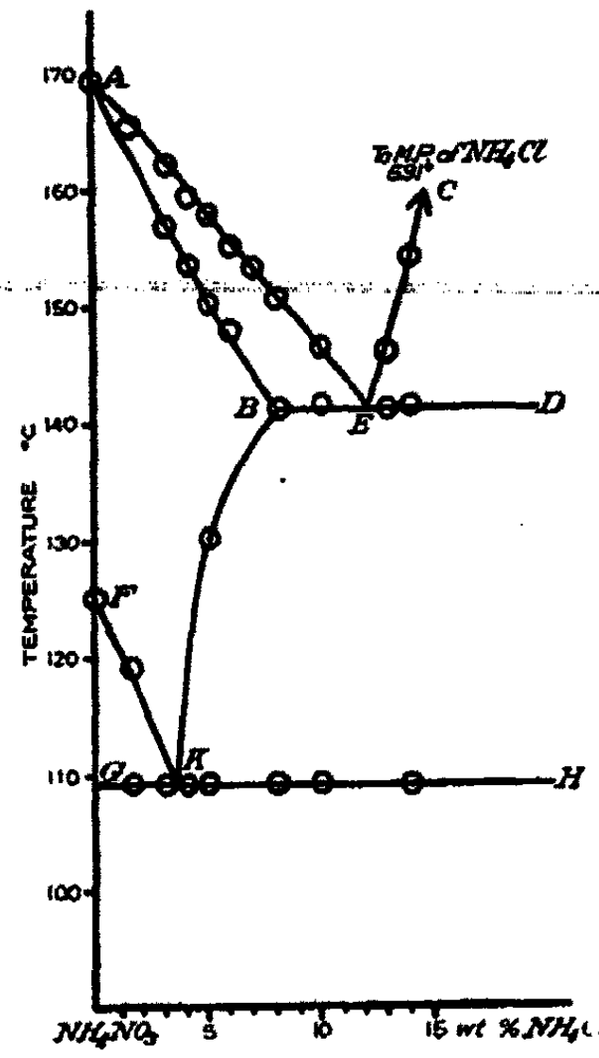



FIG. 1

Equilibrium diagram of the system: ammonium nitrate-ammonium chloride.
*ABKF* —Isometric mix-crystals
*AEB* —Isometric mix-crystals and liquid
*GKF* —Isometric mix-crystals and tetragonal $NH_4NO_3$
*DBKH* —Isometric mix-crystals and isometric $NH_4Cl$
*CED* —Liquid and isometric $NH_4Cl$
Below *GKH* —Tetragonal $NH_4NO_3$ and isometric $NH_4Cl$.

practice purposes. They would thus be put in the way of acquiring a practical acquaintance with the principles of phase equilibrium and also of gaining some familiarity with the manipulation of the polarizing microscope.

## Preparation of Mixtures

The materials used in the preparation of mixtures were J. T. Baker's analyzed ammonium nitrate and ammonium chloride. These were powdered and dried in an evacuated desiccator over $P_2O_5$ after the method recommended by Early and Lowry[1]. Weighed amounts were then mixed in various propor-

[1] J. Chem. Soc., 115, 1389 (1919).

tions and the mixture fused in a short test tube by immersing it in an oil bath to avoid excessive heating. The mixture was well stirred while liquid and then chilled rapidly to prevent segregation. About 2 g. of each mixture to be investigated was thus made; the fused cake obtained was powdered and kept in the vacuum desiccator until needed for study.

For the investigation of each mixture a small amount of the powder was placed on a specimen glass, heated gently until melted, covered with a cover slip and placed in the oil bath on the stage of the microscope. For most of the observations a magnification of 80 diameters was used, but for the study of some of the finer structures such as those produced by unmixing of solid solutions resort was had to some 200 diameters. By working in this manner and noting not only the temperature at which changes occurred but also the nature of the changes the results given in Table I were obtained. It was found that many of the changes were readily overstepped in the cooling direction but were prompt in the opposite direction. In the case of the solidus and liquidus, especially, it is essential that these be determined in the heating direction.

TABLE I

Temperatures of observed changes in $NH_4NO_3$-$NH_4Cl$ mixtures

| Composition Per cent $NH_4Cl$ | Tetragonal→Isometric inversion °C | Beginning of melting °C | Completion of melting °C |
|---|---|---|---|
| 0 | 125.5 | 169+ | |
| 1.5 | 109 (in part) | —— | 165.5 |
| 3.0 | 109 (in part) | 157 | 162 |
| 4.0 | 109 | 153+ | 159.5 |
| 5.0 | 109 | 151 | 158 |
| 6.0 | 109 | 148 | 155 |
| 7.0 | 109 | —— | 153 |
| 8.0 | 109 | 141 | 150.5 |
| 10.0 | 109 | 141.5 | 146.5 |
| 13.0 | 109 | 141 | 146 |
| 14.0 | 109 | 141.5 | 154 |

These results, together with a few others that do not lend themselves to tabulation, are expressed in diagrammatic form in Fig. 1.

### Correspondence of the Results with those of Perman

The diagram obtained by Perman is reproduced in Fig. 2 and comparison shows that the liquids of ammonium nitrate and the composition and temperature of the eutectic are in complete agreement with my results. The upper points on the $NH_4Cl$ liquidus are somewhat lower than those determined by Perman but these are very difficult of determination because some decomposition sets in and a little gas is evolved so that the error here may be perhaps four or five degrees. It is sufficient to know that the $NH_4Cl$ liquidus rises steeply from the eutectic.

It is especially to be noted that some features of Perman's results themselves point directly to the existence of solid solution. Thus he obtained a remarkable eutectic arrest in the 11 per cent mixture, the temperature remaining constant for fully seven minutes. On the other hand he obtained no break whatever in the six per cent mixture at that temperature, though in the absence of solid solution the pause should be about half as long[1]. The absence of the arrest is, of course, due to the fact that the six per cent mixture lies within the limits of solid solution.[2]

Moreover, in his later work, in which he separated the crystals from liquid by a method of filter-pressing and then analyzed the crystals, he was unable to get the $NH_4NO_3$ crystals nearly as pure as the $NH_4Cl$ crystals obtained on the other side of the eutectic[2].

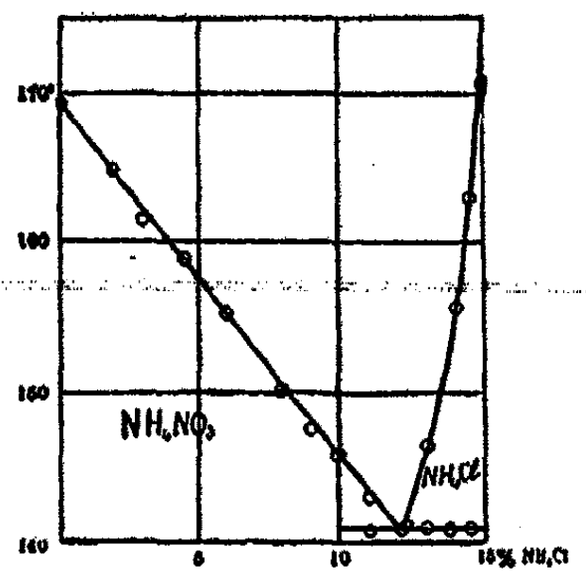



FIG. 2

The system: ammonium nitrate-ammonium chloride (after Perman).

The significant difference between the two diagrams is that the new one shows the liquidus of ammonium nitrate to be that of ammonium nitrate mix-crystals and not of the pure salt. The existence of these mix-crystals brings in the phenomena of melting intervals, inversion intervals and unmixing of solid solutions which are the really interesting features of the diagram. The existence of such features in mix-crystals or solid solutions is, of course, well known, but the phenomena resulting have seldom been observed actually in progress with the clarity exhibited in the present system, so that some description of the observations would appear to be called for.

### Melting and Crystallization of the Solid Solutions

Both the beginning and completion of melting of the solid solutions can be observed very definitely. Melting begins with the formation of narrow channels of liquid all through the originally homogeneous[3] solid. As the temperature is slowly raised these gradually widen at the expense of the intervening areas of solid until they finally occupy the whole field and the solid has completely disappeared.

Crystallization is practically the reverse of this. Upon cooling there is ordinarily five degrees or more of undercooling and then crystallization appears, not at numerous dispersed points, but at one, or at most, two or three points from which branching crystal forms spread all through the liquid. As the temperature falls this skeleton grows at the expense of the intervening areas of liquid until finally all of the liquid is exhausted.

---

[1] Perman: op. cit., p. 2474. Fig. 1.

[2] Perman and Dawkins: J. Chem. Soc., 125, 1241-2 (1924).

[3] "Homogeneous" is here used to designate the presence of only one phase and not to indicate uniformity of crystallographic orientation. When the latter condition is referred to it is specifically so designated.

It can sometimes be definitely observed that, as may be deduced from the diagram, the solid solution first separating is of different composition from that later formed. The index of refraction of ammonium nitrate mix-crystals increases as the content of $NH_4Cl$ increases. The branching crystals first formed are relatively poor in $NH_4Cl$ and therefore of relatively low refractive index, and when crystallization is complete the original skeleton is still distinguishable from the rest of the otherwise homogeneous mass by a lower refractive index, detected by the half-shade method familiar to petrographers. There are, of course, no sharp boundaries, but a general fading of the one into the other.

As a result of such zoning of crystals the crystallization interval obtained on cooling is greater than the true equilibrium interval, for such zoning represents a failure of true equilibrium. It should be noted, too, that, for the determination of the melting interval (rising temperature), material which has been crystallized in such a way as to give zoning can not be used because it will give too low a temperature of beginning of melting. Perfectly homogeneous solid solutions for the study of the melting interval were prepared by making the amount in the usual way and dropping it quickly into the oil bath, which was already at a temperature of 130°. The preparation is thus chilled instantly to 130° and crystallizes to a homogeneous solid solution.

### Melting and Crystallization of Eutectiferous Mixtures

Eutectiferous mixtures such as that containing 10 per cent $NH_4Cl$ are best crystallized in a similar manner. They then consist of areas of homogeneous mix-crystal with interstitial patches of a fine-grained intergrowth of $NH_4Cl$ and nitrate mix-crystals. When this is heated the fine-grained intergrowth is seen to melt as a whole at 141° and then with rising temperature the excess crystals dissolve in the liquid. One thus obtains direct visual evidence that the change occurring at 141° is the melting of the eutectic intergrowth.

If crystallized relatively slowly by cooling in the oil bath, so that zoning of mix-crystals occurs, even mixtures that lie within the limits of solid solution may show some residual eutectic intergrowth. Thus the seven per cent mixture, though it can readily be shown, when properly crystallized, to be within the solid solution area, may at times show some eutectic. This is due to the fact that the first crystals formed have only about 4 per cent $NH_4Cl$ and unless these can, with falling temperature, be completely made over into crystals richer in $NH_4Cl$ by reaction with the liquid, the final liquid must have considerably more $NH_4Cl$ than 7 per cent, that is, must lie within the eutectiferous region.

Thus the 7 per cent mixture may or may not develop some eutectic mixture, depending on the conditions of crystallization. In other words free $NH_4Cl$ as a separate crystalline phase may or may not develop, depending on the opportunity for reaction (interchange of material) between crystals and liquid during crystallization. This factor is so important in silicate systems where solid solution is so prevalent that I have sought to emphasize it by

giving it a name for which I have suggested the "reaction principle".[1] In mineral systems, as in the present system, the working of the reaction principle permits the development or the non-development of certain compounds as separate crystalline phases depending on the conditions of crystallization. Desch has offered objection to the principle and refers to it as "abandonment of the equilibrium diagram" though he fails to point out just where the deviation comes in[2]. It is, as a matter of fact, a direct deduction from equilibrium diagrams and is by no means confined to silicates. Here we have direct visual evidence of its working in a salt system and one could cite many systems involving either solid solution or incongruent melting and coming from Desch's own field of metallurgy where the working of the reaction principle is of paramount importance in determining the phases present in an alloy and therefore in determining the properties of the alloy.

### Limit of Solid Solution

By crystallizing rapidly at 130° in the manner described it can readily be observed that most of the mixtures in the solid solution area form a single homogeneous crystalline phase. In the 8 per cent mixture such a phase forms first at 130° but, immediately, separation of $NH_4Cl$ occurs as skeletons of cubic pattern throughout the mass. Though both the nitrate mix-crystals and the $NH_4Cl$ are isotropic, the presence of two substances and the identity of each is readily established on account of the much higher refractive index of the $NH_4Cl$. If, now, the temperature of the mass is raised to 138°, a temperature only a little below the eutectic, the $NH_4Cl$ is observed to decrease in amount slowly. After 1½ hours at that temperature there is only a bare trace left and it persists with further heating at this temperature. If the temperature could be held exactly at the eutectic without passing a little above it, and thus inducing melting, it is probable that this last trace of $NH_4Cl$ would disappear. At any rate the amount left at 138° is so small that the extent of solid solution may be said to be nearly if not quite 8 per cent.

### Metastable Solid Solutions

Even mixtures well beyond the limit of solid solution, indeed on the $NH_4Cl$ side of the eutectic, may crystallize in such a way as to give transitory, metastable, solid solutions. Thus the mixture with 13 per cent $NH_4Cl$ will cool in the oil bath to about 136° (well below the eutectic) before crystals form and it then crystallizes to a single, homogeneous phase. This phase is scarcely formed, however, when it begins to separate into two phases. This unmixing starts at one or two centers from which it spreads after the manner of an inversion. It is plainly the unmixing of a homogenous phase and not the gradual coarsening of a sub-microscopic intergrowth of two phases, for this latter would take place very gradually and all parts of the mass would, at any time, be at the same stage of coarsening. Contrary to this, the actual change

[1] N. L. Bowen: "The Reaction Principle in Petrogenesis". J. Geol., 30, 177-198 (1922).

[2] C. H. Desch: Trans. Faraday Society, 20, 472-3 (1925); and also Presidential Address Section B, Chemistry, British A. A. S., Southampton, 1925, p. 20.

at any point is an instantaneous one from a perfectly clear, homogeneous mass to a turbid intergrowth of two phases which does not thereafter change any further. The change is propagated from point to point as a circular wave which may take two, three or even five minutes to traverse one centimeter. At the end of this 5 minutes the portion not yet reached by the wave of unmixing is still the clear, homogeneous solid solution that it was originally. While there may thus elapse several minutes between the time of formation of the metastable solution and the *completion* of unmixing in all parts of the mass, I have never observed any appreciable interval between the formation of the homogeneous crystalline phase and the *beginning* of unmixing at some point in the mass. It is not suggested that this is a necessary property of metastable solid solutions. It is merely pointed out as a fact in the present instance.

### Mixing and Unmixing of Solid Solutions

Reference has already been made to the unmixing of solid solutions especially in connection with the metastable solid solutions and also to both mixing and unmixing in describing the determination of the limits of solid solution on the 8 per cent mixture. The phenomena observed on crossing the unmixing curve *BK* in any of the mixtures between 3 1/2 per cent (*K*) and 8 per cent (*B*) are in most respects the same as those already described for the 8 per cent mixture. Thus the 5 per cent mixture, when crystallized rapidly at 142°, gives a single homogeneous mix-crystal phase and it remains indefinitely as such if the temperature is maintained at that value. If, however, the temperature is lowered to 115°, unmixing occurs in the form of the separation of a skeleton of $NH_4Cl$ of cubic pattern. This separation is somewhat different from that occurring in the metastable solid solutions. It takes place gradually and uniformly in all parts of the mount, appearing first as a slight turbidity which increases until finally definite, though minute, stripes of higher refractive index ($NH_4Cl$) are to be made out. If the homogeneous mass is now slowly reheated (in the actual example the heating rate was 10° per hour) the $NH_4Cl$ can be seen to decrease in amount. At 130° it has finally disappeared and the preparation is again a single homogeneous phase. It was also ascertained that at 125° some $NH_4Cl$ persists after two hours and without apparent diminution in amount after the first few minutes. It was taken, therefore, that disappearance at 130° represents equilibrium at the point on the curve *BK* at 5 per cent $NH_4Cl$ was accordingly placed at that temperature.

### Inversion and the Inversion Intervals of the Solid Solutions

When a mount of pure $NH_4NO_3$ is slowly heated the inversion from the birefracting tetragonal form to the isotropic form is observed to take place at 125.5°. In all mixtures containing $NH_4Cl$ (none with less than 1.5 per cent was examined) the same change takes place at 109° (*GKH*). Below that temperature all mixtures are definitely inhomogeneous, both tetragonal $NH_4NO_3$ and cubic $NH_4Cl$ being recognizable. This is true even of the mixture containing only 1.5 per cent $NH_4Cl$ so that from direct observation

we know that there is little if any solid solution of $NH_4Cl$ in the tetragonal modification of $NH_4NO_3$. Immediately above 109° the condition of the mixture depends upon whether it is of a composition lying to the right or to the left of $K$. Those compositions to the right of $K$ (richer in $NH_4Cl$) consist of isotropic mix-crystals and excess $NH_4Cl$ as such. Those to the left of $K$ consist of isotropic mix-crystals and excess birefracting (tetragonal) $NH_4NO_3$. Indeed it was on this basis that the composition of the point $K$ was established. The 4 per cent mixture was found to belong to the one class and the 3 per cent to the other. The point $K$ was believed to be thus located with sufficient accuracy and was placed midway or at 3.5 per cent.

It may be of interest to note that if we calculate the concentration of the solid solution which should have an inversion point of 109° by means of the approximate formula $\Delta T = \frac{RT^2}{L} \cdot \frac{N}{N_o}$ we obtain a value of approximately 3.4 weight per cent $NH_4Cl$ which is in agreement with the experimental finding that it is between three and four per cent. In the formula $\Delta T$ is the difference between the temperature of any phase-change (melting, boiling or inversion) of a pure solvent and that of the same change in a solution containing $N$ mols of solute to $N_o$ mols of solvent. $T$ is the temperature of the phase-change in the pure solvent, $L$ the latent heat of the phase-change per mol and $R$, the gas constant. In the present case the temperature of the inversion of the pure nitrate is 125°C whence $T = 398°$ and $\Delta T = 16°$. The latent heat of inversion per gram = 13 0 calories[1], whence $L$ = 1040 calories.

The further behavior, with temperature rising above 109°, of mixtures to the right of $K$ (those with excess $NH_4Cl$) has already been described. Those to the left of $K$ remain to be discussed. They contain in addition to isotropic mix-crystals an excess of tetragonal $NH_4NO_3$. The latter is very conspicuous under crossed nicols, for it occurs as bright birefracting filaments ramifying through the dark, isotropic ground mass. When the temperature is slowly raised these filaments gradually narrow as a result of the absorption of their substance into the surrounding isotropic phase. Thus, if the 1.5 per cent mixture is held at 118° for 35 minutes there is at first marked absorption of the filaments, but the change finally comes to rest with minute filaments still persisting. On the other hand, at 120° disappearance of the filaments is complete in 20 minutes. On the basis of these determinations the point on the curve $FK$ corresponding to the 1.5 per cent mixture was placed at 119°.

Under conditions of relatively rapid heating, these filaments of tetragonal $NH_4NO_3$ behave in a different manner. There is then insufficient opportunity for diffusion into the adjacent phase and they act as they would in its absence. The temperature may accordingly be raised to 125.5° where they promptly invert to the isotropic form. We have thus additional proof that these filaments are pure, tetragonal $NH_4NO_3$ and that this form of $NH_4NO_3$ takes no $NH_4Cl$ into solid solution. Even after inversion of the filaments to the iso-

[1] This value was calculated by Bridgman from the results of his study of the effect of pressure on the transition point. Proc. Am. Acad. Arts Sci., 51, 614 (1916).

tropic form, whereby they have become the same phase as their surroundings, they are, nevertheless, a different concentration of that phase and are still distinguishable by virtue of a lower refractive index. This difference gradually fades out, however, and in a few minutes no observable difference persists.

The freedom of diffusion in these solids, which is evidenced by this and other phenomena already described, is very remarkable when it is considered that the temperatures concerned are but little above the boiling point of water.

The inversion of the solid solutions (*G-K*) with falling temperature should take place when the curve *FK* is crossed but as a matter of fact undercooling ordinarily occurs. Filaments of birefracting, tetragonal $NH_4NO_3$ can be developed, however, in a mass that was originally a homogeneous isotropic solid solution by cooling it into the region *FKG* and holding it there.

It should be pointed out that some mixtures can be crystallized in such a way as to give both the effect characteristic of mixtures to the left of *K* and that characteristic of mixtures to the right of *K*. This is accomplished by the relatively slow crystallization induced by cooling the oil bath with the mount in place and was observed to occur in the 4 per cent mixture. As has already been stated, the crystallization begins with the separation of a framework with less than 4 per cent $NH_4Cl$ which is later filled in by material with more than 4 per cent $NH_4Cl$ and the difference is apparent in the lower refractive index of the original framework. Further cooling of a mass so constituted and holding it at a temperature of 113° induce separation of birefracting $NH_4NO_3$ in the parts corresponding with the original framework and of a cubic skeleton of $NH_4Cl$ in the other parts.

### Lack of Solid Solution in the other Modifications of Ammonium Nitrate

We have already noted the evidence that there is no solid solution of $NH_4Cl$ in the tetragonal form of $NH_4NO_3$. A study of the other inversions of the nitrate, that at 84°, that at 32°, and the metastable inversion at 50°, shows that there is no appreciable change in any of them in the presence of $NH_4Cl$. From this fact it may be deduced that, like the tetragonal form, none of the other low-temperature forms of ammonium nitrate takes ammonium chloride into solid solution. Therefore for the complete diagram of stable equilibrium above room temperature Fig. 1 requires to have added to it only two horizontal lines, one at 84° and one at 32°.

### Summary

A re-examination of the system ammonium nitrate-ammonium chloride gives results that agree with those of Perman as to the position of the liquidus curves and the eutectic but reveals a series of solid solutions not found by him. The method of investigation is that of direct observation under the microscope whereby the various crystalline phases can be identified by means of their optical properties and phase-changes can be observed actually in progress.

It is thus found that all mixtures from pure $NH_4NO_3$ as far as eight per cent $NH_4Cl$ crystallize to a homogeneous, mix-crystal phase of isometric

symmetry. In consequence of the existence of this mix-crystal or solid solution series the phenomenon of the eutectic does not enter until after the limits of solid solution are passed, each member of the series beginning to melt at a successively higher temperature as pure $NH_4NO_3$ is approached.

In addition to these melting intervals of the solid solutions their inversion intervals can likewise be observed directly. The isometric (I) ⟶ tetragonal (II) inversion changes from 125.5° for pure $NH_4NO_3$ to 109° for the solid solution containing 3.5 per cent $NH_4Cl$. At 109° the curve of unmixing of solid solutions is encountered and along this curve the phenomena of mixing and unmixing of solid solutions take place and can be directly observed. Thus even changes involving diffusion in the solid state take place with comparative readiness in these materials.

All of the facts are embodied in the equilibrium diagram, Fig. 1.

# PROPERTIES OF AMMONIUM NITRATE

## III. A Note on the System: Ammonium Nitrate-Ammonium Sulphate[1]

BY N. L. BOWEN

Perman, continuing his studies of $NH_4NO_3$, has published in collaboration with Howells the results of an investigation of the system $NH_4NO_3$-$(NH_4)_2SO_4$ by the method of thermal analysis. They found that the melting point of $NH_4NO_3$ rises with addition of $(NH_4)_2SO_4$ and concluded therefore that there was formation of solid solutions[2].

Freeth, while recognizing this as a possible interpretation of the thermal results, offers the alternative suggestion that we have here an example of the limiting case of the eutectic. The eutectic is assumed to lie sensibly at the composition of the component $NH_4NO_3$ and therefore, of course, sensibly at the temperature of melting of $NH_4NO_3$ and the rising curve is assumed to be the liquidus of the double salt, $3NH_4NO_3 . (NH_4)_2SO_4$.[3] Freeth offers this system by way of an example of one in which a little more work would clear up moot points and suggests the determination of an isotherm at 170°C with water. This would almost certainly offer more than a little work and not improbably would still permit alternative interpretation. There is a simpler and more direct method, namely, that of actual observation of the phases and phase-changes under the petrographic microscope, and the present note gives the results of applying this method to decide the point at issue.

The method is that already described in former papers of the present series and consists in preparing a microscope mount of the mixture by melting it on a specimen glass, covering it with a cover slip and then observing the various phase-changes in an oil bath of controlled and measured temperature mounted on the stage of a polarizing microscope.

No attempt was made to work out the complete system: Only enough work was done to decide whether the rising liquidus was that of $NH_4NO_3$ mix-crystals or the 3:1 double salt, which required the preparation of only one mixture. The mixture made was that containing four per cent $(NH_4)_2SO_4$.

When this mixture is melted and allowed to cool in the oil bath it is seen to crystallize to a single, homogeneous, isotropic, mix-crystal phase or solid solution. The refractive indices of the 3:1 double salt have been determined by Thomas and Hallimond[4] to be $\gamma = 1.536$ and $\alpha = 1.521$. A small fraction of one per cent of such material, present in addition to isotropic $NH_4NO_3$, could not escape detection under the microscope. There is the possibility, of course, that the double salt has a higher-temperature, crystalline form which

[1] Investigations carried out with the co-operation of Peerless Explosives Company, to whom we take this opportunity of expressing our thanks.

[2] Perman and Howells: J. Chem. Soc., 123, 2130 (1923).

[3] F. A. Freeth: J. Phys. Chem. 29, 506 (1925).

[4] "Chemical and physical properties of Oppau ammonium sulphate-nitrate". Trans. Faraday Soc., 20, 57 (1924).

is isotropic, but even if this form were present as such it would require to have almost exactly the same refractive index as $NH_4NO_3$ to escape detection. The possibility of such extreme correspondence is very remote and in any case the fact that the sulphate exists in solid solution is proven by other observations now to be given.

When the preparation is further cooled no change of any kind is observed until a temperature of about 100°C is reached, when inversion to a birefracting mass occurs. The preparation is now plainly inhomogeneous, i.e., is made up of two different crystalline phases, the one definitely recognizable as tetragonal $NH_4NO_3$, the other too small in amount to permit definite determination of its properties. The exact temperature at which the inversion takes place with falling temperature is of no particular significance for undercooling readily occurs, but, upon slow reheating, the mass is observed to revert to the isotropic state at 118.5°C, a full 7° below the corresponding inversion in pure $NH_4NO_3$. Such a change of inversion point can be brought about only as a result of solid solution. Moreover, the direction of the change—a lowering—is such as to prove the greater solid solubility of the $(NH_4)_2SO_4$ in the higher temperature (isotropic) form of $NH_4NO_3$ than in the lower temperature (tetragonal) form[1].

The preparation is now again a single, homogeneous, isotropic, mix-crystal phase which has been produced in this case from two solids so that the possibility can be immediately rejected that the similar phase produced by cooling the liquid was a metastable phase that failed to unmix.

All of the facts are therefore in complete accord with the conclusion of Perman and Howells that solid solutions are formed and their rising liquidus is properly interpreted as the result of this fact. The present work proves directly only that the solid solution extends at least as far as 4 per cent, but the smooth rise of the liquidus as far as 8 per cent indicates that it is all the one liquidus and that solid solution extends beyond that point, for the solidus must, of course, lie at least a little on the sulphate side of the liquidus.

Further work would be necessary to determine the limiting concentration of this mix-crystal series, but there is nothing in the existence of such a series that is inconsistent with the proved existence of the 3:1 double salt at 70° or, indeed, with its stability in contact with liquid at higher temperatures.

## Summary

By the method of direct observation of phase-changes under the microscope it is proved that the rising liquidus in the system, $NH_4NO_3$-$(NH_4)_2SO_4$ is caused by solid solution, as Perman and Howells conclude, and not by the limiting position of the eutectic, a possible alternative suggested by Freeth.

*Geophysical Laboratory,*
*Carnegie Institution of Washington,*
*January, 1926.*

[1] It was observed that the metastable inversion which takes place at 50° in pure $NH_4NO_3$ took place at sensibly the same temperature in the present mixture, from which fact it may be inferred that neither the tetragonal nor the orthorhombic form of $NH_4NO_3$ takes sulphate into solid solution at least at that temperature.

# THE EFFECT OF TEMPERATURE UPON THE GROWTH OF YEAST IN VARIOUS MEDIA

BY F. F. SHERWOOD AND E. I. FULMER*

98-110

## Introduction

In previous communications from this laboratory[1] it has been shown that the rate of growth of yeast depends not only upon the kinds of nutrients present but also upon their concentrations. In the case of ammonium salts there are optimum concentrations which shift with temperature, a higher concentration being required for optimum results with rise in temperature. This is true not only in a synthetic medium but holds likewise for beer wort. The optimum concentrations of ammonium salt for the growth of yeast in the medium at any temperature is that concentration in which a protein, wheat gluten, is least swollen. The generalization was made[2] that "if the addition of ammonium salt to a medium increases its ability to dehydrate wheat gluten, the addition will likewise improve the medium for the growth of yeast, the effect being a maximum in any combination in which the gluten is least swollen".

It was likewise pointed out in a preliminary communication on the subject[3] that since there are at least two optimal concentrations of ammonium salt for the growth of yeast at a given temperature it follows that for a given concentration of the salt there are at least two optimal temperatures. In Table I are given the values of the optimum temperatures for several standard media for yeast growth.

TABLE I

Calculated Optimum Temperatures for Several Standard Media for the Growth of Yeast

| Investigator | Ammonium salt | Normality | Optimum Temperatures | |
|---|---|---|---|---|
| Pasteur | tartrate | 0.00109 | − 29.5 | −26.0 |
| Nägeli | tartrate | 0.00435 | − 23.8 | −25.4 |
| Mayer | nitrate | 0.00936 | − 15.0 | −24.2 |
| Amand | chloride | 0.0187 | + 1.4 | −21.9 |
| Raulin | nitrate and sulfate | 0.0359 | + 31.6 | −17.9 |
| MacDonald | sulfate | 0.0454 | + 48.2 | −15.5 |
| Laurent | sulfate | 0.0713 | + 93.7 | − 9.5 |
| Cohn | tartrate | 0.109 | +159. | − 0.47 |

* From the Laboratory of Biophysical Chemistry, Chemistry Department, Ames.

[1] Fulmer, Nelson and Sherwood: J. Am. Chem. Soc., 43, 191 (1921); Ind. Eng. Chem., 16, 921 (1924); Fulmer: "Colloid Symposium Monograph", 2, 204 (1924).

[2] Fulmer, Sherwood and Nelson: Ind. Eng. Chem., 16, 921 (1924).

[3] Fulmer: "Colloid Symposium Monograph", 2, 204 (1924).

In only one instance, that of Raulin's medium, is an optimum temperature within the viable range. A rise in temperature in a medium with a given concentration of ammonium salt is equivalent in the effect upon the growth of yeast to the lowering of the concentration of the salt at a given temperature. Evidently the term "optimum temperature" for the growth of an organism has no general meaning but is a function of the kinds of materials present and of their concentrations.

Data obtained regarding the effect of temperature upon the growth of an organism in a medium of constant composition are the resultant of two factors, the effect of temperature per se and its effect upon the physical chemical environment. This may be illustrated as follows. If the growth of yeast in Amand's medium be studied between 10° and 30° the growth rate will be increased by rise in temperature but also retarded due to the increasing "distance" from the optimum of +1.4°; with MacDonald's medium the growth rate will be accelerated by the increase in temperature and likewise by that fact of the approach to an optimum of +48.2°; with a medium such as that of Cohn the effect will be complex for with rise in temperature the growth rate will be accelerated by the increase in temperature but retarded as the temperature goes away from the medium of −1.7° and accelerated as the optimum of +159 is approached.

It would seem then that the effect of temperature per se upon the growth of yeast in a medium of a given composition can be determined only on the basis of growth rates in the medium with the optimum concentrations of the components for each temperature. Data are here presented on the growth of yeast at various temperatures in media whose composition is adjusted to optimum conditions and the results compared to those obtained in media not so adjusted as well as with data obtained by other investigators.

The yeast used had been growing continuously in a synthetic medium for five years and came originally from a cake of Fleischmann's yeast and is identical with the yeast described previously[1] as No. 11. The number of cells in each case was determined by means of the Thoma-Zeiss counting chamber and is indicated as "count". The "count" is the number of cells in sixteen small squares so that when the count is one there are 250,000 cells per cubic centimeter. In every case the flasks were inoculated so that the initial count was one, the inoculation being made from an actively growing culture in order to reduce any "lag phase" to a minimum.

In the determination of the growth rates the flasks were gently rocked after the method described by Clark[2] and for reasons discussed by him.

The beer wort was made by mashing, at 55°, 360 grams of distiller's malt with 1150 cc. of distilled water for 24 hours. The mixture was filtered through towelling, then through filter paper and heated for thirty minutes under 15

[1] Fulmer and Christensen: J. Phys. Chem., 29, 1415 (1925).
[2] Clark: J. Phys. Chem., 26, 42 (1922).

TABLE II

Determination of Optimum Concentration of Ammonium Chloride in the Synthetic Medium

| Temp. | 0° | | 10° | | 20° | | 25° | | 30° | | 35° | | 40° | | 42° | | 43° | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hrs. | 24 | 98 | 37 | 45 | 24 | 46 | 24 | 36 | 24 | 83 | 24 | 72 | 46 | 77 | 24 | 48 | 24 | 45 |
| Normality $NH_4Cl$ | Count | | Count | | Count | | Count | | Count | | Count | | Count | | Count | | Count | |
| 0.0118 | 2.6* | 3.8* | 20 | 21 | 96 | 120 | 40 | 56 | 102 | 242 | 109 | 99 | 204 | 146 | — | — | | |
| 0.0128 | 1.8 | 2.3 | — | — | — | — | — | — | — | — | — | — | — | — | — | — | | |
| 0.0206 | — | — | 24 | 28 | — | — | — | — | — | — | — | — | — | — | — | — | | |
| 0.0236 | 1.3 | 1.1 | 31* | 39* | 108 | 166 | 48 | 98 | 115 | 280 | 144 | 188 | — | 213 | 59 | 123 | | |
| 0.0265 | — | — | 27 | 30 | — | — | — | — | 117 | 294 | — | — | — | — | — | — | | |
| 0.0295 | — | — | 19 | 22 | 150* | 224* | 78 | 103 | 138 | 312 | 196 | 201 | 222 | 236 | 76 | 149 | | |
| 0.0301 | — | — | — | — | 47 | 101 | — | — | — | — | — | — | — | — | — | — | | |
| 0.0307 | — | — | — | — | 45 | 84 | 96 | 109 | — | — | — | — | — | — | — | — | | |
| 0.0313 | — | — | — | — | 47 | 76 | — | — | — | — | — | — | — | — | — | — | | |
| 0.0319 | — | — | — | — | — | 69 | 122* | 156* | — | — | — | — | — | — | — | — | | |
| 0.0324 | — | — | — | — | 46 | 67 | 80 | 89 | 156 | 313 | 225 | 243 | — | 260 | — | — | | |
| 0.0342 | — | — | — | — | — | — | — | — | 174 | 335 | — | — | — | — | — | — | | |
| 0.0354 | 1.0 | 0.5 | 14 | 17 | — | 66 | 60 | 69 | 184* | 369* | 257 | 277 | 237 | — | 135 | 173 | | |
| 0.0366 | | | — | — | 49 | — | — | — | 120 | 283 | — | — | — | 291 | — | — | | |
| 0.0384 | | | — | — | — | — | — | — | 96 | 229 | 273* | 314* | 276 | 310 | 196 | 229 | 2.5 | 2.9 |
| 0.0413 | | | 10 | 12 | — | — | 49 | 56 | 85 | 226 | 202 | 186 | 288* | 388* | 238 | 283 | 2.6 | 3.0 |
| 0.0425 | | | | | — | — | — | — | — | — | — | — | — | — | 279* | 342* | 2.7 | 3.1 |
| 0.0431 | | | | | — | — | — | — | — | — | — | — | — | — | — | — | 3.1* | 3.3* |
| 0.0437 | | | | | — | — | — | — | — | — | — | — | — | — | 206 | 289 | 2.8 | 3.1 |
| 0.0442 | | | | | — | — | — | — | — | — | — | — | — | — | — | — | 2.7 | 3.0 |
| 0.0472 | | | | | 49 | 68 | 45 | 49 | 74 | 182 | 197 | 177 | 216 | 164 | 159 | 240 | 2.6 | 3.1 |
| 0.0590 | | | | | | | | | 67 | 177 | 143 | 168 | 198 | 142 | 143 | 186 | | |

* Optimum.

TABLE III

The Effect of Ammonium Chloride upon the Growth of Yeast in Wort

| Temperature | 10 | | 20 | | 30 | | 40 | | 42 |
|---|---|---|---|---|---|---|---|---|---|
| Normality of $NH_4Cl$ | Count 36 hr. | Normality of $NH_4Cl$ | Count 30 hr. | Normality of $NH_4Cl$ | Count 22 hr. | Normality of $NH_4Cl$ | Count 42.5 hr. | Normality of $NH_4Cl$ | Count 25 hr. |
| 0.000 | 185 | 0.000 | 210 | 0.000 | 230 | 0.000 | 680 | 0.000 | 29 |
| 0.0059 | 210 | 0.0118 | 240 | 0.0118 | 270 | 0.0236 | 795 | 0.0118 | 63 |
| 0.0088 | 222 | 0.0147 | 253 | 0.0236 | 352* | 0.0259 | 825 | 0.0236 | 94 |
| 0.0118 | 235 | 0.0177 | 265 | 0.0294 | 232 | 0.02714 | 843 | 0.0294 | 157* |
| 0.0129 | 248 | 0.0182 | 273 | 0.0341 | | 0.0283 | 900* | 0.0354 | 83 |
| 0.0135 | 260 | 0.0188 | 340* | 0.0354 | 242 | 0.0294 | 720 | 0.0482 | 85 |
| 0.0141 | 321* | 0.0194 | 258 | 0.0470 | 245 | 0.0354 | 692 | 0.0470 | 83 |
| 0.0147 | 245 | 0.0200 | 245 | 0.0588 | 244 | 0.0590 | 700 | 0.0588 | 84 |
| 0.0177 | 239 | 0.0236 | 233 | 0.0820 | 246 | 0.0826 | 713 | 0.0700 | 77 |
| 0.0354 | 226 | 0.0354 | 225 | 0.106 | 281* | 0.1060 | 733 | 0.0820 | 72 |
| 0.0531 | 240 | 0.0590 | 220 | 0.118 | 235 | 0.1180 | 772* | 0.0940 | 81 |
| 0.0590 | 256 | 0.0708 | 239 | 0.129 | 233 | 0.1416 | 685 | 0.1230 | 142 |
| 0.0649 | 269* | 0.0767 | 242 | | | | | 0.140 | 111 |
| 0.0708 | 245 | | | | | | | 0.153 | 84 |
| 0.0826 | 232 | 0.0826 | 261* | | | | | | |
| | | 0.0885 | 241 | | | | | | |
| | | 0.0896 | 236 | | | | | | |

* Optimum

pounds pressure. After standing for three days to permit coagulated matter to settle out, the liquid was filtered and sterilized in live steam for thirty minutes.

The basal medium was Medium E[1] which for 30° has the following amounts of materials per 100 cc.: 0.188 g. $NH_4Cl$, 0.100 g. $K_2HPO_4$, 0.100 g. $CaCl_2$, 0.04 g. $CaCO_3$, 10 g. sugar.

## The Determination of Optimum Concentrations of Ammonium Chloride in Medium E and in Wort

In Tables II, III and IV are given typical data showing the effects of various concentrations of ammonium chloride upon the growth of yeast in Medium E and in beer wort at several temperatures. It will be noted that with both media there are two optimum concentrations of the salt.

With both media the largest crops were obtained at 42°, a temperature considerably higher than that usually considered optimum for the growth of yeast. Slator[2] states that above 40° the enzymes are destroyed. In the synthetic medium the growth at 42° is as good as at 40° but there is a sharp break at 43°. It would seem than that with a properly adjusted medium of the given components that 40°-42° marks the temperature for the maximum growth of yeast and that a profound change takes place between 42° and 43°.

The ammonium salt may be said to act as a "temperature buffer". The term "thermal" death point of an organism may have as little general meaning as "optimum temperature" unless expressed in terms of the composition of the medium. The effect of ammonium salts upon the death rate of yeast and change in permeability to methylene blue[3] is being studied in this laboratory.

The data on wort confirm a previous statement[4] that whatever the role of bios may be in beer wort it is not the same as that of the ammonium salt.

In Table IV are assembled the optimal concentrations of the ammonium chloride for the media studied. In each instance the optimum normality of the salt is a linear function of the temperature, the appropriate equations being given in the table. By means of equations (1) and (2) may be calculated the optimum concentrations of the salt for a given temperature for the synthetic medium while equation (3) and (4) may be used for the beer wort employed in this work. Since latter medium may vary considerably in composition, depending upon the malt and method of mashing, these equations could not be promiscuously used. The equation should be determined for each sample. Similarly by means of the equations (5, 6, 7, and 8) may be calculated the optimum temperatures for a given normality of the ammonium salt. Equations (5) and (6) were used in calculating the data in Table I.

---

[1] Fulmer, Nelson and Sherwood: J. Am. Chem. Soc., 43, 191 (1921); Ind. Eng. Chem. 16, 921 (1924); Fulmer: "Colloid Symposium Monograph," 2, 204 (1924).

[2] Slator: J. Chem. Soc., 89, 128 (1903).

[3] Miller: J. Phys. Chem., 24, 564 (1920); Fraser: J. Phys. Chem., 25, 1; Fulmer: 10 (1921).

[4] Fulmer, Sherwood and Nelson: Ind. Eng. Chem., 16, 921 (1924).

TABLE IV

The Effect of Ammonium Chloride upon the Growth of Yeast in Medium E—Second Maximum

| Temperature | 10 | | 20 | | 30 | | 40 | |
|---|---|---|---|---|---|---|---|---|
| | Normality of $NH_4Cl$ | Count 30 hr. | Normality of $NH_4Cl$ | Count 35 hr. | Normality of $NH_4Cl$ | Count 28 hr. | Normality of $NH_4Cl$ | Count 30 hr. |
| | 0.0000 | 48 | 0.000 | 58 | 0.000 | 61 | 0.000 | 67 |
| | 0.059 | 53 | 0.059 | 65 | 0.118 | 75 | 0.118 | 76 |
| | 0.118 | 61 | 0.118 | 71 | 0.177 | 84 | 0.177 | 84 |
| | 0.1298 | 72 | 0.1475 | 80 | 0.2265 | 89 | 0.2265 | 91 |
| | 0.1475 | 80 | 0.177 | 86 | 0.236 | 105* | 0.236 | 94 |
| | 0.1534 | 92* | 0.182 | 89 | 0.295 | 84 | 0.265 | 97 |
| | 0.1593 | 79 | 0.194 | 100* | 0.354 | 76 | 0.278 | 111* |
| | 0.1652 | 60 | 0.206 | 88 | 0.472 | 63 | 0.287 | 79 |
| | 0.177 | 55 | 0.236 | 65 | 1.118 | 58 | 0.295 | 72 |
| | 0.236 | 40 | 0.354 | 56 | 1.483 | 50 | 0.354 | 65 |
| | 0.2950 | 38 | | | | | 0.4720 | 59 |

* Optimum.

TABLE V

Optimum Concentrations of Ammonium Chloride in Medium E and in Wort

| Temp. | Medium E | | Wort | |
|---|---|---|---|---|
| | I(1) | II(2) | I(3) | II(4) |
| 0 | 0.0118 | | | |
| 10 | 0.0236 | 0.1534 | 0.0141 | 0.0649 |
| 20 | 0.0295 | 0.1940 | 0.0188 | 0.0826 |
| 25 | 0.0319 | | | |
| 30 | 0.0354 | 0.236 | 0.0236 | 0.106 |
| 35 | 0.0383 | | | |
| 40 | 0.0413 | 0.278 | 0.0283 | 0.118 |
| 42 | 0.0425 | | 0.0294 | 0.123 |
| 43 | 0.0431 | | | |

N = normality of ammonium chloride
t = temperature

*Medium E*

1 $N_1 = 0.00057t + 0.0179$; $t_1 = \frac{N - 0.0179}{0.00057}$

2 $N_2 = 0.0042t + 0.111$; $t_2 = \frac{N - 0.111}{0.0042}$

*Wort*

3 $N_1 = 0.0090 + 0.0050t$; $t_1 = \frac{N - 0.0090}{0.0050}$

4 $N_2 = 0.0475 + 0.00177t$; $t_2 = \frac{N - 0.0475}{0.00177}$

## The Optimum Concentrations of $K_2HPO_4$, $CaCl_2$ and $CaCO_3$

Data showing the effect upon the growth of yeast at several temperatures of various concentrations of $K_2HPO_4$, $CaCl_2$ and $CaCO_3$ in Medium E are found in Tables VI, VII and VIII. The results confirm our previous findings.[1]

TABLE VI

Growth of Yeast, varying $K_2HPO_4$

| | 25°C. | 30°C. | | 35°C. | 40°C. | |
|---|---|---|---|---|---|---|
| Normality $K_2HPO_4$ | I = 1 Count 30 hr. | I = 1 Count 66 hr. | I = 1 Count 42 hr. | I = 1 Count 24 hr. | I = 1 Count 24 hr. | I = 1 Count 72 hr. |
| 0.0000 | 180 | 93 | 60 | 27 | 26 | 91 |
| 0.00232 | 222 | 227 | 162 | 172 | 98 | 183 |
| 0.003480 | 246 | 280 | 165 | 181 | 126 | 241 |
| 0.00464* | 261 | 305 | 205 | 190 | 159 | 269 |
| 0.00696 | 260 | 302 | 204 | 189 | 158 | 267 |
| 0.00928 | 259 | 304 | 203 | 187 | 157 | 268 |
| 0.01160 | 261 | 303 | 202 | 188 | 158 | 269 |
| 0.01392 | 262 | 302 | 203 | 187 | 159 | 267 |

* Optimum.

TABLE VII

Growth of Yeast, varying $CaCl_2$

| | 25°C. | | 30°C. | | 35°C. | | 40°C. | |
|---|---|---|---|---|---|---|---|---|
| Normality of $CaCl_2$ | I = 1 Count 24 hr. | I = 1 Count 48 hr. | I = 1 Count 72 hr. | I = 1 Count 48 hr. | I = 1 Count 42 hr. | I = 1 Count 98 hr. | I = 1 Count 24 hr. | I = 1 Count 48 hr. |
| 0.000 | 61 | 92 | 217 | 186 | 157 | 202 | 160 | 210 |
| 0.00180 | 73 | 106 | 235 | 198 | | | | |
| 0.00360 | 91 | 117 | 247 | 202 | 161 | 257 | 209 | 269 |
| 0.00540 | 105 | 129 | 289 | 246 | | | | |
| 0.00720 | 130 | 136 | 295 | 266 | 177 | 260 | 212 | 272 |
| 0.00900 | 140 | 156 | 304 | 290 | | | | |
| 0.0108 | 158 | 173 | 312 | 298 | 191 | 274 | 226 | 285 |
| 0.0126 | 219 | 196 | 310 | 310 | | | | |
| 0.01440 | 256 | 218 | 318 | 318 | 211 | 278 | 245 | 299 |
| 0.01620 | 286 | 278 | 335 | 342 | 232 | 286 | 251 | |
| 0.01800* | 379 | 334 | 386 | 388 | 255 | 319 | 275 | 325 |
| 0.0216 | 375 | 333 | 387 | 388 | 253 | 318 | 276 | 328 |
| 0.0217 | 378 | 335 | 388 | 389 | 254 | 315 | 274 | 326 |
| 0.0324 | 376 | 335 | 387 | 389 | 255 | 318 | 275 | 324 |
| 0.0360 | | | | | 254 | 317 | 276 | |

* Optimum.

[1] Refers to first reference given on page 742.

TABLE VIII

Growth of Yeast, varying $CaCO_3$

| | 25°C. | 30°C. | 35°C. | 40°C. |
|---|---|---|---|---|
| Normality of $CaCO_3$ | I = 1 Count 32 hr. | I = 1 Count 48 hr. | I = 1 Count 36 hr. | I = 1 Count 46 hr. |
| 0.000 | 42 | 130 | 65 | 70 |
| 0.0040 | 115 | 179 | 170 | 196 |
| 0.0060 | 125 | 298 | 192 | 210 |
| 0.0080* | 170 | 371 | 220 | 251 |
| 0.0100 | 100 | 238 | 180 | 215 |
| 0.0120 | 80 | 226 | 164 | 190 |
| 0.0160 | 65 | 206 | 150 | 140 |
| 0.020 | 52 | 186 | 148 | 139 |
| 0.024 | 51 | 175 | 139 | |

* Optimum.

It will be noted that the optimum concentrations of the salts above studied do not vary with temperature as do those for the ammonium chloride. In Table IX are given the concentrations for the best possible medium for the growth of yeast at any temperature with the given components.

TABLE IX

The Concentrations of Salts in Medium E Optimum for Any Temperature

| Salt | Normality | Grams per 100 cc. |
|---|---|---|
| $NH_4Cl$ | (1) 0.0179 + 0.00057t | 0.0960 + 0.60306t |
| | or | or |
| | (2) 0.111 + 0.0042t | 0.595 + 0.675t |
| $K_2HPO_4$ (anhyd) | 0.00464 | 0.0260 |
| $CaCl_2$ (anhyd) | 0.01800 | 0.100 |
| $CaCO_3$ (ppted) | 0.0080 | 0.040 |

## The Growth of Yeast in Various Media

In Table X will be found data showing the growth of yeast in wort without added ammonium chloride while data on the growth of yeast in wort to which had been added the optimum concentration of the ammonium salt for each temperature will be found in Table XI.

## Table X

### Growth of Yeast in Wort without $NH_4Cl$

| 0° | | 10° | | 20° | | 30° | |
|---|---|---|---|---|---|---|---|
| Time (Hours) | Count | Time | Count | Time | Count | Time | Count |
| 28 | 2.2 | 26 | 13 | 17 | 57 | 7 | 15 |
| 35 | 2.7 | 29 | 19 | 19 | 92 | 11 | 71 |
| 48 | 3.9 | 36 | 35 | 21 | 149 | 13 | 153 |
| 52 | 4.3 | 40 | 53 | 23 | 243 | 14 | 225 |
| 64 | 4.4 | 52 | 128 | 25 | 281 | 23 | 677 |
| 76 | 4.6 | 62 | 162 | 29 | 792 | 29 | 1050 |
| | | 77 | 164 | 39 | 1165 | 35 | 1092 |
| | | | | 48 | 1190 | 40 | 1197 |
| | | | | 63 | 1205 | 46 | 1205 |
| | | | | | | 49 | 1220 |
| | | | | | | 59 | 1215 |
| | | | | | | 73 | 1223 |

| 40° | | 42° | | 43° | |
|---|---|---|---|---|---|
| Time (Hours) | Count | Time | Count | Time | Count |
| 6 | 4.5 | 9 | 53 | 12 | 1.6 |
| 8 | 25 | 10 | 83 | 18 | 2.2 |
| 9.5 | 67 | 11 | 131 | 24 | 2.8 |
| 12 | 223 | 13 | 308 | 30 | 3.6 |
| 13 | 320 | 15 | 316 | 38 | 3.7 |
| 14 | 505 | 17 | 340 | 45 | 3.8 |
| 23.5 | 837 | 21 | 355 | 68 | 3.8 |
| 29 | 872 | 33 | 408 | | |
| 37 | 1342 | 41.5 | 521 | | |
| 48 | 1345 | 56 | 625 | | |
| 60 | 1332 | 68 | 630 | | |
| 72 | 1342 | | | | |

TABLE XI

Growth of Yeast in Wort with Optimum Concentrations of $NH_4Cl$

| | 10° | | 20° | | 30° | | 40° | | 42° | |
|---|---|---|---|---|---|---|---|---|---|---|
| Time (Hours) | Count 1st Opt. | 2d | Count 1st Opt. | 2d | Count 1st Opt. | 2d | Count 1st Opt. | 2d | Count 1st Opt. | 2d |
| 8 | | | | | 29 | 25 | | | | |
| 9 | | | | | | | | | 64 | 59 |
| 10 | | | | | 56 | 54 | 131 | 113 | | |
| 11 | | | | | 87 | 82 | 209 | 178 | 161 | 146 |
| 12 | 3.5 | 3.4 | | | 130 | 122 | 332 | 277 | 255 | 228 |
| 13 | | | | | | | | | 406 | 356 |
| 15 | 4.8 | 4.6 | | | | | 1107 | 980 | | |
| 17 | 6.0 | 5.7 | 72 | 63 | | | | | | |
| 18 | | | 92 | 83 | | | | | | |
| 19 | 7.2 | 6.8 | 119 | 107 | | | | | | |
| 21 | | | 196 | 175 | | | | | | |
| 21.5 | | | | | 1437 | 1300 | | | | |
| 23 | | | | | | | | | 600 | 525 |
| 25 | | | 384 | 342 | | | | | | |
| 25.5 | | | | | | | 1330 | 1200 | | |
| 26 | 15 | 14.0 | | | | | | | | |
| 32 | 28 | 26 | | | | | | | | |
| 34 | | | 1059 | 1040 | 1470 | 1390 | | | | |
| 35 | | | | | | | | | 652 | 617 |
| 43 | | | 1301 | 1180 | | | | | | |
| 45 | 109 | 98 | | | | | | | | |
| 47 | | | | | | | 1465 | 1380 | | |
| 48 | | | | | | | | | 667 | 655 |
| 50 | 153 | 133 | | | | | | | | |
| 55 | | | 1404 | 1270 | | | | | | |
| 59 | | | | | 1510 | 1395 | | | 670 | 662 |
| 62 | 237 | 206 | | | | | | | | |
| 67 | | | 1449 | 1296 | | | | | | |
| 69 | | | | | | | 1705 | 1565 | | |
| 70 | | | | | 1515 | 1400 | | | | |
| 74 | 244 | 210 | | | | | | | | |
| 75 | | | 1444 | 1300 | | | | | | |
| 81 | 246 | 212 | | | | | 1710 | 1560 | 665 | 660 |

In Table XII are given the data showing the growth of yeast on the synthetic media. The figures in the columns marked A were obtained by using Medium E with the optimum concentration of ammonium salt for each temperature while in the experiments designated B Medium E was used with the concentration of the ammonium salt optimum for 30°.

TABLE XII

Growth of Yeast in Medium E. A. Opt. for Each Temp. B. Opt. for 30°

| Temp. | 0° | 10° | | 20° | | 30° | | 40° | | 42° | | 43° |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time | A | A | B | A | B | A | B | A | B | A | B | A |
| 6 | | | | | | | | | | | | |
| 7 | | | | | | | | | | | | |
| 8 | | | | | | | | | 11 | 13 | 7.5 | |
| 9 | | | | | | | | | | 17 | | |
| 10 | | | | | | | | | 21 | | 13.5 | |
| 11 | | | | | | 30 | 33 | 43 | 28 | 23 | | |
| 12 | | | | | | 45 | 45 | 63 | 38 | | | 1.5 |
| 13 | | | | | | | | 91 | | 41 | 26 | |
| 14 | | | | | | 77 | 77 | | | | | |
| 15 | | | 3.0 | | | 110 | 110 | 112 | | 70 | | |
| 16 | | | | | | 137 | | | 97 | | 55 | |
| 17 | | | | | 34 | | 24 | | | 131 | | |
| 18 | | | | | | | 24 | | | | | 1.8 |
| 19 | | | 4.2 | | 49 | | | | | | | |
| 21 | | | | | 74 | | 42 | | | 162 | | |
| 22. | | | | | | | | 169 | | | | |
| 23 | | | 5.5 | | 111 | | | | | | | |
| 24 | | | | | | | 72 | | | | 89 | |
| 25 | | | | | 128 | | | | | | | |
| 26 | | | 11 | | | | | | | | | |
| 28 | | 2.1 | | | | | 80 | | | | | |
| 29 | | | 16 | | 149 | | | | | | | |
| 30 | | | | 12 | | | | | | | | |
| 32 | | | | | | | | | 144 | | | 2.7 |
| 33 | | | | | | | | | | 258 | | |
| 34 | | | | | | | | 223 | | | | |
| 35 | | 2.6 | | | | | 156 | 156 | | | | |
| 36 | | | 28 | | | | | | | | | |
| 37 | | | | | | | | | | | | |

TABLE XII (Continued)

Growth of Yeast in Medium E. A. Opp. for each Temp. B. Opt. for 30°

| Temp. | 0° | 10° | | 20° | | 30° | | 40° | | 42° | | 43° |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time | A | A | B | A | B | A | B | A | B | A | B | A |
| 38 | | | | | | | | | | | | 3.4 |
| 39 | | 42 | 18 | 224 | | 191 | 192 | | | 132 | | |
| 40 | | | | | | | | | | | | |
| 41 | | | | 174 | | | | | | 332 | | |
| 42 | | | | | | | | 188 | | | | |
| 43 | | | | | | 254 | 258 | | | | | 3.5 |
| 45 | | | | | | | | 395 | | | | |
| 46 | | | | | | 261 | | | | | | |
| 48 | 3.6 | | | 280 | | | 261 | | | | | |
| 50 | | | | 184 | | | | | | | | |
| 51 | | | | | | | | | | 139 | | |
| 52 | 3.8 | 105 | | | | | | | | | | |
| 54 | | | | | | 274 | | | | | | |
| 55 | | | 37 | | | | | | | | | |
| 56 | | | | | | | | 195 | 349 | | | |
| 58 | | | | | | | | 393 | | | | |
| 59 | | | | | | | 274 | | | | | |
| 60 | | | | | | | | | | | | |
| 62 | | 134 | | 283 | | | | | | | | |
| 63 | | | | | | | | | | 138 | | |
| 64 | 4.2 | | 67 | | | | | | | | | |
| 65 | | | | 205 | 270 | | | | | 345 | | |
| 68 | | | | | | | | 399 | | | | 3.4 |
| 69 | | | | | | | | | 196 | | | |
| 71 | | | | | | | 270 | | | | | |
| 72 | | | 69 | | | | | | | | | |
| 73 | | | | | | | | 398 | | | | |
| 75 | 4.1 | 137 | | 203 | | | | | 202 | | | |

The data above presented permit an analysis of three growth phases of yeast in various media at several temperatures. Buchanan[1] describes and discusses in detail seven growth phases in a culture of a microorganism.

1. Initial Stationary Phase during which the number of cells remains constant.

2. Lag Phase or Positive Growth Acceleration Phase in which the "average rate of increase in numbers per organism increases with the time".

3. The Logarithmic Growth Phase during which "the rate of increase per organism remains constant".

[1] Buchanan: J. Infect. Dis., 23, 109 (1918).

3. Phase of Negative Growth Acceleration in which "the rate of growth per organism decreases".

5. Maximum Stationary Phase during which "there is practically no increase in the numbers of organisms".

6. Phase of Accelerated Death in which the numbers of cells is "decreasing with increasing rapidity".

7. Logarithmic Death Phase during which the "rate of death per organism remains constant".

## The Logarithmic Growth Phase of Yeast in Several Media at Different Temperatures

During the logarithmic or maximum rate of growth the number of cells increases a certain fraction of itself each instant, that is if C = count

$$(1)\quad \frac{dC}{dt} = kC$$

$$(2)\quad \int_{C_1}^{C_2} \frac{dC}{C} = k \int_{t_1}^{t_2} dt$$

and

$$(3)\quad \log C_2 - \log C_1 = k(t_2 - t_1)$$

During this phase of growth the generation time, that is, the time required for one cell to become two will be:

$$(4)\quad \text{g.t.} = \frac{\log 2}{k}$$

From the growth data previously given values of k were obtained as the slope of the straight lines resulting from the graph of log 10 C plotted against time. The following discussion will deal then with the effect of temperature upon the value of *k* per various media. A summary of such values is given in Table XIII.

TABLE XIII

Values of *k* for Various Media at Different Temperatures

| Temperature | Wort No $NH_4Cl$ added | Wort 1st Optimum $NH_4Cl$ | Wort 2d Optimum $NH_4Cl$ | Medium E Optimum for 30° | Medium E Optimum for each Temperature |
|---|---|---|---|---|---|
| 0 | 0.0122 | 0.0453 | 0.0443 | | 0.0113 |
| 10 | 0.0430 | 0.1092 | 0.1068 | 0.0324 | 0.0405 |
| 20 | 0.1035 | 0.1780 | 0.1740 | 0.0777 | 0.0883 |
| 30 | 0.1686 | 0.2051 | 0.1992 | 0.1361 | 0.1361 |
| 40 | 0.1936 | 0.2005 | 0.1964 | 0.1316 | 0.1452 |
| 42 | 0.1923 | | | 0.1098 | 0.1239 |
| 43 | 0.0180 | | | 0.0143 | |

In Table XIV the values of $k$ for the various media are compared to that for wort as standard.

TABLE XIV

The Value of K for Various Media Where $K = \frac{k(\text{Medium Used})}{k(\text{Wort})}$

| Temperature | Wort 1st Optimum $NH_4Cl$ | Wort 2d Optimum $NH_4Cl$ | Medium E Optimum for 30° | Medium E Optimum for each Temperature |
|---|---|---|---|---|
| 0 | 3.71 | 3.63 | —— | 0.93 |
| 10 | 2.54 | 2.48 | 0.75 | 0.94 |
| 20 | 1.72 | 1.68 | 0.75 | 0.85 |
| 30 | 1.22 | 1.18 | 0.807 | 0.807 |
| 40 | 1.03 | 1.01 | 0.54 | 0.75 |
| 42 | —— | —— | 0.57 | 0.64 |
| 43 | —— | —— | —— | 0.79 |

The increase in growth rate in wort due to the addition of the optimum concentrations of the ammonium chloride is especially striking at the lower temperatures. The above points are shown clearly on the graphs in Fig. 1 where the values of $k$ are plotted against temperature.

With a rise in temperature the advantage of the salt decreases with practically no effect at 40°. The two optimum concentrations for the wort give practically identically results. In the synthetic medium again is seen the advantage of using the optimum concentrations for each temperature as compared to results obtained by use of a medium optimum for the one temperature of 30°.

## The Temperature Coefficients for the Growth of Yeast in Several Media at Various Temperatures

Using the values for $k$ found in Table X the temperature coefficients are calculated on the usual basis where $Q_{10} = k(t_1 + 10)/k(t_2)$. Values for $Q_{10}$ are listed in Table XVI. In the same table are listed values for "$\mu$" calculated from the van't Hoff equation as follows:

$$(5) \quad 2.303 \log \frac{K_0}{K_1} = \frac{\mu}{2}\left(\frac{T_1 - T_0}{T_1 T_0}\right)$$

In every instance through a range of 10-40 there is a smaller "spread" of values for $Q_{10}$ in cases where optimum conditions are maintained compared to values for unadjusted media. With wort the differences in value of $Q_{10}$ for adjusted and non-adjusted medium is greatest at the lower temperatures.

In Table XVII are found average values of $Q_{10}$ obtained by various investigators.

TABLE XVI

Values of $Q_{10}$ and of $\mu$ for Various Media

| Medium | $W_0$ | | $W_1$ | | $E_0$ | | $E_1$ | | Slator (6) | |
|---|---|---|---|---|---|---|---|---|---|---|
| Temperature | $Q_{10}$ | $\mu$ | $Q_{10}$ | $\mu$ | $Q_{10}$ | $\mu$ | $Q_{10}$ | $\mu$ | $Q_{10}$ | $\mu$ |
| 10 | 3.52 | 12,500 | 2.43 | 8,600 | | | 3.52 | 12,500 | 5.6 | 19,900 |
| 15 | | | | | | | (2.8) | 10,300 | 3.8 | 14,000 |
| 20 | 2.41 | 9,800 | 2.41 | 9,800 | 2.40 | 9,800 | 2.18 | 8,800 | 2.8 | 11,400 |
| 25 | | | | | | | (1.8) | 7,600 | 2.2 | 9,300 |
| 30 | 1.63 | 7,100 | 1.63 | 7,100 | 1.75 | 7,600 | 1.54 | 6,700 | 1.9 | 8,300 |
| 35 | | | | | | | (1.3) | 5,900 | 1.6 | 7,200 |
| 40 | 1.15 | 5,300 | 1.14 | 5,300 | 0.966 | 4,600 | 1.07 | 5,000 | (1.3) | 6,000 |
| 42 | 0.99 | 4,600 | 0.98 | 4,600 | 0.834 | 3,900 | 0.85 | 4,000 | | |
| 43 | 0.093 | | | | | | 0.115 | | | |
| $\Delta Q_{10}$ (10-40) | 2.53 | | 1.45 | | | | 2.67 | | 4.3 | |
| $\Delta Q_{10}$ (20-40) | 1.25 | | 1.26 | | 1.43 | | 1.11 | | 1.5 | |

$W_0$ = Wort without ammonium chloride
$W_1$ = Wort with optimum concentration of ammonium chloride
$E_0$ = Medium E optimum for 30°
$E_1$ = Medium E optimum for each temperature

## TABLE XVII

### Average Values of $Q_{10}$

| Investigator | | Temperature Range | Average $Q_{10}$ |
|---|---|---|---|
| Slator[1] | | 10-35 | 2.97 |
| Herzog[2] | | 14-28 | 2.88 |
| Aberson[3] | | 12-33 | 2.72 |
| Sherwood and Fulmer | $W_0$ | 10-40 | 2.18 |
| | $W_1$ | 10-40 | 1.90 |
| | $E_1$ | 10-40 | 2.05 |

$W_0$ = wort without ammonium chloride.
$W_1$ = wort with optimum concentration of ammonium chloride.
$E_1$ = medium E optimum for each temperature.

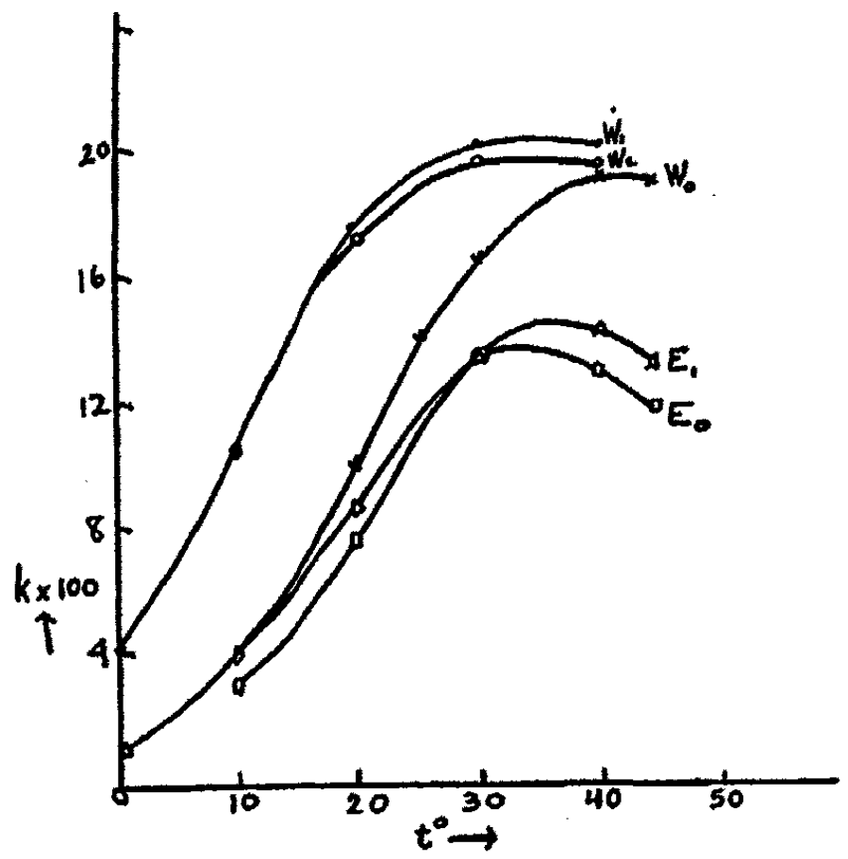



FIG. 1

An examination of this table shows the widely differing values for $Q_{10}$ obtained by various investigators of yeast growth. It is evident that the lowest average values obtained are typical of media whose composition has been adjusted in an appropriate manner for each temperature thus eliminating certain variables discussed in the Introduction.

[1] Slator: J. Chem. Soc., 89, 128 (1903).
[2] Herzog: Z. physik. Chim., 37, 149 (1902).
[3] Aberson: Rec. Trav. chim., 22, 78 (1903).

## The Phase of Negative Growth Acceleration and the Maximum Stationary Growth Phase of Yeast

In studies on temperature coefficients for the growth of yeast use has usually been made of the phase, the logarithmic phase. However environment may not influence the growth phases equally or even in the same direction. For example, with reference to the logarithmic phase and the Maximum Stationary Phase or "total crop" a change of environment may cause one of nine effects as follows:

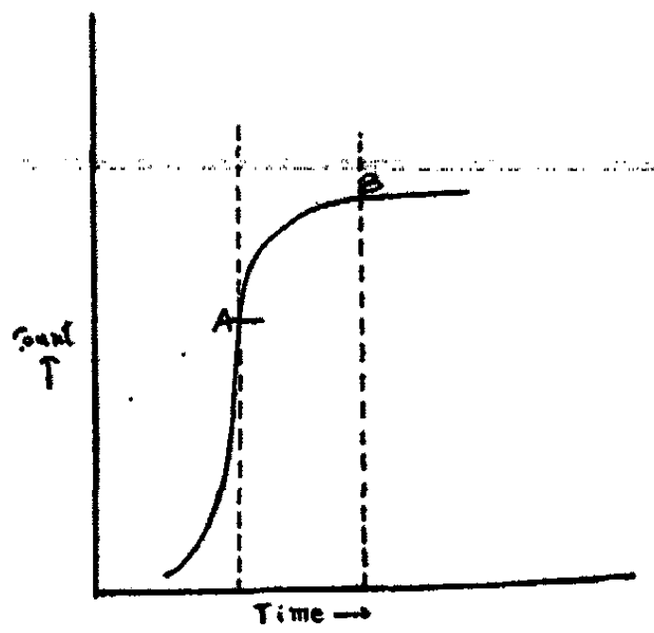



FIG. 2

TABLE XVIII

| Logarithmic Phase | Total Crop |
|---|---|
| I. Increase | No effect |
| II. Increase | Decrease |
| III. Increase | Increase |
| IV. Decrease | No effect |
| V. Decrease | Decrease |
| VI. Decrease | Increase |
| VII. No effect | No effect |
| VIII. No effect | Decrease |
| IX. No effect | Increase |

From the graphs of growth data given above a study may be made of the effect of ammonium chloride and of temperature upon the phase of negative growth acceleration and the total or maximum crop. The former phase is represented by the count at the inflection of the curve between the logarithmic phase and the maximum stationary phase, that is, the count at which the growth just ceases to be logarithmic. These points are designated on a typical curve on Fig. 2. Values for the above functions are given in Table XIX.

## TABLE XIX

### Maximum Crop and Critical Count for the Growth of Yeast in Various Media at Several Temperatures

| Medium | $W_0$ | | $W_1$ | | $W_2$ | | $E_0$ | | $E_1$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| Temp. | A | B | A | B | A | B | A | B | A | B |
| 0 | | | | | | | | | 4.2 | 4.2 |
| 10 | 102 | 161 | 153 | 246 | 133 | 212 | 37 | 69 | 105 | 137 |
| 20 | 290 | 1218 | 384 | 1442 | 342 | 1300 | 80 | 203 | 128 | 282 |
| 30 | 1245 | 1350 | 1437 | 1515 | 1300 | 1400 | 156 | 270 | 137 | 280 |
| 40 | 950 | 1555 | 1380 | 1710 | 1200 | 1560 | 97 | 202 | 223 | 394 |
| 42 | 450 | 622 | 600 | 665 | 525 | 660 | 89 | 138 | 131 | 343 |
| 43 | | | | | | | | | 3.3 | 3.4 |

A = Inflection count.
B = Total crop.
$W_0$ = Wort with $NH_4Cl$.
$W_1$ and $W_2$ = Wort with 1st and 2d optimum $NH_4Cl$.
$E_0$ = Medium E optimum for 30°.
$E_1$ = Medium E with optimum $NH_4Cl$.

The data show that the effect of the ammonium salt falls into class III given in Table XVIII that is the salt increases both the logarithmic growth rate and the total crop. It is also apparent that the salt leads to an increased count at the inflection point in the logarithmic curve. However, the figures given in Table XX show that the inflection count and the total crop are not increased equally. At 20° in all the media used with the possible exception of $E_1$ the phase of negative growth acceleration is more extended than at any other temperature. The maximum logarithmic growth rate, inflection count, and total crop occur at 40° for all the media used except Medium E optimum for 30°.

## TABLE XX

### Ratio of "Inflection Count" to "Total Crop", B/A

| Temp. | Medium $W_0$ | $W_1$ | $W_2$ | $E_0$ | $E_1$ |
|---|---|---|---|---|---|
| 10 | 1.6 | 1.6 | 1.6 | 1.8 | 1.3 |
| 20 | 4.6 | 3.8 | 3.8 | 2.5 | 2.2 |
| 30 | 1.1 | 1.1 | 1.1 | 1.7 | 2.0 |
| 40 | 1.6 | 1.2 | 1.3 | 2.1 | 1.8 |
| 42 | 1.4 | 1.1 | 1.2 | 1.6 | 2.6 |

## Summary

1. A detailed study has been made upon the growth of yeast at various temperatures in several media.

2. The optimal concentrations of ammonium chloride in the synthetic medium have been formulated.

3. Temperature coefficients for the growth of yeast were determined in media adjusted to optimum concentrations for each temperature and compared to those obtained in media not so adjusted.

4. A quantitative study was made of the phase of negative growth acceleration and the maximum stationary growth phase of yeast in several media at different temperatures.

# MECHANISM OF THE PHOTOCHEMICAL REACTION BETWEEN HYDROGEN AND CHLORINE. PART III. THE MEAN LIFE OF ACTIVITY IN ILLUMINATED CHLORINE*

BY ABRAHAM LINCOLN MARSHALL

It was suggested in Part I of this series of papers[1] that it might be possible to distinguish between the two types of mechanism which have been advanced to account for the photochemical reaction between hydrogen and chlorine by a re-investigation of the rate of decay of activity in illuminated chlorine. Chlorine atoms as postulated in the Nernst mechanism should have a relatively long life while excited chlorine molecules according to our present views might have a mean life period of the order of $(10)^{-6}$ sec.

Bodenstein and Taylor[2] investigated this problem and were unable to detect any enhanced reactivity in chlorine 0.00065 sec. after illumination. They illuminated chlorine with light from a 25 candle power Osram lamp placed 30 cm. from the reaction system. The chlorine after illumination was passed thru a bent capillary into a stream of hydrogen. The capillary was blackened to prevent light from reaching the mixed gases. The capillary used by them was of 0.3 mm. radius, 20 mm. long with a volume of 0.0065 cc.

Gohring[3] has analysed the results of Taylor and showed them to be consistent with the Nernst mechanism. The chlorine which they used was electrolytic and is assumed to contain 0.1 percent of oxygen. From this value Gohring calculates the concentration of atomic chlorine in the steady state to be $6.9(10)^{-13}$ mol-litre and the half life period as 0.00012 second. This would give rise in Taylor's experiments to an undetectable amount of hydrogen chloride.

Let E = radiation of frequency $\nu$ absorbed per second.
V = volume of the vessel.
$Z_{11}$ = number of impacts per second one chlorine atom makes with all the other chlorine atoms.
$Z_{12}$ = number of impacts per second one chlorine atom makes with oxygen molecules present in the gas.
$N_1$ = number of chlorine atoms—c.c.
$N_2$ = number of oxygen molecules—c.c.
$1/2N_1Z_{11}$ = total impacts between chlorine atoms per c.c.—second.

$$Z_{11} = kN_1$$

where $k = \Omega\pi\sigma_1^2\sqrt{2}$ and $\Omega_1$ = velocity of chlorine atoms.
$\sigma_1$ = diameter of chlorine atoms.

$$Z_{12} = k_1N_2$$

$$k = 2\sigma_{AB}^2\sqrt{\frac{m_1+m_2}{m_1m_2}\cdot 2\pi RT}$$

* Contribution from the Laboratory of Physical Chemistry, Princeton Univ.

[1] J. Phys. Chem., 29, 842 (1925).
[2] Z. Electrochem., 22, 202 (1916).
[3] Z. Electrochem., 27, 516 (1921).

$k_1N_1N_2$ = total impacts between atomic chlorine and oxygen. Gohring calculates $1.5(10)^{-8}$ of these impacts to be effective,

$$\text{then } \frac{dN_1}{dt} = 2\,\frac{E}{h\nu}\cdot\frac{1}{V} - N_1^2 - 1.5(10)^{-8}\,K_1N_1N_2$$

in the steady state—

$$2\,\frac{E}{h\nu}\cdot\frac{1}{V} = k\,N_1^2 + 1.5(10)^{-8}\,k_1N_1N_2$$

For the moment let us neglect the deactivation caused by impacts between chlorine atoms; then in the steady state—

$$2\,\frac{E}{h\nu}\cdot\frac{1}{V} = 1.5(10)^{-8}\,k_1N_1N_2$$

$$\bar{N}_1 = \frac{2E}{h\nu V k_1 N_2 \times 1.5(10)^{-8}}$$

= concentration of Cl in steady state.

The problem now is to calculate the concentration of Cl 1/1600 second after the illumination is cut off.

$$-\frac{dN_1}{dt} = 1.5(10)^{-8}\,k_1N_1N_2$$

$$\ln\frac{\bar{N}_1}{N_1} = 1.5(10)^{-8}\,k_1N_2t$$

$$k_1 = 2(2.55)^2(10)^{-16}\sqrt{\frac{67}{32\times 35}\times 82.15(10)^6\times 2\pi\times 300}$$

$$= 1.25(10)^{-10}$$

$$N_2 = 0.1 \text{ percent} = \frac{6(10)^{23}}{22{,}400\times 7{,}600} = 2.68(10)^{16}$$

$E = 10^{-3}$ g. cals.—sec.
$= 4.18(10)^4$ ergs.—sec.
$h\nu = 3.93(10)^{-12}$ ergs. for $\lambda = 500\mu\mu$.
$V = 200$ c.c.
$t = 1/1600$ sec.

$$\log N_1 = \log \frac{2\times 4.18(10)^4}{3.93(10)^{-12}\times 200\times 1.25(10)^{-10}\times 2.68(10)^{16}\times 1.5(10)^{-8}} - \frac{1.5(10)^{-8}\times 1.25(10)^{-10}\times 2.68(10)^{16}}{2.33\times 1600}$$

$$= 10.318 - 1.36$$

$$= 8.96$$

$N_1 = 9.1(10)^8$ atoms Cl—c.c.

If each atom is responsible for the formation of $10^6$ molecules of HCl

$N_{HCl} = 9.1(10)^{14}$ molecules = 0.0034 percent HCl

which is an undetectable amount under the experimental conditions of Bodenstein and Taylor.

Warburg[1] has also treated this problem neglecting the effect of oxygen and concludes that one should expect a considerable amount of hydrogen chloride to be formed. Assuming we are dealing with pure chlorine the concentration of atomic chlorine in the steady state is given by the equation $\bar{N}_1 = \sqrt{\frac{2E}{h\nu Vk}}$

the rate of decay of activity is $-\frac{dN_1}{dt} = kN_1^2$

and the concentration $N_1$ of atomic chlorine at time $t$ after illumination is given by $1/N_1 - 1/\bar{N}_1 = kt$

$$k = \Omega_1 \pi \sigma_1^2 \sqrt{2} = 14{,}500 \sqrt{\frac{300}{35}} \cdot \frac{22}{7} \cdot 4(10)^{-16}\sqrt{2} = 7.55(10)^{-11}$$

$$N_1 = \sqrt{\frac{2 \times 4.18(10)^4}{3.93(10)^{-12} \times 200k}} = \sqrt{1.41(10)^{24}} = 1.19(10)^{12}$$

$$1/N_1 = 4.7(10)^{-14} + 8.4(10)^{-13}$$

$N_1 = 1.1(10)^{12}$ atoms of chlorine

It will be observed that in this calculation practically none of the atomic chlorine has combined in 1/1600 second, and this on the assumption that every impact of chlorine atoms with one another leads to combination. From analogy with the observed results on the combination of atomic hydrogen and atomic bromine, one would only expect about one in every thousand impacts to be fruitful.

If the analysis given by Gohring and Warburg is correct it should be possible to obtain very considerable amounts of hydrogen chloride in an experiment of this nature provided pure chlorine free from inhibitors for the reaction is used and is subjected to intense illumination.

## Experimental

A diagram of the apparatus used is given in Fig. 1. The whole set up between the capillary *H* and the liquid air trap *C''* was so arranged that it could be surrounded by a furnace and heated to 300°-400°C. While the apparatus was being heated a stream of chlorine gas from an electrolytic generator was passed thru the apparatus. On several occasions the capillary *H* was cooled in liquid air to block it with solid chlorine and the whole set up was evacuated with a diffusion pump. This treatment was continued for several days to ensure the complete removal from the system of all impurities which were volatile or were capable of reacting with chlorine. In the subsequent experiments inhibitors of the type described by Chapman and Burgess[2] due to albuminous material on the walls of the vessel were absent. This procedure is an improvement over that previously used since it greatly

[1] Z. Electrochem., **27**, 139 (1921).
[2] J. Chem. Soc., **89**, 1399 (1906).

shortens the time necessary to clean up the apparatus and makes it more probable that a proper cleansing has been accomplished.

Only two stopcocks were used in the entire apparatus and these never came in contact with chlorine and were protected by liquid air traps from the rest of the system so that impurities from the grease used for lubrication might not diffuse into the carefully purified reaction system.

The capillary *B* thru which the chlorine gas was forced after illumination was made of a special ruby glass supplied by the Corning Company, which sealed directly to G702P glass of which the whole set-up was constructed. The capillary was constricted to the required diameter by a process of trial and error; the two capillaries used in this investigation were about 8 mm. long

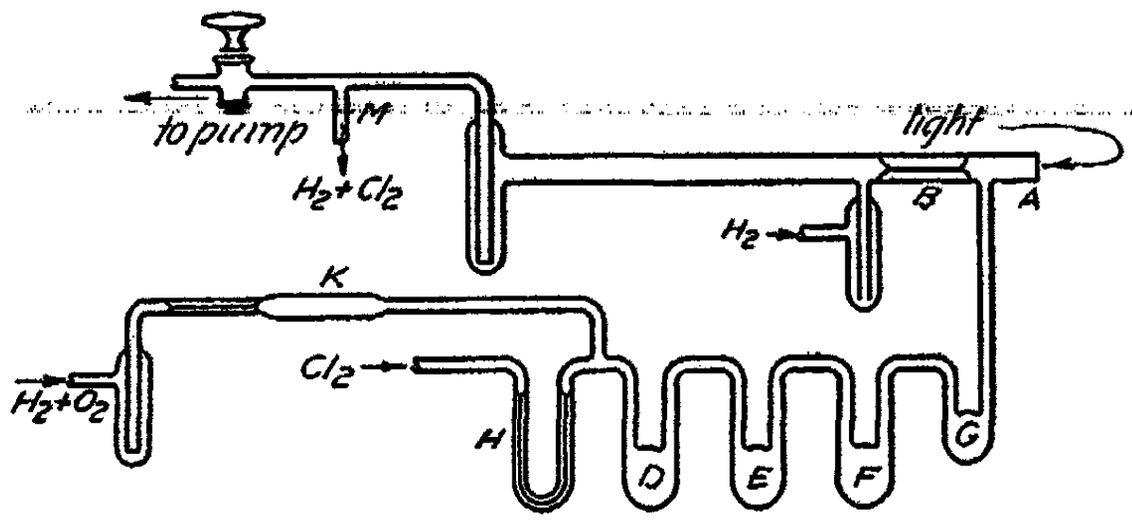



FIG. 1

and had volumes respectively of 0.00018 and 0.00034 cc. These volumes were determined by weighing the amount of mercury required to fill the capillary. The part *A* consisted of a quartz to glass graded seal with a quartz window at the end. The distance from the window to the capillary opening was 5 cm. An Hanovia quartz mercury arc was used as a source of illumination and was contained in a black box with a diaphragm attached with an opening the size of the window at *A*. The end of *A* was placed against the opening in the diaphragm, and the arc was 4 cm. from *A*. It consumed 3 amps. at 60 volts.

The whole apparatus on the hydrogen side of the capillary was painted black after the preliminary baking out process and the experiments were carried out in a darkened room free from all stray light.

The chlorine used was taken from a cylinder of electrolytic chlorine. It was washed with water and passed over heated glass powder to decompose any oxides of chlorine present. While collecting the chlorine in the container *D* the whole apparatus was evacuated the capillary *B* having been shunted by a glass by-pass which was later sealed off. The chlorine was condensed in liquid air any oxygen present being removed by the pump. After filling *D* the apparatus was sealed off at the capillary *H* from the source of chlorine; container *E* was cooled in liquid air and *D* with a $CO_2$-ether mixture and chlorine distilled into *E* in a high vacuum. Due to the poor heat exchange consequent on the high vacuum conditions the chlorine in *D* remained solid thruout the distillation. The first fraction of the distillate was collected. A similar dis-

tillation was made from *E* to *F*. The chlorine collected in *F* was kept in an ice bath which gave a chlorine pressure of 3.7 atmos. This pressure was used to drive the chlorine at a high rate of flow thru the capillary *B* after illumination. Electrolytic hydrogen was led in thru the liquid air trap C′ and the mixture of hydrogen and chlorine passed out at *M* into a solution of potassium iodide.

The chlorine as prepared above was exceedingly dry and it became necessary to moisten it. This was accomplished by first collecting some water in the container *G*, which was cooled in liquid air, before the chlorine was collected. The water was made by passing hydrogen containing some oxygen over a piece of heated quartz tubing *K* which was sealed into the apparatus with graded seals. The combustion was carried out at low pressures to avoid an explosion.

The protection given by the liquid air traps was necessary to prevent any contamination from entering the system after baking out; the traps were in the furnace in the preliminary heat treatment. During the experiments the water was kept at room temperature.

## Results

The first series of experiments was made with dry chlorine. Four experiments were made with chlorine flowing at a rate of 0.55 cc.—sec. corresponding to a time of 0.00033 sec. for passage thru the capillary. The iodine released by the chlorine was titrated with N/4 thiosulfate and methyl red was used as an indicator for the acid titration. All the solutions used were carefully neutralised before an experiment so that a drop of N/10 acid or alkali was sufficient to produce a marked change in the indicator. In these experiments the solution remained neutral and no trace of acid was found. The time of passage thru the capillary was decreased to 0.00020 sec. by increasing the chlorine temperature to 20°C. Still no acid was detected.

It was then decided to wet the chlorine before illumination. A series of experiments with moist chlorine passing thru the capillary into hydrogen 0.00030 sec. after illumination produced no detectable amount of hydrogen chloride.

These results with pure chlorine were entirely unexpected in the light of the previous discussion and might lead one to conclude that the Nernst mechanism, on which that analysis was based, was incorrect. The effect of the glass walls has however not been considered and it is quite possible that these may be catalysing the recombination of the chlorine atoms. It will apparently be necessary to resort to some other method of experimentation to settle this point. The author has suggested a method of attack[1] involving a quantitative study of the rate of reaction at low pressures and being a continuation of previous work[2]. If the mechanism involves chlorine atoms it

[1] Trans. Am. Electrochem. Soc., Spring Meeting (1926).
[2] J. Phys. Chem., 29, 1453 (1926).

should be possible to calculate the rate of reaction as a function of the pressure from a knowledge of the quanta absorbed and the rate of diffusion of the atoms to the surface of the container where they are removed from the system.


## Summary

The experiments of Bodenstein and Taylor on the mean life of reactivity in illuminated chlorine have been repeated using an improved technique. Pure chlorine was used and passed into hydrogen $3(10)^{-4}$ sec. after intense illumination by a quartz mercury arc. *No reactivity was detectable.*

This result was directly contrary to a mathematical analysis based on the Nernst atomic mechanism which predicted a large reaction. Only two possibilities seem to arise: either this mechanism is incorrect and it is necessary to assume a mechanism involving excited chlorine molecules, or the walls of the capillary remove the chlorine atoms by causing their recombination. Further experimentation is necessary to reach a decision and a possible method of attack is pointed out.


*Princeton, N. J.*

# A STUDY OF THE PRECIPITATION OF MASTIC SUSPENSOIDS*

BY H. V. TARTAR AND CARL Z. DRAVES

## Introduction

None of the generalizations dealing with the precipitation of colloids by electrolytes, have been reduced to exact quantitative form. It has long been known that two of the primary factors which determine the precipitation of a colloid of the suspensoid type (hydrophobic colloid) are the concentration and the valence of the ion of the electrolyte in solution which has an electric charge opposite in sign to that of the colloidal particles. Although there is abundant evidence in the literature that hydrogen and hydroxyl ions may be strongly adsorbed but scant consideration has been given, in work dealing with the precipitation of colloids, to the full effect of these ions.

Michaelis and Timenez-Diaz[1] have pointed out very clearly that the concentration of hydrogen-ion (or hydroxyl-ion) may be quite as important in its effect as that of the ions of the added electrolyte. For example, they found that the concentration of potassium salt just sufficient to precipitate a negative suspensoid varies widely with the hydrogen-ion concentration of the dispersion medium. Michaelis and his coworkers[2] used negative suspensoids for which the minimal concentration of the salt required for precipitation at a given Sörensen value (pH) is but slightly affected by the character of the negative ion from the added electrolyte. This permitted the use of Sörensen buffer solutions for effecting precipitation at varying hydrogen-ion concentrations. The results of this work, using congo red and colloidal mastic, showed that the relationship between hydrogen-ion concentration and salt concentrations was represented approximately by the following equation for an equilateral hyperbola:

$$\left[\log \frac{(H_o^+)}{(H^+)}\right] \left[\log \frac{(i_o)}{(i)}\right] = K$$

in which (i) represents the salt concentration which is just sufficient to cause precipitation and $(H^+)$ the simultaneous value of the hydrogen-ion concentration in the same experiment. $(H_o^+)$ is a constant which is equal to the hydrogen-ion when precipitation is effected with hydrochloric acid alone; while $(i_o)$ is the limiting value of the salt concentration necessary for precipitation as the solution is made more and more alkaline; K is a constant which must be determined from the experimental values. This equation expresses the fact that the concentration of salt required for precipitation increases rapidly with decrease in the hydrogen-ion concentration of the dispersion medium.

---

* Contribution from the Chemical Laboratory, University of Washington.

[1] Michaelis and Timenez-Diaz: Kolloid-Z., 29, 181 (1921).

[2] Michaelis and Timenez-Diaz: Kolloid-Z., 29, 181 (1921); Michaelis and Hirabayashi: 30, 209 (1922).

Tartar and Gailey[1], in a preliminary paper, found that for the negative suspensoids, mastic and gamboge, widely varying concentrations of salts yielding the same cation but different anion were required for precipitation; also that the variation in hydrogen-ion concentration, due to hydrolysis of the salts used, was as great as the variation of the salt concentrations. On the other hand, when the experiments were made using the same concentrations of the different salts as was required for potassium chloride alone, together with a sufficient amount of the acid with anion corresponding to that of the salt employed, all the precipitations occurred at approximately the same Sörensen value (pH).

Tartar and Gailey also found that different common acids when used alone produced precipitation of mastic or gamboge at the same hydrogen-ion concentration regardless of the valence of the anion. The data of Michaelis and Hirabayashi[2] also showed that with either acids alone or mixtures of salts and acids, the anion (with the exception of the sulfosalicylate-ion which is very antagonistic) has only a slight effect on the precipitation of congo red and mastic suspensoids.

In each investigation referred to above on the precipitation of colloidal mastic, the conditions were simplified and made uniform by using a carefully prepared sol. As yet, no satisfactory study has been made of the effects of using different samples of the gum, of varying the concentration or dispersity of the sols, on the precipitation with electrolytes at different hydrogen-ion concentrations. Neisser and Friedemann[3] "showed that the precipitation value of salts with univalent cations is less the more concentrated the emulsion (mastic) while with divalent and trivalent cations the precipitation value decreases slightly as the concentration of colloid decreases". Bechhold[4] found that the rate of precipitation of mastic with electrolytes depends, within certain limits, upon the concentration of the sol. Odén[5], in attempting to separate colloidal mastic particles of varying size by fractional precipitation, investigated the effect of particle size on the critical concentration of electrolyte for precipitation and was unable to prove that there was a relationship of particle size to precipitation. Burton and Bishop[6] enunciated the rule as a result of their experiments on the effect of the dilution of mastic sol that "for univalent ions the concentration of ion necessary to produce coagulation increases with decreasing concentration, this increase being very rapid with low concentrations of colloid". In all these investigations by different workers, however, the marked influence of the hydrogen-ion concentration of the dispersion medium was not taken into consideration.

---

[1] Tartar and Gailey: J. Am. Chem. Soc., **44**, 2212 (1922).

[2] Michaelis and Hirabayashi: Kolloid-Z., **30**, 209 (1922).

[3] Neisser and Friedemann: München med. Wochenschr., **51**, 827 (1904); cf. Weiser and Nicholas: J. Phys. Chem., **25**, 743 (1921).

[4] Bechhold: Z. physik. Chem., **48**, 385 (1904).

[5] Odén: Z. physik. Chem., **78**, 682 (1912).

[6] Burton and Bishop: J. Phys. Chem., **24**, 701 (1920).

The purpose of the work presented in this paper was to determine the effect of varying dispersity, of concentration and of variety of mastic on the concentration of potassium chloride required for precipitation of mastic suspensions at varying concentrations of hydrogen-ion. The work of Michaelis and his coworkers had already shown conclusively a reciprocal relation of hydrogen-ion concentration and salt concentration in the precipitation of a given sol. The results of their work render valueless the conclusions of so many papers dealing with precipitation in which the effect of hydrogen-ion concentration has been neglected and also are so far reaching in the development of a more complete knowledge of the precipitation of colloids by electrolytes, that it seemed very necessary that their work be subjected to verification and be extended considerably in its scope. Because of lack of time the work was limited to precipitation with a single electrolyte. The authors believed it better to make a thorough study with one precipitating agent than to use several and be obliged to otherwise limit the extent of the investigation.

## Experimental Part

### *Preparation of Colloids*

Twenty per cent solutions in neutral alcohol of two different varieties of gum mastic, one a powdered sample (Merck's) and the other a sample of the tears of the original gum, were allowed to settle until clear. Each sol was prepared in the usual manner by allowing the alcoholic solution to run slowly into water from a burette with a capillary tip which was held under the surface while the mixture was constantly and rapidly stirred. Variation in the degree of dispersity of the sols was sought by regulating the rate of flow of the alcoholic solution into the water; the time required for the flow of one cc. of the alcoholic solution through the capillary tip was varied from 12 to 85 seconds. The suspensions were permitted to stand for at least four weeks. Then the upper portion to within four cm. of the bottom of the container was siphoned off and transferred to well-seasoned bottles for use. Thereafter the sols were always well shaken before sampling. A very little chloroform was added to each sol to inhibit the growth of mold. Later the total concentrations of the mastic in grams per liter was determined by evaporation to constant weight at 105°.

Data descriptive of the different samples of mastic suspensoid employed are given in Table I. Those prepared from Merck's powdered mastic and designated as 1M to 4M inclusive were of a very light cream color. The others marked from 5T to 15T inclusive which were prepared from gum mastic tears, were milky white in color. The Sörensen values (pH) of the different sols have also been included in the table; they will be discussed in a later portion of this paper.

### *Precipitation with Potassium Chloride alone*

In all cases the method of effecting precipitation and the decision as to completeness of precipitation were the same. The precipitating agent diluted with distilled water in a large test tube to 20 cc., was poured rapidly into 20 cc.

TABLE I

Preparation of Mastic Suspensoids

| Sol. No. | Mastic per liter (G.) | Alcohol Content per liter of sol (cc.) | Rate of Addition of Alcoholic Mastic (Seconds per cc.) | pH of Sol |
|---|---|---|---|---|
| 1M | 5.738 | 50 | 30 | |
| 2M | 3.490 | 25 | 85 | 3.60 |
| 3M | 3.148 | 25 | 77 | 3.65 |
| 4M | 2.486 | 25 | 30 | —— |
| 5T | 3.074 | 25 | 36 | 4.08 |
| 6T | 3.026 | 25 | 52 | —— |
| 7T | 2.752 | 25 | 18 | —— |
| 8T | 2.945 | 25 | 12 | —— |
| 9T | 0.783 | 6.3 | 46 | —— |
| 10T | 1.562 | 12.5 | 50 | —— |
| 11T | 6.317 | 50 | 46 | 3.87 |
| 12T | 2.352 | 25 | 85 | 3.91 |
| 13T | 11.406 | 100 | 38 | 3.47 |
| 14T | 3.048 | 25 | 46 | 3.92 |
| 15T | | 55 | 46 | 3.84 |

of the colloid contained in another tube. After pouring back and forth 6 times to insure complete mixing the mixture was set aside in a thermostat at 25° for 24 hours and then examined. If completeness of coagulation was doubtful because of the non-settling of the mastic coagulum the content of the tube was centrifuged for 15 minutes in an International Centrifuge No. 1 at 2500 r.p.m. When the supernatant liquid after centrifuging appeared very clear and not opalescent, precipitation was deemed complete. After some preliminary tests, the minimal concentration for precipitation was determined from a series of four mixtures of each sol with the precipitating agent in which the concentration of the latter varied from tube to tube by 5 to 8 per cent. Each of these final series was duplicated at least once.

The potassium chloride used for precipitation was prepared from recrystallized C.P. salt except for the precipitation in alkalin solution for which a commercial C.P. product was employed. The water used throughout this investigation was distilled water which in this laboratory, has a specific conductivity of always less than $2 \times 10^{-6}$ reciprocal ohms.

Hydrogen-ion concentrations of the suspension medium in the presence of the coagulum at the minimal precipitation concentrations were determined electrometrically on larger samples of the mixtures which had stood the usual 24 hours. It was repeatedly demonstrated that it was not necessary to remove the coagulum from the suspension medium by centrifuging before determining the pH. This confims the findings of Michaelis and Hirabayashi[1]. E.M.F.

[1] Michaelis and Hirabayashi: Kolloid-Z., 30, 209 (1922).

measurements were all conducted in an air thermostat at 25°. Two hydrogen electrodes opposed to two different volume normal calomel electrodes with normal potassium chloride bridges were employed in each determination. For those mixtures in which the concentration of potassium chloride was greater than normal, the mixture itself was used in the bridge vessel. Sörensen values were calculated from the formula:

$$pH = \frac{\text{Observed E.M.F.} - 0.2848}{0.05911}$$

The data from the precipitations with potassium chloride alone are given in Table II. The concentrations are expressed in milliequivalents per liter of the mixture of precipitating agent and sol. For convenience in presenting later the results in graphical form, values are given for the logarithm of the reciprocal of the concentration of potassium chloride in mols per liter, $\log_{10} 1/KCl$. Dilutions of sols 1M and 11T to two, four and eight times the original volume of the sol, were also precipitated, the dilution indicated in the table being that of the sol before admixture with the precipitating agent.

TABLE II

Potassium Chloride and Hydrogen-Ion Concentrations in the Coagulation of Mastic Suspensoids with Potassium Chloride alone

| Sol No. | Dilution of sol before mixing (times original volume) | Potassium Chloride, (milli-equivalents per liter) | $\log_{10} 1/(KCl)$ | pH |
|---|---|---|---|---|
| 1M | 1 | 46 | 1.33 | 3.54 |
| 1M | 2 | 65 | 1.19 | 3.75 |
| 1M | 4 | 93 | 1.03 | 4.01 |
| 1M | 8 | 115 | 0.94 | 4.23 |
| 2M | 1 | 68 | 1.17 | 3.77 |
| 3M | 1 | 68 | 1.17 | 3.77 |
| 4M | 1 | 58 | 1.24 | 3.72 |
| 5T | 1 | 95 | 1.02 | 4.31 |
| 6T | 1 | 70 | 1.15 | 4.11 |
| 7T | 1 | 90 | 1.05 | 4.19 |
| 8T | 1 | 93 | 1.03 | 4.23 |
| 9T | 1 | 148 | 0.83 | 4.82 |
| 10T | 1 | 140 | 0.85 | 4.55 |
| 11T | 1 | 73 | 1.14 | 3.99 |
| 11T | 2 | 95 | 1.02 | 4.25 |
| 11T | 4 | 154 | 0.81 | 4.51 |
| 11T | 8 | 295 | 0.53 | 5.00 |
| 12T | 1 | 70 | 1.15 | 4.13 |
| 13T | 1 | 34 | 1.47 | 3.58 |
| 14T | 1 | 90 | 1.05 | 4.33 |
| 15T | 1 | 70 | 1.15 | 3.95 |

*Variation in the Natural Acidity of Mastic Sols*

The data of Table II showed that the mastic sols had different pH values after precipitation even though they had all been treated in the same manner with the neutral, unhydrolyzed salt, potassium chloride. Comparison with the pH values of the sols alone recorded in Table I made it evident that approximately these same differences in the acidity of the sols existed before precipitation as afterward. Because of the low conductivity of the mastic sols when unmixed with electrolyte, the electrometric determinations were not more accurate than to within 0.03 pH.

Not only did the same differences of acidity exist before and after precipitation but the process of precipitation was attended by no great change in acidity. The variation of the pH of three sols was determined both with amounts of salt insufficient and with amounts in excess of that necessary for complete precipitation. To avoid the change of pH involved in dilution, solid potassium chloride was used in each experiment. The data of Table III show that the increase in acidity upon the addition of less than the precipitating concentration of unhydrolyzed salt was less than that equivalent to 0.1 unit of pH. The addition of amounts of potassium chloride larger than necessary for precipitation was accompanied by a further decrease of less than 0.03 units of pH. Although the conductivity of the sol alone was too low to give satisfying accuracy in the determination of the pH of the suspension medium in the absence of salt, there was indicated in each instance a slight but definite increase in acidity, the greatest change occurring upon the addition of the first small amount of potassium chloride. This may have some significance. That there is no marked liberation of hydrogen or hydroxyl ions in the precipitation of suspensoids has likewise been observed by Pauli and Matula[1] and by Browne[2] working with ferric oxide sols.

TABLE III

Change of pH of Mastic Suspensoids upon Addition of Solid KCl

| Sol No. | solid KCl per 100 cc. sol (grams) | pH | Sol No. | solid KCl per 100 cc. sol (grams) | pH |
|---|---|---|---|---|---|
| 3M | 0.0 | 3.65 | 5T | 0.0 | 4.08 |
| | 0.1 | 3.56 | | 0.1 | 4.02 |
| | 1.0 | 3.57 | | 0.2 | 4.03 |
| | 1.0 | 3.56 | | 0.5 | 4.02 |
| 11T | 0.0 | 3.87 | | 1.0 | 4.03 |
| | 0.1 | 3.83 | | 1.0 | 4.02 |
| | 1.0 | 3.80 | | 2.0 | 3.99 |

[1] Pauli and Matula: Kolloid-Z., 21, 49 (1917).

[2] Browne: J. Am. Chem. Soc., 45, 311 (1923).

Because of the great importance of acidity at precipitation, it also became necessary to investigate the differences in the acidity of the different mastic suspensoids and even to learn the source of the acidity in order to gain a more complete knowledge of the conditions governing their precipitation. Observations made from the processes of ultrafiltration and dialysis proved that the hydrogen-ion concentration of a mastic suspensoid is due principally, within the limit of experimental error, to organic acid in true solution in the suspension medium. Four of the sols were slowly ultrafiltered under a hydrostatic head of three meters through a paper extraction thimble which had been heavily treated with collodion and then soaked in distilled water for two days. The ultrafiltrate was clear to the eye and gave only a faint Tyndall beam. Electrometric determinations were made of the hydrogen-ion concentrations; also of the total available hydrogen-ion by titration with dilute sodium hydroxide using phenolphthalein as indicator. The data are recorded in Table IV and show that in each instance the ultrafiltrate does not apparently contain so great a concentration of hydrogen-ions as the sol itself. Such a condition might be expected from the principle of Donnan membrane equilibrium. A comparison of the electrometrically determined hydrogen-ion concentration with the total available hydrogen-ion ascertained by titration indicates that from 11 to 25 per cent of the acid in the ultrafiltrate was ionized. The residue obtained by evaporation showed that approximately 4 per cent of the gum mastic of the mastic suspensoid was in true solution. The equivalent weight[1] of this residue was very roughly about 400. When the residue from the ultrafiltrate was again dissolved in a small amount of alcohol and the solution then poured into water a colloidal suspension was obtained which closely resembled in appearance the original mastic sol.

TABLE IV

Acidity of Ultrafiltrates from Mastic Suspensoids

| Sol | pH of sol | pH ultrafiltrate | Hydrogen-ion concentration of ultrafiltrate | | Grams residue per liter ultrafiltrate | Equivalent weight of residue |
|---|---|---|---|---|---|---|
| | | | Electrometric | Total Acidity (titrated) | | |
| 5T | 4.08 | 4.48 | $0.33 \times 10^{-4}$ | $2.0 \times 10^{-4}$ | 0.09 | 440 |
| 11T | 3.87 | 4.06 | $0.87 \times 10^{-4}$ | $5.3 \times 10^{-4}$ | 0.26 | 490 |
| 14T | 3.92 | 4.06 | $0.87 \times 10^{-4}$ | $7.6 \times 10^{-4}$ | 0.19 | 250 |
| 15T | 3.84 | 4.11 | $0.78 \times 10^{-4}$ | $3.0 \times 10^{-4}$ | 0.12 | 400 |

An unsuccessful attempt was made to find whether the amount of acid in true solution varied with the alcohol content of the sol. To this end sols 14T and 15T were both made from the same original sol by dilution, sol 14T with pure water and sol 15T with alcohol and water such that the final alcohol

[1] Tschirch and Reutter (Arch. Pharm. 242, 104 (1888); see also Tschirch: "Die Harze und die Hartzbehälter", 1, 468 (1906)) have found gum mastic to contain: $\alpha$ and $\beta$ masticic acids ($C_{22}H_{36}O_4$; mol. wt. = 376.3) — 4.0%. Masticolic acid ($C_{22}H_{36}O_4$; mol. wt. = 376.3) — 0.5%. $\alpha$ and $\beta$ masticonic acids ($C_{32}H_{58}O_4$; mol. wt. = 490.6) — 38.0%. $\alpha$ mastic resin ($C_{35}H_{56}O_4$) — 31.0%. These constituents are soluble in alcohol and the acids are monobasic.

content of 15T was more than twice that of 14T. Otherwise these two sols were absolutely identical. The hydrogen-ion concentration was slightly greater in 15T, the one with the greater alcohol content; but in the ultrafiltrate the order was reversed. Either the accuracy of the work was not sufficiently great to bring out any consistent difference, or else, as will be shown later in another manner, the percentage of alcohol within these lower limits is without marked effect on the hydrogen-ion concentration of a mastic sol.

Dialytic experiments also showed that the acidity of the mastic sols was due principally to organic acid (or acids) in true solution. A collodion sack filled with distilled water at room temperature was placed in a liter of mastic sol. The level of water in the sack was kept constant with a constant level siphon. Distilled water flowed freely through a capillary tube into the sack at the rate of 1 liter in twelve hours. The total volume of the dialysate was twenty liters. This arrangement was essentially that employed by Neidle[1] for hot dialysis. The first of the dialysate contained about 16 mg. of dissolved material per liter while the last contained perhaps less than 1.0 mg. per liter. The acidity of the dialysate distinctly decreased during the dialysis as shown with the methyl red indicator. Sol 5T gave an electrometric pH of 4.08 before dialysis but after dialysis the acidity had decreased to a value corresponding to a pH of 5.7. Since the conductivity of the sol largely decreased during dialysis it became increasingly difficult to determine electrometrically the Sörensen value with satisfactory accuracy. However, the values here were checked roughly with indicators. One portion of sol 5T after dialysis was diluted with carefully prepared neutral alcohol and water to an alcohol content of 25 cc. per liter and another portion to an alcohol content of 50 cc. per liter. During the next few days the pH values of the first portion were 4.87, 4.88 and 4.7. A dilution of the original sol itself with an equal volume of water gave a pH value of 4.37. The portion of dialyzed sol diluted with the double quantity of alcohol gave pH values of 4.9, 4.8, and 4.5. These figures show that although the presence of the alcohol distinctly increased the acidity of the dialyzed sol, there was no marked difference between the effects of 2.5% and 5% alcohol. The pH value of sol 11T was determined after dialysis and dilution with an equal volume of water and found to be 5.7. But upon dilution of the dialyzed sol with alcohol and water to an alcohol content of approximately 25 cc. per liter, a pH of 4.7 was obtained. The original sol 11T itself before dialysis gave a pH value of 3.87 while a dilution of two gave a pH value of 4.08.

The effect of dilution of distilled water upon the acidity of the suspensoids was determined. Sols 12T, 13T and 16T were diluted by two, four and eight times the original volumes and the hydrogen-ion concentrations then measured. The data are recorded in Table V.

[1] Neidle: J. Am. Chem. Soc., **38**, 1270 (1916).

TABLE V

Decrease of Acidity of Mastic Suspensoids with Dilution

| Sol | Dilution | Sörensen value (electrometric) pH | Concentration of hydrogen-ion (mols per liter) |
|---|---|---|---|
| 12T | 1 | 3.91 | $12.5 \times 10^{-6}$ |
| | 2 | 4.20 | 6.3 |
| | 4 | 4.49 | 3.25 |
| | 8 | 4.89 | 1.3 |
| 13T | 1 | 3.47 | 34.0 |
| | 2 | 3.67 | 21.5 |
| | 4 | 3.87 | 13.5 |
| | 8 | 4.10 | 8.0 |
| 16T | 1 | 4.25 | 5.65 |
| | 2 | 4.43 | 3.7 |
| | 3 | 4.57 | 2.7 |
| | 4 | 4.75 | 1.7 |
| | 5 | 4.85 | 1.4 |
| | 6 | 5.06 | 0.87 |

The decrease in hydrogen-ion concentration, or increase of pH, was nearly proportional to the amount of dilution. The experiments on the precipitation of the diluted sols with potassium chloride (see Table II) also showed nearly the same rate of decrease of hydrogen-ion concentration, namely about 0.25 unit of pH for each halving of the concentration.

*Coagulation of Mastic Suspensoids in Acid and Basic Solution with Potassium Chloride*

In order to cover a wide range of pH in this work, precipitations were conducted with hydrochloric acid alone, with hydrochloric acid and potassium chloride, and with potassium chloride and potassium hydroxide, using sols which differed widely in concentration and with dilutions of two and four times the volume of one sol of each variety. In these experiments the methods outlined for the precipitations with potassium chloride alone were followed. The data are recorded in Tables VI, VII and VIII. The electrometric determinations of pH were very satisfactory except those conducted in neutral or basic solution the values for which are given in Table VIII. The e.m.f. of the chain in these latter determinations rose rapidly in about ten minutes to a maximum and then decreased. Since the pH indicated by the maximum e.m.f. corresponded to the pH obtained with indicators, it was assumed to be approximately correct. The irregular behaviour of the hydrogen electrode in the pH range beyond 6.0 in solutions which are not well buffered is to be expected according to the timely work of Beans and Hammett[1].

[1] Beans and Hammett: J. Am. Chem. Soc., 47, 1215 (1925).

TABLE VI

Coagulation of Mastic Suspensoids with Hydrochloric Acid alone

| Sol | Dilution of sol before mixing (times original volume) | HCl, milli-equivalents per liter mixture | Hydrogen-ion, milli-equivalents per liter | pH |
|---|---|---|---|---|
| 1M | 1 | 6.60 | 5.89 | 2.23 |
| | 2 | 6.60 | 5.89 | 2.23 |
| | 4 | 6.49 | 5.62 | 2.25 |
| 2M | 1 | 8.06 | 6.76 | 2.17 |
| 5T | 1 | 4.92 | 4.37 | 2.36 |
| 9T | 1 | 3.77 | 3.31 | 2.48 |
| 10T | 1 | 4.50 | 3.98 | 2.40 |
| 11T | 1 | 4.16 | 3.55 | 2.45 |
| | 2 | 4.40 | 3.98 | 2.40 |
| | 4 | 4.19 | 3.89 | 2.41 |

TABLE VII

Coagulation of Mastic Suspensoids with Hydrochloric Acid in Addition to Potassium Chloride

| Sol | Dilution of sol before mixing (times original volume) | HCl, Milli-equivalents per liter mixture | pH, electrometric | $\text{Log}_{10}\frac{1}{(KCl)}$ |
|---|---|---|---|---|
| 1M | 1 | 1.26 | 2.87 | 1.70 |
| | 2 | 1.26 | 2.90 | 1.70 |
| | 4 | 1.41 | 2.87 | 1.70 |
| 2M | 1 | 1.62 | 2.81 | 1.70 |
| 5T | 1 | 6.60 | 2.25 | 1.70 |
| 9T | 1 | 0.73 | 3.18 | 1.70 |
| 11T | 1 | 0.63 | 3.22 | 1.70 |
| | 2 | 0.73 | 3.16 | 1.70 |
| | 4 | 0.84 | 3.11 | 1.70 |
| 2M | 1 | 3.93 | 2.43 | 2.0 |
| | 2 | 3.93 | 2.44 | 2.0 |
| 11T | 1 | 2.20 | 2.69 | 2.0 |
| 11T | 2 | 2.41 | 2.66 | 2.0 |

Note: The concentration of potassium chloride in the mixture was 20 milli-equivalents per liter in the one set of experiments and 10 milli-equivalents per liter in the other set of experiments.

TABLE VIII

Coagulation of Mastic Suspensoids with Potassium Chloride and Potassium Hydroxide

| Sol | Dilution of sol before mixing (times original volume) | KCl, milli-equivalents per liter mixture | pH, electrometric | Log $\frac{1}{(KCl + KOH)}$ |
|---|---|---|---|---|
| 1M | 1 | 1310 | | −0.12 |
| | 2 | 1925 | 7.4 | −0.28 |
| | 4 | 2100 | 7.7 | −0.32 |
| 2M | 1 | 1575 | 7.6 | −0.20 |
| 5T | 1 | 1660 | 9.7 | −0.22 |
| 9T | 1 | 1575 | 10.3 | −0.20 |
| 11T | 1 | 1490 | 8.5 | −0.17 |
| | 2 | 1400 | 9.16 | −0.15 |
| | 4 | 1400 | | −0.15 |

Note: The concentration of potassium hydroxide in the mixture was 0.92 milli-equivalents per liter in each case.

## Discussion of Results and Conclusions

The importance emphasized by Michaelis and his coworkers of hydrogen-ion concentration in the study of the precipitation of mastic suspensoids has been more than justified by the results of the experimental work presented in this paper. The data show a reciprocal relation between pH and log 1/(KCl), namely, the greater the hydrogen-ion concentration the less potassium chloride is required for precipitation.

The first purpose of this research was to determine the effect of variation of dispersity, of concentration, and of kind of mastic on coagulation. Of these only the last, the variety of mastic, has a definite influence per se, on precipitation. The dispersity and concentration of the sol apparently affect coagulation only indirectly through their effect on the hydrogen-ion concentration of the sol itself.

The concentration and dispersity of the sol do have an influence upon the acidity of the dispersion medium of the sol. A consideration of the data will bring out that in general the greater the concentration of the suspensoid the greater is the hydrogen-ion concentration of the sol in the absence of added electrolyte. Further, the hydrogen-ion concentration increases with the slowness with which the alcoholic mastic is stirred into water in the preparation of the sol. The actual dispersity of the sols was not quantitatively determined. But undoubtedly the average dispersity of the different samples varied with the rate of formation of the sols. When it is remembered that the acidity of mastic suspensoids is due principally to organic acid in true solution it would be expected that the amount of acid going into true solution would be effected by the amount and rate of addition of alcoholic mastic to water. It might also be expected that the amount of acid in true solution would be greatly

increased with increase in the alcohol content. The addition of dilute alcohol was found to largely increase the acidity of a sol from which the alcohol and acid had been previously dialyzed. However, the addition of twice the concentration of alcohol did not have a much greater effect. It should be again emphasized that the concentration of potassium chloride alone required to coagulate any mastic suspensoid varies with the dispersity and concentration of the sol simply because the pH of the dispersion medium is dependent upon the concentration and dispersity, or manner of preparation.

From the work presented above it is evident that any study of the effect of dilution upon the precipitation (with a univalent ion) of mastic which dis-

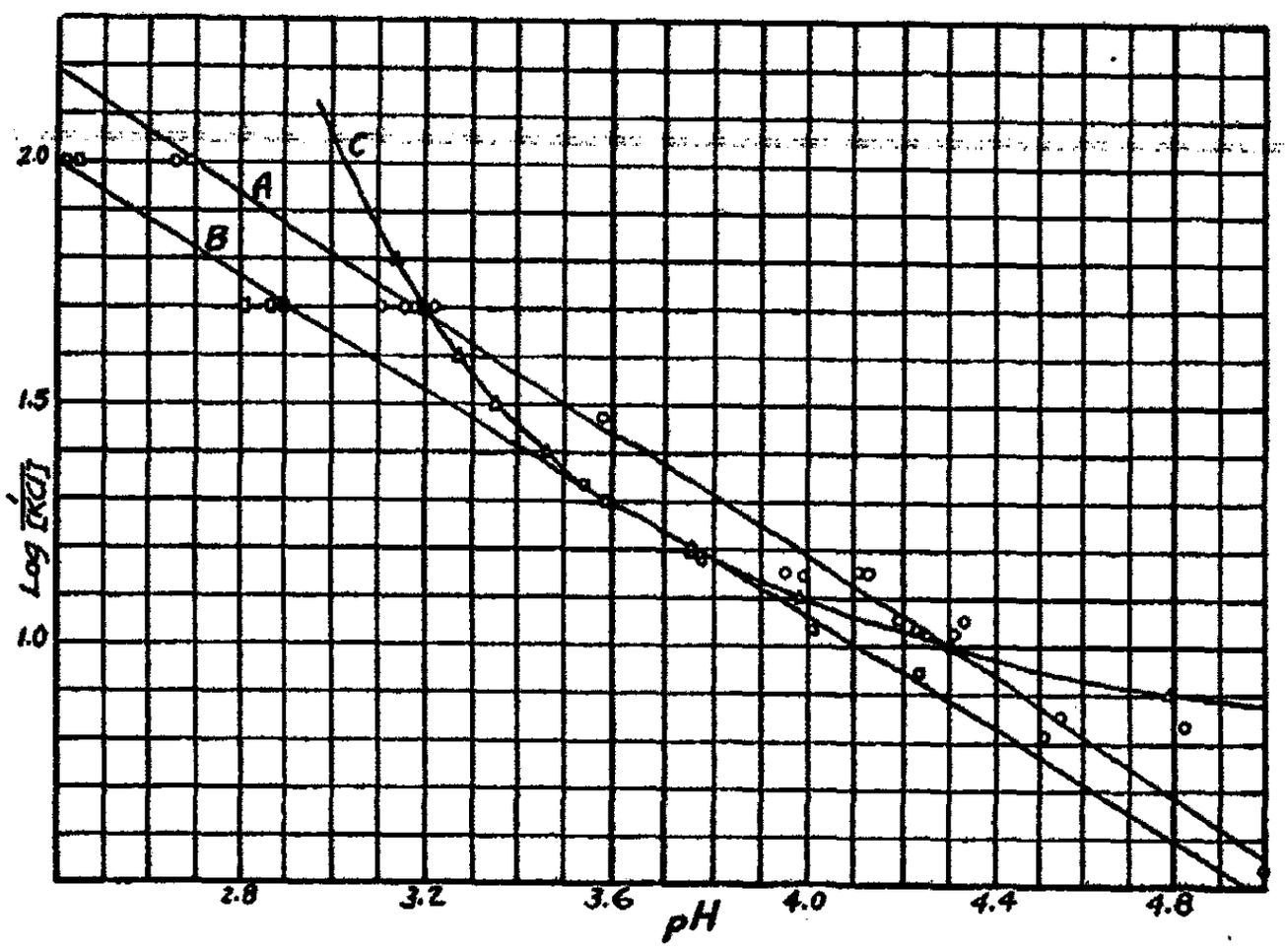



FIG. 1

A—tears mastic; $\log_{10} 1/(KCl) = 3.675 - 0.625$ pH: B—Merck's powdered mastic; $\log_{10} 1/(KCl) = 3.405 - 0.590$ pH: C—Equilateral hyperbola calculated by method of Michaelis and coworkers; $(\log_{10} 1/(KCl) + 0.18)(pH - 2.43) = 2.24$

regards the effect of dilution upon hydrogen-ion concentration, overlooks the chief factor governing the amount of electrolyte required. The decrease of acidity of mastic suspensoids with dilution furnishes a full explanation of the rule of Burton and Bishop[1] that dilution increases the concentration of uni-univalent salt required for precipitation. A more general and clearer statement of the situation would be that a decrease of hydrogen-ion concentration increases the concentration of salt required for coagulation of mastic suspensoids. The results reported herein indicate that the interpretation of the Burton and Bishop rule in its application to the change of concentration of salts furnishing bivalent and trivalent cations required for coagulation should

[1] Burton and Bishop: J. Phys. Chem. **24**, 701 (1920).

be made only after a consideration of the effects of both dilution of the sol and of hydrolysis of the salt on the hydrogen-ion concentration.

When the values of log 1/(KCl) and pH corresponding to coagulation concentrations of potassium chloride and hydrogen-ion concentrations for all the suspensoids prepared from mastic tears and dilutions of these suspensoids, are plotted as in Fig. 1 it is seen that they all lie approximately on a straight line in the pH range from 3.1 to 5.0. The equation of this line is log 1/(KCl) = 3.675 − 0.625 pH. The values for all the suspensoids and dilutions of suspensoids prepared from Merck's powdered mastic lie on a different line which is nearly parallel and whose equation is, log 1/(KCl) = 3.405 − 0.590 pH for

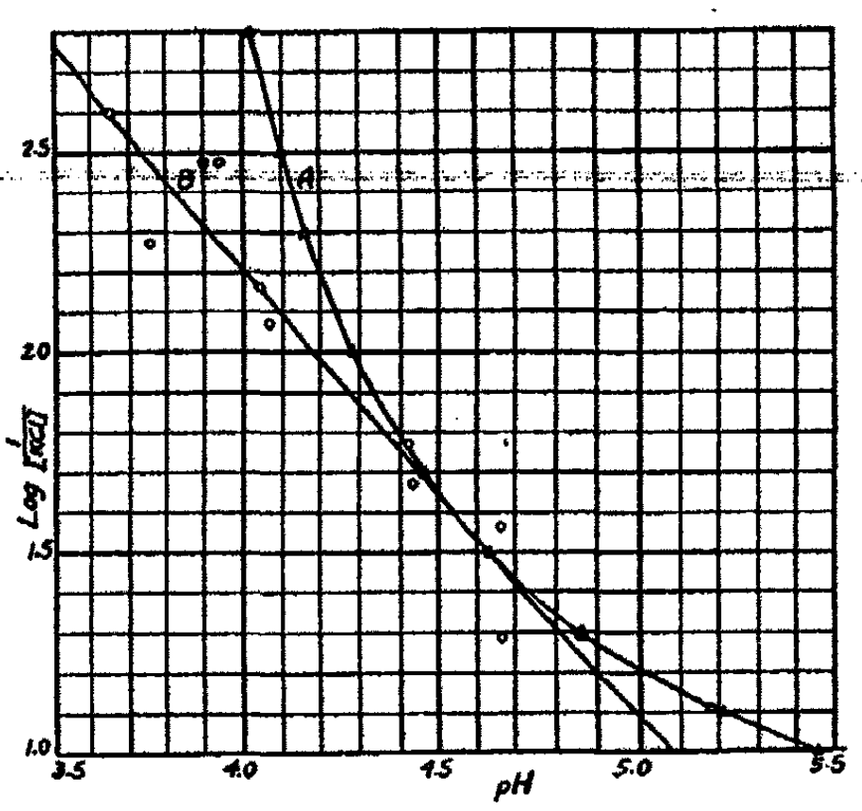



FIG. 2

A—Michaelis' hyperbola, (pH − 3.46) (log 1/(KCl) − 0.3) = 1.4: B—Michaelis and coworkers data for precipitation of mastic with KCl.

the pH range of 2.4 to 4.3. The effect of variety of mastic on coagulation is clearly shown by these equations. At a given pH a greater concentration of salt is required for the coagulation of the Merck sols. Michaelis[1] and his coworkers expressed the relation between log 1/(KCl) and pH by the hyperbolic equation given in the introduction of this paper. However, they had to explain that for the values near a pH of 4.0 the points lie below the hyperbola. If a straight line is drawn through the middle portion of the Michaelis hyperbola it will be seen that for this portion the "curve" becomes more nearly a straight line (see Fig. 2). It is true that as log 1/(KCl) approaches infinity, that is when precipitations are made with acid alone, the curve becomes asymptotic to an ordinate. Further, when the pH becomes greater than 7.0 the curve as shown by the data of Table VIII, becomes asymptotic to an abscissa. It is believed, however, that for the pH range of 2.4 to 5.0 the re-

[1] Michaelis and Timenez-Diaz: Kolloid-Z., 29, 181 (1921); Michaelis and Hirabayashi: 30, 209 (1922).

lation between log 1/(KCl) and pH can better be expressed by the straight line than by the hyperbola drawn in Fig. 1 in the manner employed by Michaelis.

It is unfortunate that there is no universally accepted criterion of complete precipitation. The point of view which governed the adoption of the standard here employed is that there is not definite precipitation unless the coagulum completely flocks leaving the dispersion medium clear. Furthermore, we believe that at least 24 hours is necessary for the attainment, or near attainment, of an equilibrium condition. The change in the appearance of the mixture of sol and precipitant is rapid the first few minutes and even the first few hours. After 24 hours, there is practically no further change apparent. The difference due to varying standards for complete precipitation is well illustrated by the data here in comparison with that of Michaelis and Hirabayashi[1]. The latter workers found precipitation with acid alone at a pH of 2.86. The average pH values at precipitation with acid alone in Table VI is 2.43 for the sols prepared from tears and 2.23 for the Merck sols, the differences from the 2.86 value being greater than can be easily accounted for on an assumption of great differences in kind of mastic.

## Summary

1. Mastic suspensoids prepared from different varieties of gum mastic and differing widely in concentration and dispersity are found to possess different hydrogen-ion concentrations and to require different concentrations of potassium chloride for coagulation.

2. The acidity of mastic suspensoids is due principally to organic acid in true solution. The mastic in true solution as free acid can be separated from the sol by dialysis and ultrafiltration. There is no great liberation of hydrogen-ions or hydroxyl-ions during coagulation with potassium chloride. The acidity of a mastic sol decreases with dilution.

3. All the suspensoids of one variety of mastic precipitate at about the same pH with hydrochloric acid alone regardless of the concentration or dispersity. In the pH range beyond 6.0 they all precipitate with nearly the same concentration of potassium chloride.

4. The minimum concentration of potassium chloride for coagulation of a mastic suspensoid is dependent entirely upon the pH of the dispersion medium. When coagulations are conducted at different pH values by varying the acidity of the precipitating agent, the curve relating pH to log 1/(KCl) for minimum coagulation concentrations is shown for one variety of mastic to be the same for the suspensions of different concentration and dispersity. This curve is found to be a straight line, rather than hyperbolic, in the pH range from 2.4 to 5.0. The curves for the suspensoids prepared from two varieties of mastic are not coincident but are nearly parallel.

*University of Washington,*
*Seattle, Washington.*
*Feb. 20, 1926.*

[1] Michaelis and Hirabayashi: Kolloid-Z., 30, 209 (1922).

# THE ACID-BASIC FUNCTION OF MOLECULES AND ITS DEPENDENCY ON THE ELECTRIC CHARGE TYPE

BY J. N. BRÖNSTED

## 1. Introduction

The simplest and most adequate definition of acids and bases is given by the scheme[1]

$$A \rightleftarrows B + H^+ \qquad (1)$$

where A and B represent acid and base respectively. This scheme indicates that an acid is defined as a substance, which is able to split off $H^+$-ions simultaneously forming a base, and a base as a substance capable of uniting with $H^+$-ions, thus forming an acid.

The unique position of acids and bases among chemical substances is accounted for by the unique properties of the $H^+$-ion. As the only chemical molecule consisting of an atomic nucleus alone, the hydrogen ion possesses an extraordinary position, particularly an extraordinary mobility, shown by the ease with which it passes from one molecule to another. A similar mobility with any other atom or ion would mean the existence of another group of chemical substances to which the name of acids and bases could be applied with a similar justification.

When the equilibrium given by scheme (1) is established in water or another solvent, the $H^+$-ion will be solvated. In the case of water as a solvent the equilibrium is [2]

$$A + H_2O \rightleftarrows B + H_3O^+ \qquad (2)$$

which is a double acid-basic equilibrium[3], A and $H_3O^+$ acting as acids, B and $H_2O$ as bases. The scheme (1) in such a case does not furnish an accurate representation of the *kinetics* of the reaction. It retains, however, unrestricted thermodynamic significance, and its application instead of the more complicated scheme (2) is justified in all cases of non-kinetic nature[4], when the solvent in which the equilibrium takes place remains unchanged.

Application of scheme (1) as a definition of the conception of acids and bases involves the admittance of the acid and basic properties being in principle assignable to ions as well as to neutral molecules. If, for instance, A is acetic acid, B, the base, must be the acetate ion. If B indicates ammonia, A, the acid, must indicate the ammonium ion etc. This is a point of view of considerable consequence. It brings to existence at once the problem of the

---

* Contribution from the Physico-Chemical Laboratory of the Polytechnical Institute of Copenhagen.

[1] Brönsted: Rec. Trav. chim., 42, 718 (1923).

[2] Compare Goldschmidt and Udby: Z. physik. Chem. 60, 728 (1907); Fajans: "Die Naturwissenschaft," 10, 165 (1923); Lowry: Trans. Faraday Soc., 20, Nr. 58 (1924).

[3] Brönsted: l. c. p. 721.

[4] The kinetic significance of the hydration of the H+-ion will be considered in another paper.

influence of the electric charge upon the acid-basic properties of molecules. This problem, in some sense, is not entirely new. When comparing the first and the second dissociation step of a dibasic acid for instance, what actually is compared is the dissociation of an electrically neutral acid and an acid of one negative electric charge. The present definition, however, involves the necessity of a general extension of the point of view from which such special cases[1] have been considered.

## 2. The Acid Nature of Aquo-ions

*The influence of the total charge of the acid molecule.*

When an aluminium salt is dissolved in water the aluminium ion unites with the solvent forming an aquo-ion, probably the hexaquo aluminium ion. This is an acid, dissociating according to:

$$\underset{\text{(acid)}}{\left[Al(H_2O)_6\right]^{+++}} \rightleftharpoons \underset{\uparrow\,\text{(base)}}{\left[\begin{matrix}OH\\Al(H_2O)_5\end{matrix}\right]^{++}} + H^+$$

and forming the hydroxo-pentaquo-ion as a base. Another acid of a similar type is the aquo-pentammine cobaltic ion, which dissociates according to the scheme:

$$\left[Co\begin{matrix}H_2O\\(NH_3)_5\end{matrix}\right]^{+++} \rightleftharpoons \left[Co\begin{matrix}OH\\(NH_3)_5\end{matrix}\right]^{++} + H^+$$

forming as a base the hydroxo pentammine cobaltic ion.

Particularly through the study of the cobaltic ammonia and similar metal ammonia salts, which possess a notable degree of definiteness and stability a certain insight has been obtained into the properties of aquo ions. For a small number of these the acid constant (dissociation constant) is known with a fair accuracy.

Thus for the aquo pentammine cobaltic ion in about 0.01 molal solution the value:

$$K = \frac{\left[Co\begin{matrix}OH^{++}\\(NH_3)_5\end{matrix}\right][H^+]}{\left[Co\begin{matrix}H_2O^{+++}\\(NH_3)_5\end{matrix}\right]} = 1.10^{-6}$$

has recently been found in this laboratory. When substituting $H_2O$ for one $NH_3$ the diaquo tetrammine cobaltic ion is formed, possessing an acid constant about three times as great as the constant for the aquo pentammine cobaltic ion. For the triaquo triammine and tetraaquo diammine cobaltic ion the value of the constant is still higher. Part of this increase, however, is accounted for by a statistical effect, which requires for instance a hexaaquo ion to be six times as strong as a monoaquo ion. The acidity, statistically corrected, is therefore not so different as the acid constants ordinarily measured, and the dissociation constant for this type of acids can be considered, at least, of the same order of magnitude.

[1] Ostwald: Z. physik. Chem., 9, 558 (1892); Bjerrum: 106, 219 (1923).

If, however, in the aquo-pentammine-cobaltic ion one ammonia group be substituted by an anion as $Cl^-$ or $NO_2^-$ the following ions thus being formed:

$$\left[\begin{matrix} & Cl \\ Co & H_2O \\ & (NH_3)_4 \end{matrix}\right]^{++}, \quad \left[\begin{matrix} & NO_2 \\ Co & H_2O \\ & (NH_3)_4 \end{matrix}\right]^{++},$$

the picture becomes entirely changed. The strength of these acids is not exactly known, but they are at least very much weaker than the above mentioned trivalent ions in which only ammonia and water molecules are combined with the central atom.

The reason for this great difference in acid strength obviously presents itself as the difference in electric charge of the acid molecule. While the aquo pentammine and the other trivalent aquo ions possess three positive charges by which the positive $H^+$-ions are strongly repelled, the chloro and nitro aquo tetrammine ions contain but two positive charges and accordingly exert a smaller repelling effect. As the process of dissociation in the case of weak acids, even if immeasurably fast from an experimental point of view, still is far from being instantaneous, a small change in the repelling force means a very considerable change in the probability of detachment and taking up of a $H^+$-ion and so easily accounts for the considerable change in acidity.

As a matter of fact, the electric effect assumed here to be operating as an acidifying factor must be looked upon as an effect of quite general nature. Under otherwise similar conditions a molecule will possess the more acid character the more positive is its electric charge, and the more basic character the more negative it is.

Werner[1], who has studied the basic properties of the various hydroxo salts as for instance

$$\left[Co\begin{matrix} OH \\ (NH_3)_5 \end{matrix}\right]Cl_2 \quad , \quad \left[\begin{matrix} & NO_2 \\ Co & OH \\ & (NH_3)_4 \end{matrix}\right] Cl$$

states that the latter of these is much more basic than the former. This, of course, is tantamount to stating that that the $\left[Co\begin{matrix} H_2O \\ (NH_3)_5 \end{matrix}\right]Cl_3$ is much more acid than is $\left[\begin{matrix} & NO_2 \\ Co & H_2O \\ & (NH_3)_4 \end{matrix}\right]Cl_2$. This corresponds entirely to our results. However, Werner does not interpret the phenomenon from the point of view here adduced, and seems rather disposed to find it in contrast to the well known influence of "electronegative" groups when introduced in organic acids. This conclusion, however, may only be justified when considering the salts as not dissociated electrolytically. Werner, certainly, was an adherent to the dissociation theory, but, strange to say, usually states his chemical formulae in undissociated form. He utilizes the dissociation theory mostly for the purpose of elucidating molecular structure. Then, of course, all molecules appear as

[1] Werner: Ber., **40**, 4098, 4117 (1907); "Neuere Anschaungen", 265 (1913).

electrically neutral, and any electric effect as the above mentioned vanishes. Not until writing the salt formulae in correspondance with their electrolytic dissociation is the true nature of the phenomenon disclosed as a simple consequence of the electrostatic forces.[1]

Passing one step further down to acids having only a single positive charge according to the theory presented here, one should expect a still further decrease in acidity. This actually is the case. Dinitrohydroxo triammine cobalt $\left[\begin{matrix}(NO_2)_2\\ Co\ OH\\ (NH_3)_3\end{matrix}\right]'$ which is electrically neutral is a much stronger base than the nitro hydroxo tetrammine cobaltic ion, indicating that the corresponding acid:[1]

$\left[\begin{matrix}(NO_2)_2\\ Co\ H_2O\\ (NH_3)_3\end{matrix}\right]^{+}$ is much weaker than $\left[\begin{matrix}NO_2\\ Co\ H_2O\\ (NH_3)_4\end{matrix}\right]^{++}$

In order to test our theory by consideration of ions of still higher positive charge than the aquo pentammine cobaltic ion, in which case a still more pronounced acidity is to be expected, we have to pass on to elements of higher valencies. It is known that platinum in its tetravalent state is able to form a great many complex ions of high stability, and several of these are usable for the demonstration of the applicability of the present point of view.

Tschugajeff[2] has recently discovered a series of salts of the hydroxo pentammine platinic ion:

$$\left[\begin{matrix}OH\\ Pt\\ (NH_3)_5\end{matrix}\right]^{+++}$$

This, in its composition, is quite analogous to the hydroxo pentammine cobaltic ion, but differs from it in possessing one more positive charge. It is now very remarkable that salts of this ion even of appreciable solubility separate from solutions containing a great excess of hydrochloric acid. From this observation we are justified in concluding that the equilibrium:

$$\underset{\text{(acid)}}{\left[\begin{matrix}H_2O\\ Pt\\ (NH_3)_5\end{matrix}\right]^{4+}} \rightleftharpoons \underset{\text{(base)}}{\left[\begin{matrix}OH\\ Pt\\ (NH_3)_5\end{matrix}\right]^{3+}} + H^+$$

---

[1] "The strengths of cobaltammine bases" has been the subject of a study by Lamb and Yngve: (J. Am. Chem. Soc., **43**, 2352 (1921)). The bases investigated are, with a single exception, strong, i.e. completely or practically completely dissociating electrolytes. The conductivity method as used by the authors is therefore, unable to give any information about the relative strength of the bases, which are in their character quite different from the weak bases dealt with above.

The conclusion was made by the authors, that the substitution of acid groups for ammonia in the hexammine ion should tend to increase the strength of the corresponding base as a consequence of the diminished positive valence of the ion, is in principle quite in harmony with the general results of the present article. The failure of the measurements to show such an effect is merely due to the inadequacy mentioned of the method in determining the relative strengths of the bases, and is not to be taken in favor of the assumption of a "chemical" influence of the acid radical, offsetting the electric effect, as supposed by the authors.

[2] Tschugajeff: Z. anorg. Chem., **137**, 1 (1924).

is located absolutely in favor of the hydroxo system, i.e. that the tetravalent aquo ion is an acid of a character much like hydrochloric acid or other strong acids, the crucial feature of which actually is their failure to exist. When considered in connection with the properties of analogous ions of lower charge this phenomenon announces in a very remarkable manner the presence of a high positive charge in the acid molecule.

The same distinction between the trivalent cobaltic and the tetravalent platinum ion is exhibited in another way. While the hexammine cobaltic ion $[Co(NH_3)_6]^{+++}$ is practically an absolutely neutral substance, hydrogen ions having no measurable tendency to leave the ammonia molecules, the hexammine platinic ion $[Pt(NH_3)_6]^{4+}$ seems to possess an acid character shown by the fact that salts of this ion are more soluble in alkali than in pure water. This phenomenon must be interpreted by assuming the following equilibrium:

$$[Pt(NH_3)_6]^{4+} \rightleftharpoons \left[Pt\begin{matrix}NH_2\\(NH_3)_5\end{matrix}\right]^{3+} + H^+$$

to exist, indicating the ability of the high positive charge to expel a hydrogen ion, even when this forms a part, as it does, of an ammonia molecule of much less acid character than a water molecule.

The acidifying influence of a high positive charge is thus clearly demonstrated by these examples. The acidity of the tetravalent platinic ions, however, seems considerably stronger than one should anticipate from the change in strength exhibited within the group of cobaltic ions. This fact and others let one surmise that the total charge of the molecule is not the only acidifying factor of electrostatic origin, but that also the charge of the central atom of the complex molecule may affect the acidity. The existence of such an effect is actually the basis of the theory of Kossel, which we shall consider in the next chapter.

### 3. The Influence of the Charge of the Central Atom

The great majority of the acids are characterized by a structure more or less similar to that of the aluminum ion or the hexammine cobaltic ion, i.e. an arrangement in which a *central atom* is surrounded by a number of atoms or molecules, which in correspondance with the theory of Werner have a *co-ordinate* position to it.

In order to show that the effect of the total charge of the molecule is paralleled by an influence of the charge of the central atom, it is necessary to compare ions of the same total charge but with varying charge of the central atom. When for instance comparing the hexammine cobaltic and the chloro-pentammine platinic ions:

$$\left[Co(NH_3)_6\right]^{+++}, \quad \left[Pt\begin{matrix}Cl\\(NH_3)_5\end{matrix}\right]^{+++}$$

we have in both cases trivalent ions, the central atom, however, possessing in the first case 3 and in the second case 4 positive charges. Now, as mentioned,

the cobaltic ion is quite neutral. The platinic ion on the other hand possesses acid character, for adding sodium hydroxide to a solution of the chloride an amido chloride is precipitated[1]:

$$\left[\mathrm{Pt}\begin{matrix}\mathrm{Cl}\\(\mathrm{NH_3})_5\end{matrix}\right]^{+++} \rightleftharpoons \left[\begin{matrix}\mathrm{Cl}\\ \mathrm{Pt}\ \mathrm{NH_2}\\ (\mathrm{NH_3})_4\end{matrix}\right]^{++} + \mathrm{H^+}$$

The same influence of the charge of the central atom exists in the case of aquo ions. The non-basic nature of the hydroxo ions of the platinic series is not only characteristic of the hydroxo-aquo-tetrammine ion as shown by Werner[2], both these ions being trivalent, but also the bivalent dihydroxo tetrammine platinic ion is almost non-basic, as shown by the fact that the corresponding salts are not transformed by strong acids into aquo salts. The chloride only adds one molecule of hydrochloric acid, but this is so loosely bound that it disengages even on exposing the solid salt to the air. Therefore the equilibrium:

$$\left[\begin{matrix}\mathrm{H_2O}\\ \mathrm{Pt}\ \mathrm{OH}\\ (\mathrm{NH_3})_4\end{matrix}\right]^{+++} \rightleftharpoons \left[\begin{matrix}\mathrm{OH}\\ \mathrm{Pt}\ \mathrm{OH}\\ (\mathrm{NH_3})_4\end{matrix}\right]^{++} + \mathrm{H^+}$$

is located almost absolutely in favor of the right-hand system, showing the great strength of the aquo ion in spite of its total charge being only three.

The point of view here stated of the charge of the central atom as an origin of acidity has, as mentioned above, already been advanced in the elaborate and important theory of Kossel[3]. According to this theory the acidity of such molecules as HCl, $H_2O$ and $H_3N$ is determined by the different negative charges: 1, 2 and 3 respectively of the atoms holding the $H^+$-ion. The weak attraction between $H^+$ and a singly charged $Cl^-$-ion allows the $H^+$ to escape easily from the HCl molecule thus making it a strong acid, while the double charge of the O-atom and still more the triple charge of the N-atom prevent the $H^+$ from ionizing to any appreciable extent. Similarly the positive charge of a central atom to which a water molecule, a hydroxyl group, etc., is bound at the same time as it holds the negative atom of such a group by electric attraction tends to disengage the positive $H^+$-ion. On that account perchloric and sulphuric acid and other acids with a central atom of high positive charge are strong acids.

The conclusions of Kossel here exemplified only by a few instances rest upon a fundamental assumption, that the various atoms within the structure of the molecule are still free to exert attracting and repelling forces as a direct consequence of their ionic charges. This standpoint may be open to some modification. Fajans[4] has pointed out the great influence of the electric deformation of molecules, a factor undoubtedly of importance but not as yet

[1] Tschugajeff: Z. anorg. Chem., 137, 401 (1924).
[2] Ber., 40, 4093 (1907).
[3] W. Kossel: Ann. Physik, (4) 49, 229 (1916).
[4] Fajans: "Die Naturwissenschaften," 10, 165 (1923).

very well defined. In spite of such criticism, for an orientation in the theory of the origin of acidity the Kossel view points are undoubtedly of great value.

It would seem natural to try to work up generally the Kossel theory with the point of view of the present article on the acid-basic function of molecules. Considering the different groups of periodic table we must expect each ion with its natural positive charge, i.e. the charge corresponding to the electronic configuration of the next lower rare gas, to combine, when dissolved in water, with water molecules, thereupon loosing a number of $H^+$-ions, increasing with

| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|
| | | | $SiO_4$ | $PO_4$ | $SO_4$ | $ClO_4$ |
| — | — | — | −4 | −3 | −2 | −1 |
| — | — | — | $HSiO_4$ | $HPO_4$ | $HSO_4$ | — |
| | | | −3 | −2 | −1 | |
| — | — | $AlO_3$ | $H_2SiO_4$ | $H_2PO_4$ | $H_2SO_4$ | — |
| — | — | −3 | −2 | −1 | 0 | |
| — | — | $HAlO_3$ | $H_3SiO_4$ | $H_3PO_4$ | — | — |
| — | — | −2 | −1 | 0 | | |
| — | — | $H_2AlO_3$ | $H_4SiO_4$ | — | — | — |
| | | −1 | 0 | | | |
| — | — | $H_3AlO_3$ | — | — | — | — |
| | | 0 | | | | |
| — | — | $H_4AlO_3$ | — | — | — | — |
| | | +1 | | | | |
| — | $H_3MgO_2$ | $H_5AlO_3$ | — | — | — | — |
| | +1 | +2 | | | | |
| $H_2NaO$ | $H_4MgO_2$ | $H_6AlO_3$ | — | — | — | — |
| +1 | +2 | +3 | | | | |

the number of positive charges in the series of elements considered. The outcome of such a process is most clearly illustrated by considering a special group for instance the second group of elements ranging from neon to chlorine. The behaviour of these elements is shown in the following scheme, where the figures at the tops of the columns indicate the natural positive charge of the element below, and the figures under the formulae of the various molecules the corresponding charge. In stating the formulae no special consideration has been given to the problem of the degree of hydration.

When a positive chlorine ion $Cl^{7+}$ dissolves in water, it forms a hydrate say $Cl(H_2O)_4^{7+}$ and then loses eight $H^+$-ions. The repelling forces of the positive central atom are so strong that even the last of the 8 $H^+$-ions, after the

molecule $HClO_4$ has been formed, leaves the molecule completely. The ion $ClO_4^-$, therefore, is the only form in which the $Cl^{7+}$ ion can exist in aqueous solution.

A sulphur ion $S^{6+}$ behaves similarly, has a great tendency to losing eight $H^+$-ions thus forming $SO_4^{--}$. The smaller charge in comparison with the $Cl^{7+}$-ion, however, is indicated by the existence of $HSO_4^-$ and possibly also in very slight concentration: $H_2SO_4$. In these molecules only seven and six $H^+$-ions respectively are lost.

A phosphorus ion $P^{5+}$ has a still smaller tendency to lose $H^+$-ions. Eight $H^+$-ions are lost only in a solution containing great excess of a strong base. Dissolved in water at ordinary concentration the $P^{5+}$-ion gives rise to formation of $HPO_4^{--}$, $H_2PO_4^-$ and $H_3PO_4$ molecules, corresponding to a disengagement of 7, 6 and 5 $H^+$-ions respectively.

In the case of the $Si^{4+}$ ion the force expelling the $H^+$-ions from the hydrated ion has decreased so far that the molecule $H_4SiO_4$ corresponding to a loss of four $H^+$-ions is the stable form under ordinary conditions. Only in the presence of a large excess of alkali are more $H^+$-ions split off and ions of negative charges formed.

A still more marked change in acid character is shown by the trivalent aluminum ion $Al^{3+}$. Under normal conditions this ion loses no or only one $H^+$-ion. On the other hand, in basic solution it may be brought to lose up to six $H^+$-ions forming as the most negatively charged molecule the aluminate ion $AlO_3^{3-}$. In spite of its lower positive charge than that of the previous atoms aluminum is the first element in this series to exist in aquous solution with a positive charge. However, this property does not show up suddenly as quite a novel property, but merely indicates a further step in the graduation of acidity.

By the magnesium ion $Mg^{2+}$ a further alteration in the same direction is exhibited. When dissolved in water the hydrated ion shows no appreciable tendency to losing $H^+$-ions. Undoubtedly, however, the magnesium ion possesses a weak acid character, as shown particularly at higher temperatures, and we must believe that an ion as $MgOH^-$ or $H_3MgO_2^-$ is capable of existence[1].

Finally the sodium ion in aqueous solution seems completely neutral, i.e. the number of $H^+$-ions disengaged by it is zero. One should expect even in this case an increase of acidity of the $H_2O$-molecule by combining with a singly charged positive ion. This increase seems, however, in the case of sodium too small to be demonstrated experimentally[2].

A clear picture of the dependency between acidity and electric charge in this series of elements is given in Fig. 1. Here the natural positive charge of the ions is used as an abscissa. The ordinate indicates the number of $H^+$-ions

[1] See Gjaldbaek: Z. anorgan. Chem, 144, 000 (1925).

[2] Bjerrum states (private communication) that he has found some facts that indicate strong solutions of sodium salts to be more acid than corresponding solutions of potassium salts. This agrees excellently with the graduation in acidity to be expected in the series Li–Na–K.

lost by each ion, when transferred from a free state into an aquous solution in which the $H^+$-ion concentration is kept at the value $10^{-7}$. The ordinate 6.5 f. instance belonging to P thus indicates a loss of 6.5 $H^+$-ions by one $P^{5+}$-ion, i.e. a state of the dissolved $P^{5+}$-ion corresponding to a mixture of $HPO_4^{--}$ and $H_2PO_4^-$ in equal proportions. This mixture is known to possess a pH value of 7. The ordinate 1 belonging to aluminum indicates this ion to exist at pH = 7 preferably as a bivalent positive ion. The composition of this is known to be $H_{11}AlO_6^{2+}$ or $\left[ Al\begin{matrix} OH \\ (H_2O)_5 \end{matrix} \right]^{2+}$.

All points, as shown by the figure, can be combined by a smooth curve showing the gradual and continuous change in acidity when passing from an element such as sodium of quite metallic character to metalloid elements as sulphur and chlorine, the acidity thus proving to be a definite function of its natural electric charge.

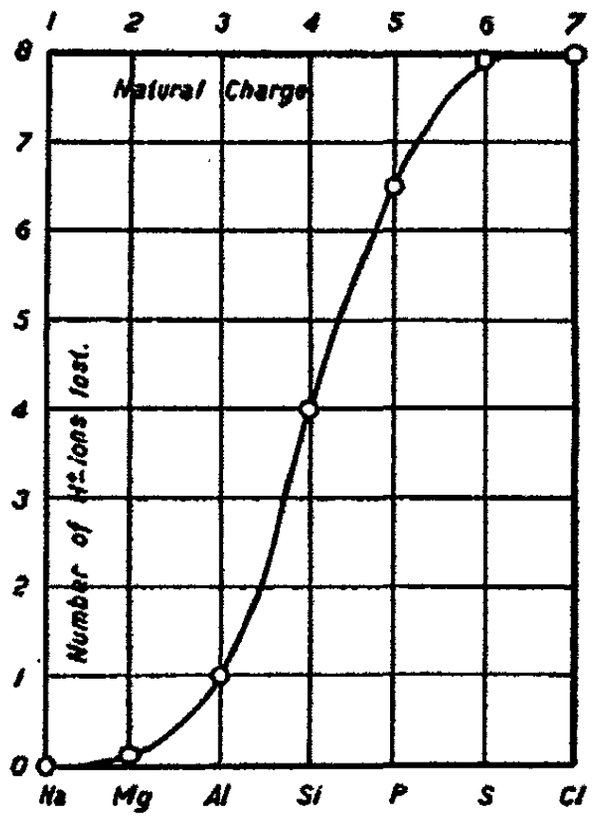



FIG. 1

Besides the magnitude of the electric charge of the central atom also the distance between it and the $H^+$-atoms plays a part, as already shown by Kossel. When comparing the first series in the periodic table:

Li Be B C N

with the second

Na Mg Al Si P

the elements in the first series in correspondance with their smaller atomic volume are found to form hydrated ions of much higher acidity than the elements in the second. Even the lithium ion is certainly not neutral, but possesses a definite acidity[1] and this in the case of glucinum is known to be very pronounced.

[1] LiCl shows for instance a tendency to lose HCl in contact with water at a higher temperature. Compare Kolthoff (Rec. Trav. chim., 42, 969 (1923)) who has attempted to determine the "hydrolysis" of a lithium salt solution.

### 4. The Influence of the Solvent upon the Acid-Basic Properties

The solvent influences the acid-basic equilibrium in two different ways. 1. Through its dielectric constant. 2. Through its acid-basic properties. We shall consider the last mentioned factor first.

It was stated already in the introduction that the scheme of dissociation of an acid, on account of the hydration of the $H^+$-ion is somewhat more complex than corresponding to (1) and must properly be represented by:

$$\underset{(\text{acid})_1}{A} + \underset{(\text{base})_2}{H_2O} \rightleftarrows \underset{(\text{base})_1}{B} + \underset{(\text{acid})_2}{H_3O^+}$$

i.e. the scheme of a double acid-basic equilibrium. In fact the $H^+$-ion or proton has no possibility of existing in the presence of other molecules. In the case of water as a solvent this is illustrated by the extremely high heat of hydration[1] showing its practical non-existence in solution.

The "dissociation" of an acid, therefore, is indespensably connected with the presence of a basic molecule, capable of taking up the $H^+$-ion expelled[2]. On the other hand a base will undergo no "ionization", i.e. it will add no hydrogen ions unless an acid molecule is present to provide the hydrogen ion required. In order to cause acid and basic "ionization" to occur the solvent thus evidently must possess basic and acid properties itself.

Accordingly for instance in the case of acetic acid, EH, the process of "dissociation" is actually represented by:

$$EH + H_2O \rightleftarrows E^- + H_3O^+ \qquad (3)$$

Putting:

$$\frac{a_{E^-}\, a_{H^+}}{a_{EH}} = K_{EH(a)}$$

and:

$$\frac{a_{H_3O^+}}{a_{H_2O}\, a_{H^+}} = K_{H_2O(b)}$$

where $a$ is the activity, $K_{EH(a)}$ and $K_{H_2O(b)}$ indicate the acid constant of EH and basic constant of $H_2O$ respectively. The tendency of acetic acid to ionize in aqueous solution according to scheme (3) therefore is given by:

$$\frac{a_{E^-}\, a_{H_3O^+}}{a_{EH}\, a_{H_2O}} = K_{EH(a)}\, K_{H_2O(b)}$$

i.e. by the product of the two acid and basic constants involved in the reaction. Of course the same product measures the tendency of water to ionize in the presence of acetic acid, these two tendencies being actually identical.

Correspondingly in the case of ammonia in water solution the equation:

$$\frac{a_{NH_4^+}\, a_{OH^-}}{a_{NH_3}\, a_{H_2O}} = K_{NH_3(b)}\, K_{H_2O(a)}$$

where the terms have an analoguous significance, gives the tendency for ammonia and water to ionize in the presence of one another. For the solvent itself a similar equilibrium exists:

$$2H_2O \rightleftarrows H_3O^+ + OH^-$$

---

[1] Fajans: Ber., 21, 709 (1919).
[2] Compare Lowry: l. c.

showing that the "dissociation" of water is actually an amphoteric reaction one molecule of $H_2O$ acting as an acid and another as a base. Putting:

$$\frac{a_{OH^-}\ a_{H^+}}{a_{H_2O}} = K_{H_2O(a)}$$

and:

$$\frac{a_{H_3O^+}}{a_{H^+}\ a_{H_2O}} = K_{H_2O(b)}$$

the ionization of water is seen to be determined by the constant:

$$\frac{a_{H_3O^+}\ a_{OH^-}}{a'_{H_2O}} = K_{H_2O(a)}\ K_{H_2O(b)}$$

the product of acid and basic constant thus also in the case of a pure solvent being the factor which determines the ionization.

The widespread opinion that water is equally acid and basic—and therefore quite a neutral substance—thus has to be abandoned. As a matter of fact such a conclusion is by no means justified even if we acknowledge that the ionization of a pure substance is to the same degree depending on its acidity and basicity.

The points of view here presented for the acid-basic function in general, may be useful to explain phenomena, which have not as yet been understood. Thus it is well known that pure substances as a rule are poor conductors for electricity, in other words are but little ionized. This for instance is the case with pure HCl, $H_2O$ and $H_3N$ in a liquid state. Mixtures of these substances, however, may be excellent conductors. How is this phenomenon to be accounted for?

According to the above views ionization in the three cases must occur according to:

$$_2HCl \rightleftarrows H_2Cl^+ + Cl^-$$
$$_2H_2O \rightleftarrows H_3O^+ + OH^-$$
$$_2H_3N \rightleftarrows H_4N^+ + NH_2^-$$

depending upon the values of the three constants:

$$K_{HCl(a)} \quad K_{HCl(b)}$$
$$K_{H_2O(a)} \quad K_{H_2O(b)}$$
$$K_{H_3N(a)} \quad K_{H_3N(b)}$$

Now it is not unreasonable to expect that, as the acid constants in the series HCl, $H_2O$, $H_3N$ decreases from HCl to $NH_3$ the basic constants will increase correspondingly in the same direction. It is possible, therefore, that the products are approximately equal. That the conductivity of the three substances in a pure state are of the same order of magnitude, as a matter of fact, shows this conclusion to be justified.

If now mixing for instance HCl and $H_2O$, the equilibrium:

$$HCl + H_2O \rightleftarrows H_3O^+ + Cl^-$$
$$(acid)_1 \quad (base)_2 \qquad (acid)_2 \quad (base)_1$$

being established, the tendency of the stronger acid HCl to dissociate becomes enhanced by the presence of the stronger base $H_2O$ instead of the very

weak base HCl in pure HCl. The ionization as measured by the product $K_{HCl(a)}\ K_{H_2O(b)}$ takes place therefore in the mixture at a much greater extent than in the pure solvent. The reaction can also be considered from the point of view that the tendency of the $H_2O$-molecule to act as a base, i.e. to unite with a $H^+$-ion is greatly favored by the presence of the stronger acid HCl instead of $H_2O$ and therefore the ionization stronger than in pure water. In quite a similar way the reason for a mixture of $H_2O$ and $NH_3$ to ionize much more than the pure liquids is seen to be the greater value of the product $K_{(a)}\ K_{(b)}$ in the mixture than in any of the pure solvents.

The second factor determining the ionization values is the dielectric constant of the solvent. It is generally recognized that the ionization of acids and bases increases with increasing dielectric constant of the solvent. This is owing to the diminishing in the electric attraction forces between the ions. It is evident, however, that the conclusion applies only to acids and bases which are negatively charged or electrically neutral. When comparing the following series of acid-basic equilibria:

$$A^\circ \rightleftarrows B^- + H^+$$
$$A^+ \rightleftarrows B^\circ + H^+$$
$$A^{++} \rightleftarrows B^+ + H^+$$
$$A^{+++} \rightleftarrows B^{++} + H^+$$

it is noticed immediately that only the first is affected, by changing solvent in correspondence with the usual point of view. The second is not affected And the following are affected in the opposite direction. The more positive the acid molecule is, the more is its acid character enhanced by decrease in dielectric constant.

Several experimental observations are in agreement with this conclusion. As examples may be mentioned the dissociation of trivalent aquo ions the dissociation of which increases in aqueous solution by addition of alcohol. A ferric perchlorate solution which is made colorless by an excess of perchloric acid becomes decidedly brown by adding alcohol. A violet solution of chromium nitrate or perchlorate turns green and a red solution of dipyridin tetraquo chromic chloride also green on a similar treatment. In all cases the color change accompanying the change in the medium is caused by the transformation of the trivalent aquo ion into a bivalent hydroxo ion for instance:

$$\underset{\text{(red)}}{\left[Cr\begin{matrix}Py_2\\(H_2O_4\end{matrix}\right]^{+++}} \longrightarrow \underset{\text{(green)}}{\left[\begin{matrix}Py_2\\Cr\ OH\\(H_2O)_3\end{matrix}\right]^{++}} + H^+$$

Dilution with water of course has an effect in the same direction, but the effect of alcohol, acetone, and other organic liquids is much stronger. The several influencing factors are simultaneously operating in any real case and the acid-basic and the other solvation effects may be of influence besides the dielectric effect. However, alcohol is a weaker base than water, and we must consider, therefore, the dielectric effect to be predominating in causing the phenomenon here mentioned.

These results reached by means of theoretical and experimental evidence entails another law as its actual basis: Namely, that under conditions otherwise alike the chemical potential of an ion is higher in a medium of low than in a medium of high dielectric constant, and that this effect is the more marked the higher the valence is of the ion considered. This agrees with the electrostatic theory of the potential of charged particles and with a number of experimental facts for instance that electrolytically dissociating salts are appreciably soluble only in the solvents of high dielectric constant.

When comparing the strength of two acids or two bases consideration of the factors described above is quite obligatory. Comparison, therefore, should be made only when the acids or bases are present in the same solvent. There remain then still solvation effects which are different for the different molecules, and acid and basic constants found experimentally therefore always refer to the acid or base in its solvated state. An absolute comparison of acidity and basicity of definite molecules evidently requires the absence of any solvent medium, including the pure acid or basic liquids themselves.

Accordingly also methods depending upon static or kinetic behavior of acids or bases in the pure liquid state, as for instance those recently proposed by Hantzsch[1], are inadequate to express a definite measure of acid or basic properties of molecules.

## Summary

1. The definition of acids and bases by means of the scheme:

$$\underset{\text{(acid)}}{A} \rightleftarrows \underset{\text{(base)}}{B} + H^+$$

involves the admission of ions as well as electrically neutral molecules as acids and bases.

2. The positive electric aquo ions, for instance $Al(H_2O)_6^{+++}$, are acids. The acid property is the more pronounced, the higher the positive charge. The corresponding hydroxions are bases.

3. In correspondence with the theory of Kossel the charge of the central atom of a molecular configuration plays a very great part in imparting to it acid and basic properties.

4. The acidity and basicity of the various molecules formed by the elements in any group of the periodic table show a graduate change in correspondance with the statements in 1., 2. and 3.

5. The electrostatic effect tends to make acids with two or more positive charges more strongly ionizing in solvents of low dielectric constant than in water.

[1] Hantzsch: Z. Elektrochem., 29, 221 (1923); 30, 194 (1924).

6. The free $H^+$-ion does not exist. Ionization of acids and bases takes place as a double acid-basic equilibrium involving the solvent molecules. The ionization tendency is measured by the product of an acid and basic constant. This accounts for the slight ionization in pure solvents as HCl or $H_2O$ and the strong ionization in mixture: $HCl + H_2O$.

7. Absolute comparison of the strengths of two acids or two bases is impossible because it requires the absence of any solvent medium.

*Copenhagen,*
*Denmark,*
*Dec. 11, 1925.*

# INTERFACIAL TENSIONS BETWEEN ORGANIC LIQUIDS AND WATER OR AQUEOUS SOLUTIONS

BY JAMES ROBERT POUND

In this paper the author records the measurements of the interfacial tensions at 30° between certain organic liquids, which for brevity are frequently called 'oils', and water or aqueous solutions. The capillary tube method was used, as described by Reynolds[1], and as used by the author in 1922[2]. Some references to the author's previous work will be made below. The aim of the present work was to improve this method of determining interfacial tensions by measuring the densities of the two mutually saturated liquids as well as those of the original liquids, and also to investigate the changes of interfacial tension due to increasing purity of the liquids used and to chemical action between the liquids in contact. For the last purpose the interfacial tensions, and their changes with time, have been observed between certain esters and aqueous solutions.

The determinations of the interfacial tensions were made in the apparatus previously described, i.e. for one apparatus

$$I = k.(d - d').(h + r/3\mu), \qquad (1)$$

where k is a constant for that apparatus,
d and d′ are the densities (C.G.S. units) of the two liquids,
h is the difference between the levels of the two interfaces or menisci, the one in and the other out of the capillary tube in the scale divisions of the outer tube,
r is the radius of the capillary tube in centimeters,
$\mu$ is the value of one scale division of the outer tube in cm.,
and I is the interfacial tension, I.T., in dynes per centimetre. For the one apparatus $r/3\mu$ is a constant, which too is small compared to h.

The water or aqueous solution used was prepared largely air-free; the water by boiling and cooling, and the solution by exhausting the air from the stock bottle for some time before using; otherwise bubbles of air may come out of the solution after keeping some time in the thermostat at 30° and get into the capillary tube and spoil the experiment. The water or aqueous solution being in place, the oil was introduced from the top or the bottom depending on whether it was the lighter or denser liquid, allowed to attain the thermostat temperature, and then introduced round and into the capillary tube by running out the water or aqueous solution. From the time of the first setting, the two menisci, or interfaces between the liquids, were under observation for hours; several readings being taken in each of several settings. The densities of the two liquids were often determined at the finish of an interfacial tension experiment; the lower liquid was run out directly into the S.G.

[1] J. Chem. Soc., 119, 469 (1921).

[2] Pound: J. Chem. Soc., 123, 578 (1923).

bottle, and the upper liquid into a separating funnel and thence into the S.G. bottle. All densities, given in C.G.S. units, were determined at 30° in the thermostat and with the usual precautions. The densities of the pure liquids, Table I, are accurate to within a unit or two in the fifth decimal place; those of the liquids from the I.T. tests, Table V, may be considered correct to the fourth decimal place.

At 15° the hydrochloric acid solution was 1.030 Normal, the sulphuric acid solution was 2.796 Normal, and the sodium hydroxide solution was 1.024 Normal. The last solution was freshly made from the best material, but no special precautions were taken to ensure its being carbonate-free. The sodium chloride solutions were nearly saturated and were made as required.

The interfacial tensions, etc., are summarised in Tables I-IV. Each organic liquid or oil used is mentioned in Table I and is there definitely numbered. Where there were used more than one sample of such from *entirely different sources*, these are distinguished by dashes after the number, e.g. the turpentines 5 and 5′. But where there were used different preparations or distillates from the one source, these samples are distinguished by letters after the number, e.g. the turpentine 5 and the distilled turpentine 5a. The interfacial tension experiments between the oils and water are referred to afterwards by these numbers. The I.T. experiments between the oils and the hydrochloric acid solution are numbered as above followed by X; those with the sulphuric acid solution by Y; those with sodium hydroxide solution by Z; and those with the sodium chloride solutions by S. Thus experiment 25aS is the I.T. experiment with the fraction 25a from the distillation of the ethyl acetate 25 and a solution of sodium chloride. It will be convenient, too, to let I = the I.T. between an oil and water, x = the I.T. between it and the hydrochloric acid solution, y = the I.T. between it and the sulphuric acid, z = the I.T. between it and the sodium hydroxide, and s = the I.T. between it and the salt solution.

Table V summarises the density determinations carried out with the mutually saturated liquids. For the first eleven pairs of liquids of the table, the oil and the water were placed overnight in a stoppered flask in the thermostat, and in the morning the two layers were separated and their densities determined. The remaining pairs of liquids were taken directly from the I.T. apparatus. The densities of the original liquids may be obtained from Table I. The mutual solubility of two liquids should cause a decrease in the difference between their densities; for solution of the denser liquid in the lighter will, in general, raise the density of the latter, and solution of the lighter liquid in the denser will lower the density of the denser, and so (d − d′) will decrease. The Table V indicates that these normal cases are twice as numerous as the abnormal cases; in the latter the oil is a complex mixture or chemical action occurs between the two liquids. Also the oils dissolve water from the dilute acid and alkali solutions as from pure water, with similar density changes in the oil in these cases; from the sodium hydroxide solution the oils dissolve somewhat less water and the density changes in them are then somewhat less. Also the oils dissolve similarly in water and in dilute acid and

## TABLE I

### Interfacial Tensions of Liquids against Water at 30°, with their Densities, Boiling-points etc.

| No. | Liquid | B. P. | Density 30°/4° | Initial I. T. γ | Interfacial tension (dynes/cm.) Over hrs. | Final I. T. | After hrs. |
|---|---|---|---|---|---|---|---|
| 1a | Petrol | 51.5– 78.0° | 0.6669 | 41.6 | 2 | 45.0 * | 23 |
| 1b | Petrol | 80.0–100.5 | 0.70995 | 40.65 | ½ | 43.85* | 20 |
| 1c | Petrol | 101.5–125.5 | 0.73178 | 37.50 | ½ | 43.3 * | 20 |
| 1d | Petrol | 83–100 | 0.7102 | 45.48 | 2 | 43.5 * | 96 |
| 1′ | Petrol | 97–124 | 0.72715 | 46.10 | 2 | 46.3 * | 96 |
| 2 | Benzene | 80.03–80.13 | 0.86704 | 33.10* | 20 | — | — |
| 3a | Toluene | 110.6–110.7 | 0.85122 | 33.50 | ½ | 34.40* | 22 |
| 3b | Toluene | 110.8 | 0.85172 | 34.24* | 20 | — | — |
| 4a | Xylene | 138.6–139.3 | 0.84844 | 34.75 | 24 | — | — |
| 4b | Xylene | 139.4–139.5 | 0.85000 | 36.40 | 24 | — | — |
| 5 | Turpentine | —— | 0.91207 | 9.84 | 5 | 10.3 | 22 |
| 5a | Turpentine | 161.5–173.5 | 0.86614 | 16.61 | 1 | 16.56 | 20 |
| 5′ | Turpentine | —— | 0.85268 | 11.07 | 1 | 10.2 * | 46 |
| 6 | Terebene | —— | 0.85438 | 10.45 | 1 | 14.24 | 23 |
| 6a | Terebene | 174.5–181.5 | 0.84040 | 21.70 | ¼ | 26.0 | 22 |
| 7 | Limonene | 75–85°(25mm) | 0.91151 | 2.84 | ½ | 1.4 | 21 |
| 8 | Pine Oil | —— | 0.92263 | 10.88 | 1 | 11.20* | 64 |
| 9 | Eucalyptus Oil | —— | 0.90533 | 16.24 | 1½ | 16.1 | 20 |
| 10 | Cineol | —— | 0.91145 | 9.0 | 1 | 6.6 | 20 |
| 11 | Isobutyl alcohol | 107.2–107.6 | 0.79452 | (1.5) | — | — | — |
| 12a | Amyl alcohol | 130.7–131.6 | 0.80432 | 4.97 | 1 | 4.05* | 20 |
| 12b | Amyl alcohol | 131.6–132.0 | 0.80364 | 4.95 | 1 | 4.11* | 20 |
| 12′a | Amyl alcohol | 129.4–130.7 | 0.8053 | 4.87 | 1 | 4.15* | 21 |
| 12′b | Amyl alcohol | 130.8–131.7 | 0.8036 | 4.83 | 1 | 3.82* | 21 |
| 13 | Phenyl-ethyl alcohol | 218.4–219.2 | 1.01103 | 4.51 | 1 | 4.60* | 25 |
| 14 | Acetophenone | 201.4–201.6 | 1.01952 | 12.00 | 4 | 12.08* | 24 |
| 15 | Furfural | 160.2–161.2 | 1.14842 | 5.13 | 26 | — | — |
| 16 | Benzaldehyde | 179.3–182.0° | 1.03784 | 14.18 | 48 | — | — |
| 16′ | Benzaldehyde | 178.5–181.5 | 1.03790 | 13.99 | 4 | 14.18 | 48 |
| 17 | Acetic anhydride | 137.0–139.8 | 1.06713 | 3.1 z | — | 0 | ½ |
| 17′ | Acetic anhydride | 137.6–140.0 | 1.06722 | 3.7 z | — | 0 | ½ |
| 18 | Quinoline | (237.5)v | 1.08677 | 2.87 | 1½ | — | — |
| 19 | Aniline | 184.1–184.6 | 1.01298 | 6.00 | ½ | 5.69* | 28 |
| 20 | Chloroform | 61.1 | 1.4688 | 31.37 | 19 | — | — |
| 21 | Carbon tetrachloride | 76.5– 76.6 | 1.57426 | 42.76* | 21 | — | — |
| 22 | Nitrobenzene | (210–211)v | 1.19219 | 24.10 | 10 | 23.90* | 18 |
| 23a | Chlorobenzene | 131.5–131.7 | 1.09304 | 35.50 | 2 | 35.95* | 22 |
| 23b | Chlorobenzene | 131.9 | 1.09548 | 35.52 | 1 | 37.15* | 23 |
| 24a | Benzyl chloride | 174.0–174.8 | 1.08699 | 29.99 | 5 | 28.6 | 20 |
| 24b | Benzyl chloride | 175.2–178.3 | 1.08815 | 30.07 | 5 | 27.1 | 98 |

TABLE I (continued)

| No. | Liquid | B. P. | Density 30°/4° | Interfacial tension (dynes/cm.) Initial I. T. γ | Over hrs. | Final I. T. | After hrs. |
|---|---|---|---|---|---|---|---|
| 25 | Ethyl acetate | —— | 0.88651 | 6.19 | 5 | 5.96* | 21 |
| 25a | Ethyl acetate | 76.8– 77.1 | 0.88781 | 6.79 | 2 | 6.06* | 21 |
| 25b | Ethyl acetate | 77.1– 77.3 | 0.88834 | 6.39 | 4 | 6.05* | 49 |
| 26a | Butyl acetate | 120.2–122.2 | 0.85746 | 7.46 | 1 | 6.78* | 21 |
| 26b | Butyl acetate | 122.2–124.7 | 0.86057 | 8.10 | 2 | 7.96* | 140 |
| 26c | Butyl acetate | 124.7–127.2 | 0.86668 | 11.07 | 2 | 10.6 * | 67 |
| 27a | Amyl acetate | 139.0–140.3 | 0.8545 | 10.88 | 3 | 10.67* | 21 |
| 27b | Amyl acetate | 140.3–142.0 | 0.85856 | 12.05 | 4 | 12.04* | 27 |
| 28a | Ethyl butyrate | 104.5–107.5 | 0.87577 | 12.45 | 1 | 12.35* | 50 |
| 28b | Ethyl butyrate | 107.5–112.0 | 0.87425 | 13.54 | 50 | 13.33* | 50 |
| 28c | Ethyl butyrate | 112.5–117.4 | 0.87301 | 13.70 | ½ | 13.56* | 24 |
| 28d | Ethyl butyrate | 117.4–123.5 | 0.87209 | 14.80 | 2 | 14.75* | 24 |
| 29 | Amyl butyrate | —— | 0.85703 | 17.70 | 2½ | 17.50* | 20 |
| 29a | Amyl butyrate | 166.0–172.5 | 0.85593 | 16.80 | 2½ | 17.02* | 48 |
| 29b | Amyl butyrate | 172.5–176.6 | 0.85778 | 20.78 | 21 | 20.57* | 48 |
| 29c | Amyl butyrate | 176.6–183.6 | 0.85838 | 22.04 | 20 | 21.92* | 20 |
| 30 | Amyl valerianate | —— | 0.86145 | 17.80 | 20 | 17.94* | 20 |
| 30a | Amyl valerianate | 171.5–178.5 | 0.85790 | 16.23 | 5 | 16.46* | 23 |
| 30b | Amyl valerianate | 178.5–184.0 | 0.86042 | 19.52 | 2 | 19.70* | 67 |
| 30c | Amyl valerianate | 184.0–188.5 | 0.86202 | 21.15 | 67 | 21.10* | 67 |
| 31a | "Oenanthic ether" | (222–231)[v] | 0.85912 | 19.55 | 20 | 19.41* | 20 |
| 31b | "Oenanthic ether" | (231–240)[v] | 0.85912 | 19.93 | 20 | 20.02* | 20 |
| 32a | Benzyl acetate | 214.0–214.9 | 1.04677 | 15.41 | 2 | 15.10* | 50 |
| 32b | Benzyl acetate | 214.9–215.3 | 1.04692 | 15.40 | 2 | 15.15* | 50 |
| 33 | Methyl benzoate | 197.2–198.0 | 1.07845 | 16.63 | 1 | 16.91* | 65 |
| 34 | Isobutyl benzoate | 240.3–240.5 | 0.98959 | (24.1) | — | — | — |
| 35 | Benzyl benzoate | —— | 1.10851 | 25.68 | 2 | 21.70* | 74 |
| 35a | Benzyl benzoate | 317.8–319.6 | 1.10797 | 25.41 | 5 | 23.82* | 91 |
| 36 | Methyl salicylate | 220.6–221.9 | 1.17382 | 22.03 | 21 | 22.3 | 23 |
| 37 | Amyl salicylate | —— | 1.04225 | 29.98 | 4 | 29.83* | 47 |
| 38 | Ethyl phthalate | 226°(120mm) | 1.11051 | 14.64 | 2 | 14.68* | 47 |
| 39 | Ethylacetoacetate | 180.8–182.8 | 1.01418 | 3.75[z] | — | 2.9 * | 48 |
| 39′ | Ethylacetoacetate | 181.4–185 | 1.01585 | 3.50[z] | — | 3.2 * | 26 |
| 40 | Maize Oil | —— | 0.9141 | 5.8 | ¼ | 0 | 8 |
| 40a | Maize Oil | —— | 0.91446 | 8.95 | ¼ | 0 | 18 |
| 40′ | Maize Oil | —— | 0.91136 | 20.7 | ¼ | 19.2 | 18 |
| 41 | Cotton-seed Oil | —— | 0.91107 | 22.4 | ¼ | 20.8 | 24 |
| 42 | Sperm Oil | —— | 0.91407 | 5.7 | ¼ | 3.6 | 24 |
| 42a | Sperm Oil | —— | 0.91424 | 3.9 | ¼ | 2.7 | 18 |

* The density changes due to the mutual solubility of the two liquids have been allowed for in the calcualtions of these interfacial tensions.

[v] Of these boiling points the absolute values are uncertain.

[z] Here the interfacial tension is decreasing rapidly; these values are the extrapolated values at time zero, i.e. at the start.

alkali solutions,—if anything to a less extent in the solutions than in the pure water. But the density changes resulting from the solution of oils in water are less than those resulting from the solution of water in oils. From the values of Table V, therefore, it was possible to forecast the change in (d − d′) due to mutual solution of an oil and a solution from the known change in (d − d′) due to the solution of this oil and water. In all the I.T. tables those interfacial tensions marked with an asterisk (*) are calculated from the densities of the mutually saturated liquids, and those not so marked are calculated from the densities of the original liquids. In many cases where (d − d′) decreased owing to mutual solubility of the two liquids during an interfacial tension experiment, the value of h was found to increase proportionately so that the value of I remained constant (v. eqn. 1). The constancy of the interfacial tension between many pairs of liquids over a considerable time of contact was thus satisfactorily proved, e.g. Table I, expts. 14, 28d, 30c, 38.

In the interfacial tension experiments the organic liquid sometimes became opalescent either throughout, or at the interface, or at its surfaces next the glass where a film of water (etc.) was left between the oil and the glass as the liquids were run into position. In many cases this opalescence was undoubtedly due to the solubility of water in the oil. This opalescence appeared more or less quickly after the contact of the two liquids; it generally started from the outer interface and spread therefrom through the oil; it sometimes, but not always, disappeared after some hours in the thermostat,—presumably as

TABLE II

Interfacial Tensions (dynes/cm.) at 30° of Oils and Water or Concentrated Salt Solutions

| No. | Liquid | With Water Initial I. T. | Salt Solution Density 30°/4° | Salt Solution %NaCl | With NaCl solution (Series S) Initial I. T. | Over hrs. | Final I. T. | After hrs. |
|---|---|---|---|---|---|---|---|---|
| | | (Y) | | | (S) | | | |
| 1′ | Petrol | 46.10 | 1.18544 | 25.34 | 54.36 | 1½ | 55.8 | 20 |
| 11 | Isobutyl alcohol | 2.1 | 1.19439 | 26.42 | 7.30 | 48 | — | — |
| 12b | Amyl alcohol | 4.95 | 1.18685 | 25.51 | 10.52 | ½ | 9.5 | 20 |
| 13 | Phenyl ethyl alcohol | 4.51 | 1.19613 | 26.63 | 9.98 | 1 | 9.64 | 26 |
| 14 | Acetophenone | 12.00 | 1.18544 | 25.34 | 17.84 | 20 | — | — |
| 17 | Acetic anhydride | 3.4 | 1.17578 | 24.18 | 8.0 | 0 | 0 | 3½ |
| 18 | Quinoline | 2.87 | 1.19439 | 26.42 | 9.93 | 47 | — | — |
| 19′ | Aniline | 6.00 | 1.18685 | 25.51 | 12.1 | 1 | — | — |
| 25a | Ethyl acetate | 6.79 | 1.17955 | 24.635 | 14.50 | 22 | 14.50 | 22 |
| 32a | Benzyl acetate | 15.41 | 1.17955 | 24.635 | 21.12 | 3 | 21.50 | 22 |
| 34 | Isobutyl benzoate | (24.1) | 1.19234 | 26.175 | 30.57 | 24 | 30.28 | 24 |
| 35a | Benzyl benzoate | 25.41 | 1.19480 | 26.47 | 31.53 | 2 | 31.07 | 24 |
| 39 | Ethyl acetoacetate | 3.75 | 1.19480 | 26.47 | 10.90 | 2 | 10.2 | 48 |

## TABLE III

Interfacial Tensions (dynes/cm.) at 30° of Oils and Water or Acid or Alkali Solutions

| No. | Liquid | With Water Initial I. T. (γ) | Series X With 1.03 N. Hydrochloric Acid Initial I. T. (x) | Over hrs. | Final I. T. | After hrs. | Series Y With 2.796 N. Sulphuric Acid Initial I. T. (y) | Over hrs. | Final I. T. | After hrs. | Series Z With 1.024 N. Sodium Hydroxide Initial I. T. (z) | Over hrs. | Final I. T. | After hrs. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1′ | Petrol | 46.10 | 45.90 | 19 | 45.7 | 19 | 46.80 | 19 | 46.8 | 19 | 47.22 | ½ | 43.70 | 19 |
| | | | | | | | | | | | †39.6 | – | †24.45 | 19 |
| 14 | Acetophenone | 12.00 | — | — | — | — | 12.46 | 2½ | 10.87 | 22 | 14.20 | 1½ | 14.64 | 25 |
| 16x | Benzaldehyde | 14.1 | — | — | — | — | 12.57 | 1½ | 14.73 | 47 | † 7.4 | 0 | † 3.2 | 24 |
| 19′ | Aniline | 6.00 | — | — | — | — | — | — | — | — | 8.52 | 6 | — | — |
| 25b | Ethyl acetate | 6.39 | 6.84 | ¼ | 0 | 18 | — | — | — | — | 7.02 | ¼ | 6.06 | 19 |
| 26b | Butyl acetate | 8.10 | 7.60 | 4 | 6.1 | 24 | — | — | — | — | 9.20 | 1½ | 7.64 | 20 |
| 27a | Amyl acetate | 10.88 | — | — | — | — | — | — | — | — | 12.4 | ¼ | 10.43 | 98 |
| 27b | Amyl acetate | 12.05 | 12.10 | ¼ | 10.93 | 98 | — | — | — | — | — | – | — | — |
| 28a | Ethyl butyrate | 12.45 | 12.36 | 1½ | 6.90 | 72 | — | — | — | — | 12.9 | ¼ | 11.36 | 24 |
| 28b | Ethyl butyrate | 13.54 | 13.50 | ½ | 8.71 | 48 | — | — | — | — | — | – | — | — |
| 29b | Amyl butyrate | 20.78 | 20.34 | 5 | 19.82 | 75 | 20.47 | 3 | 19.7 | 72 | 16.58 | 2 | 17.02 | 75 |
| 30b | Amyl valerianate | 19.52 | 19.76 | 2 | 18.13 | 19 | — | — | — | — | 14.27 | ½ | 15.0 | 19 |
| 31a | "Oenanthic ether" | 19.55 | 20.47 | 1½ | 19.3 | 72 | — | — | — | — | — | – | — | — |
| 32a | Benzyl acetate | 15.42 | — | — | — | — | 15.76 | 7 | 15.80 | 72 | — | – | — | — |
| 33 | Methyl benzoate | 16.63 | 16.86 | ½ | 15.4 | 72 | — | — | — | — | 13.15 | 0 | 10.1 | 18 |
| 34 | Isobutyl benzoate | 24.1 | — | — | — | — | 24.61 | ¾ | 24.85 | 24 | 13.47 | ¼ | 12.85 | 1 |
| 35 | Benzyl benzoate | 25.68 | — | — | — | — | — | — | — | — | 11.2 | ½ | — | — |
| 37 | Amyl salicylate | 29.98 | — | — | — | — | 29.3 | ¼ | 25.7 | 45 | — | – | — | — |
| 38 | Ethyl phthalate | 14.64 | 14.71 | 2 | 14.45 | 72 | — | — | — | — | 8.4 | ¼ | 10.88 | 22 |
| 39 | Ethyl acetoacetate | 3.75 | — | — | — | — | — | — | — | — | 3.31 | ½ | — | — |
| 39′ | Ethyl acetoacetate | 3.50 | — | — | — | — | 4.14 | 1 | 1.65 | 65 | — | – | — | — |

† These experiments with 1.339 N sodium hydroxide solution.

TABLE IV

Some Varying Interfacial Tensions at 30°

| No. | Organic liquid | Aqueous liquid | Interfacial tension (dy/cm after hours:— 0 | ·½ | 1 | 3 | 18 | limiting | |
|---|---|---|---|---|---|---|---|---|---|
| 16Z | Benzaldehyde | 1.3N. NaOH | 7.4 | 5.36 | 4.84 | 3.9 | 3.3 | 3.2 | (24 hrs.) |
| 17 | Acetic anhydride | Water | 3.1 | 0.96 | — | — | — | 0 | (28 mins.) |
| 17′ | " " | " | 3.7 | 1.27 | — | — | — | 0 | (29 mins.) |
| (17) | " " | Water at 7.5° | 3.15 | 2.8 | 1.5 | — | — | 0.6 | ( 2 hrs.) |
| 17′S | " " | 24% NaCl | 8.0 | 7.8 | 5.9 | [3.2 (2 hrs.)] | | 0 | (3½ hrs.) |
| 25bX | Ethyl acetate | N. HCl | 6.84 | 6.84 | 6.22 | 4.9 | 0 | 2.8 | (10 hrs.) |
| 25bz | " " | N. NaOH | 7.68 | 7.02 | 6.55 | 6.38 | 6.06* | | |
| 28bx | Ethyl butyrate | N. HCl | — | 13.5 | 13.0 | 12.3 | 10.3 | 8.7 | (48 hrs.) |
| 33z | Methyl benzoate | N. NaOH | 13.15 | 12.76 | 12.4 | 11.8 | 10.1 | | |
| 37Y | Amyl salicylate | 2.8N. $H_2SO_4$ | — | 29.3 | 28.5 | 28.0 | 26.7 | 25.7 | (45 hrs.) |
| 39′ | Ethyl acetoacetate | Water | 3.50 | 3.45 | 3.35 | 3.25 | — | 3.18 | (26 hrs.) |
| 39′Y | " " | 2.8N. $H_2SO_4$ | — | 4.14 | 4.14 | 3.6 * | 2.7 | 2.5 | (38 hrs.) |
| | | | | | | | | 1.65 | (65 hrs.) |
| 39 | " " | Water | 3.75 | 3.58 | 3.41 | 3.16 | 2.9 | 2.9 | (49 hrs.) |
| 40 | Maize Oil | Water | — | 5.8 | 3.0 | 1.7 | 0 | 0 | ( 8 hrs.) |
| 40a | " " | " | — | 8.95 | 5.33 | 2.2 | 0 | 0 | (18 hrs.) |
| 40′ | " " | " | — | 20.7 | 20.0 | 19.6 | 19.2 | | |
| 41 | Cotton Seed Oil | Water | — | 22.4 | 22.0 | 21.7 | 20.8 | 20.8 | (24 hrs.) |
| 42 | Sperm Oil | Water | — | 5.70 | 5.05 | 4.31 | 3.67 | 3.57 | (24 hrs.) |
| 42a | " " | " | — | 3.91 | 3.36 | 3.02 | 2.73 | | |

the oil became saturated with water. But why should there be any opalescence under the circumstances, i.e. at constant temperatures? Does emulsification precede true solution? Further it was the general rule for the oils, clear and saturated with water, to become opalescent after cooling—either after the I.T. or density determinations. This is readily explained by the decreasing solubility of the water in the oil as the temperature fell. The only liquids (of Table V) that after saturation with water did not become opalescent after cooling, were the petrols and the phenyl-ethyl-alcohol.

However, in the I.T. experiments with water opalescence only occurred with 17 out of the 42 liquids, and similarly with the acid solutions: it occurred in none of the experiments with the concentrated salt solutions, and in half of the experiments with the caustic soda solutions, and in none of the cases where there is great mutual solubility,—e.g. experiments 11-14 and 17 and 25-28. This opalescence, due to solution, occurs in the primary stage therof, and where solution is great this stage presumably is soon passed. There were no obvious relations between this opalescence and the purity of the oil, the density changes due to mutual solution, and the variations observed in the I.T.

But opalescence may sometimes be due to special impurities thrown out of solution from the oil by solution therein of water, e.g. expts. 7, 10, 16; v. notes, later.

And opalescence is undoubtedly due in certain cases with the solution of sodium hydroxide to chemical action with the oil, i.e. its saponification and separation of the soap, mainly at the interface, e.g. with the liquids 31, 33, 34, 37. This is the case too with the fatty oils and water, e.g. 40a and the 1922 oils (loc. cit.). Such opalescence attains its maximum intensity at the interface, giving there finally a crinkled, quite contaminated and often semi-solid interface. Here there is decreasing and variable interfacial tension. This last opalescence, that due to the dissemination of insoluble products of interaction between the oil and the solution, was noted in our previous paper; but the former opalescence, due to the first solution or dissemination of the water in the oil, was not noted.

In Table I are given the densities and boiling points of the organic liquids used. In most cases they were distilled and the boiling points were determined by carefully standardised thermometers and are correct to within fractions of a degree Centigrade. The initial interfacial tension was generally calculated from the mean value of h obtaining over one or two hours and during the first four or five settings. But in certain cases where the variations in h were small and not definitely in one direction, the mean value of h over the whole period of the experiment was used to calculate the initial interfacial tension; here a final interfacial tension may or may not be given. The final interfacial tension was usually calculated from the densities of the saturated liquids and marked with an x in the table; where they have been calculated from the densities of the original (unsaturated) liquids, the final interfacial tensions will be less accurate.

Variations in the interfacial tension between two liquids must be due to changes; (a) in the liquids due to mutual solubility; (b) in (or at) the interface

due to the concentration there of suspended or dissolved substances from the contiguous liquids, or (c) in the two liquids due to chemical action between them, e.g. the development of acidity in aqueous layers from the hydrolysis of esters. Now the effect of (a) must be instantaneous, i.e. at the interface between two liquids mutual saturation must be rapidly completed. This is obvious from the present experiments, and it is well confirmed by Reynolds' measurement of the surface tensions of saturated liquids by placing one of them in a reservoir and capillary tube in a closed space saturated with the vapour of the second, loc. cit., p. 467. Thus on making contact between two liquids it is impossible to distinguish between (1) the I.T. between the original liquids, (2) the I.T. between the saturated interfaces or accommodated interfaces, and (3) the I.T. between the saturated liquids with saturated interfaces. In the present capillary tube method (3) is only marked from (2) by the related changes of h and (d − d′), on allowing for which (3) = (2). But it is in general possible to note the further stage, when the saturated liquids have evolved a contaminated interface carrying adsorption products or products of reaction due to (b) or (c). These effects are cumulative and generally slow enough to observe.

The conclusions from the interfacial tension experiments are as follows, certain particular cases being referred to in detail under the special notes about each organic liquid (p. 805 et seq.). From the results of Table I of the I.Ts. with water it will be seen that:—

(a) The oils of variable I.T., 7 samples, are impure oils, e.g. 16, or oils suffering chemical changes, e.g. 5; here the average variation observed in the I.T. over the time of contact was 10% of the value.

(b) The oils of decreasing I.T. are the fatty oils, 40 to 42, the oils of greatest solubility in water, 11, 12, 17, 19 and 39, certain oils that are complex mixtures, e.g. 5′, 7, 9, 29, and oils that react chemically with the water, e.g. 5′, 24, 26, 39. Here the average variation in I.T. is from 1 to 100%; there are 32 cases of this type.

(c) The oils of increasing I.T. are rare,—14 samples. Special reasons operate for the terpenes, 6 & 6a, and for the three petrols, 1a, 1b, 1c. Many of the remaining nine cases approximate to constant I.T.,—the average increase of I.T. being 2% of the I.T. value.

(d) The oils of constant I.T., 25 samples, are the purest liquids, usually with not too great solubility in water, e.g. 2, 3b, 14, 21, and 32b, and certain oils that are mixtures, e.g. 28, 29b, 30c and 31. Here the average variation of I.T. is 1.6% (from 0.2 to 6%),—partly depending on the absolute value of h.

It may be concluded that:—

(1) Purification of an oil tends to produce a more constant I.T.; e.g. 1b to 1d, 5 to 5a, 30 to 30c, 35 to 35a. With two pure liquids, where there is no chemical action or excessive mutual solubility, the I.T. is constant over a long period; in the present experiments the variation in the I.T. in such cases over one to three days does not exceed 1% of the initial I.T.

(2) A mixed oil has often a similarly constant I.T. against water or a solution; e.g. expts. 1′, 28 a, b, c and d, 29 to 31b, and also 32a, 32aY and 32aS, 34Y etc.

(3) Evidently a mixed oil only gives a varying I.T. against water or a solution where selective adsorption, or concentration, at the interface occurs with some of the components of either or both of the liquids in contact, or where chemical action occurs that results in such adsorbable products. Experiments 1′ and 1′Y (with constant I.T.) contrast with experiments 1′Z, 1a, b, c, and d (with varying I.T.). Such selective adsorption is partly the reason why the fatty oils and water give decreasing I.Ts.; thus the filtered maize oil, 40a, gives a higher and slower varying I.T. with water than the original oil, 40. For I.Ts. against colloidal solutions see Reynolds, loc. cit.

(4) Apart from the variability of the I.T., however, purification of an oil tends to raise the I.T.; e.g. 1b to 1d, 3a to 3b, 25 to 25a and 25b.

(5) In most cases, however, the I.T. of oil-solution tends to rise with the higher fractions of the oil quite apart from purification; e.g. with oils 26 to 31.

(6) A mixture of oils often has a lower I.T. against a given solution than the average I.T. of the components. Thus with the amyl butyrate the mean value of the I.Ts. of the fractions is 19.3 and the original liquid has I.T. of 17.7; this is a rough test as initial and final fractions were rejected; the ethyl acetate and amyl valerianate, however, similarly confirm the rule.

(7) The greater the mutual solubility between two liquids the lower is the I.T. Thus oils have lower I.Ts. against salt solutions than against pure water; and the following groups of liquids are in order of decreasing solubility and increasing I.T.,—benzene, toluene and xylene; isobutyl, amyl and phenylethyl alcohols; ethyl, butyl, amyl and benzyl acetates (v. Seidell's "Solubilities"). The I.T. = $S.T._{A'} - S.T._{B'}$, where $S.T._{A'}$ is the surface tension of the liquid, A, saturated with the liquid, B, and $S.T._{B'}$ is that of B saturated with A,—Reynolds' rule (loc. cit.); when the liquids are completely miscible $S.T._{A'} = S.T._{B'}$ and the I.T. = 0. The difference between the S.Ts. of the pure liquids, $S.T._A - S.T._B$, gives the maximum possible I.T. between them, that which would obtain if they were completely immiscible. The more the observed I.T. is less than $(S.T._A = S.T._B)$, the greater is the mutual solubility. Where the mutual solubility is great this method of measuring the I.T. is unsuitable, unless the liquids were mutually saturated beforehand.

Table II gives the interfacial tensions at 30° of thirteen liquids against concentrated solutions of common salt in water. From the density of the salt solution the percentage weight of salt therein was taken from the Landolt-Börnstein tables. The conclusions are as follows.

(8) The I.T. of an oil against the salt solution is greater than its I.T. against water at the same temperature, or $I < s$. These salt solutions are approximately of the same concentration, and $s = 1.07 \cdot I + 5$—(2). A relation like this equation (2) can be deduced from Reynolds' rule. Let $S.T._s$, $S.T._O$, and $S.T._W$ be the surface tensions of the salt solution, oil and water

respectively; then, after Reynolds, if the mutual solubility is negligible,— $s = S.T._S - S.T._O$, and $I = S.T._W - S.T._O$, and thus $s - I = S.T._S - S.T._W$ = a constant. Now at 30° $S.T._W = 71.5$ and the S.T. of a 25% salt solution = 80.5 (dynes per cm.), so that $(s - I) - 80.5 - 71.5 = 9$. Equation (2) approaches this with liquids of high I.T.

(9) With a given oil the variation of the I.T. against a salt solution is usually less than the variation of its I.T. against water. The experimental error is probably greater with the salt solution than with water, but the lower solubility of the oil in the salt solution is the cause of this I.T. behaviour. The oil also would take up less water from the salt solution than from pure water; also hydrolysis of an oil would be less rapid with a salt solution than with water. From equation (2) and the values of s for the isobutyl alcohol and isobutyl benzoate there have been obtained the values of I for these liquids, which values are in brackets in Table II.

Table III gives the interfacial tensions at 30° of organic liquids against the solutions of hydrochloric and sulphuric acids and the solution of sodium hydroxide. The following conclusions may be drawn.

(10) There are five cases of decreased initial I.T. with the hydrochloric acid solution, and six cases of increased I.T., the average increase being 0.33 dyne per cm., compared with the I.Ts. against water. The general behaviour is that the aqueous solutions of salts, acids and bases the I.T. of an oil is greater than with water, and the above cases of increased I.T. with the HCl solution are similar to the normal results recorded by other observers[1]. But all the oils examined by the author gave with the HCl solution I.Ts. decreasing with time, and thus the initial I.Ts. given in Table III may be rather low.

(11) With the normal hydrochloric acid solution the interfacial tension of an ester varies more than the I.T. with water, the former I.T. decreasing with the time and from two to fifty times more than the corresponding decrease (if any) of the oil-water I.T. Now the experimental errors are not greater—at any rate, not 5 or 50 times greater—with the solutions than with water, and should not lead always to decreasing I.Ts. in the former cases. Also the mutual solution is rather less with the esters and the acid solutions than with the esters and water (Table V). The varying decreasing I.Ts. of the esters and the acid solutions must then be due to the adsorption at the interfaces of the products of the hydrolysis of the esters. The alcohols, resulting from the hydrolysis, will increase the mutual solubilities of the two layers[2] and therefore decrease the I.Ts.; this effect will be the more pronounced with the alcohols of lower molecular weight. The presence of the lower fatty acids, too, will produce probably the same effect. Esters of the lowest molecular weight have the greatest velocities of saponification[3] and it is these esters that with HCl solution give the most rapid decrease of I.T.,—though the mutual solubilities are the greatest with these also. In contact with water for

[1] See Harkins and others: J. Am. Chem. Soc., (1916-1917); Reynolds: loc. cit.
[2] Seidell: "Solubilities".
[3] Reicher: J. Chem. Soc., 48, 1034 (1885).

## Table V

### Densities (30°/4°) of mutually Saturated Liquids

| Liquids | Number | Densities Satd. Oily Layer | Densities Satd. Aqueous Layer |
|---|---|---|---|
| From special tests:— | | | |
| Petrol—Water | 1a | 0.6692 | 0.9955 |
| Petrol—Water | 1b | 0.71025 | 0.99564 |
| Petrol—Water | 1c | 0.73146 | 0.99566 |
| Benzene—Water | 2 | 0.86708 | 0.99563 |
| Toluene—Water | 3b | 0.85164 | 0.99561 |
| Amyl alcohol—Water (0.80398) | (12) | 0.82167 | 0.99167 |
| Aniline—Water (1.01302) | (19) | 1.01385 | 0.99716 |
| †Chloroform—Water (1.4897) | (20) | 1.4831 | 1.0002 |
| Carbon tetrachloride—Water (1.57432) | (21) | 1.57412 | 0.99594 |
| Nitrobenzene—Water (1.19189) | (22) | 1.19120 | 0.99600 |
| Chlorobenzene—Water | 23b | 1.09533 | 0.99577 |
| From I.T. Tests:— | | | |
| Petrol—Water | 1d | 0.7100 | 0.9957 |
| Petrol—Water | 1′ | 0.72774 | 0.99569 |
| Turpentine—Water | 5′ | 0.85215 | 0.99581 |
| Pine Oil—Water | 8 | 0.92308 | 0.99567 |
| Phenyl-ethyl alcohol—Water | 13 | 1.01082 | 0.99577 |
| Acetophenone—Water | 14 | 1.01979 | 0.99571 |
| " —$H_2SO_4$ | 14Y | 1.01977 | 1.07972 |
| " —NaOH | 14Z | 1.01993 | 1.03907 |
| Benzaldehyde—$H_2SO_4$ (1.04855) | 16Y | 1.04710 | 1.08104 |
| " —NaOH (1.03838) | 16Z′ | 1.03548 | 1.05415 |
| Ethyl acetate—Water | 25b | 0.89397 | 0.99484 |
| Butyl acetate—Water | 26b | 0.86609 | 0.99316 |
| " —HCl | 26bX | 0.86678 | 1.01254 |
| Amyl acetate—Water | 27b | 0.85963 | 0.99556 |
| " —HCl | 27bX | 0.85968 | 1.01348 |
| " —NaOH | 27aZ | 0.85589 | 1.03824 |
| Ethyl butyrate—Water | 28a | 0.87753 | 0.99535 |
| " —Water | 28b | 0.87587 | 0.99550 |
| " —HCl | 28bX | 0.87721 | 1.01309 |
| Ethyl butyrate—NaOH | 28aZ | 0.87719 | 1.03815 |
| Amyl butyrate—Water | 29b | 0.85833 | 0.99559 |
| " —HCl | 29bX | 0.85835 | 1.01345 |
| " —NaOH | 29bZ | 0.85799 | 1.03847 |
| Amyl valerianate—Water | 30c | 0.86171 | 0.99579 |
| " —HCl | 30bX | 0.86053 | 1.01345 |
| " —NaOH | 30bZ | 0.85948 | 1.03836 |

† For chloroform and water the figures are specific gravities at 22° by Herz,—from Seidell's "Solubilities".

TABLE V (continued)

| Liquids | Number | Densities Satd. Oily Layer | Satd. Aqueous Layer |
|---|---|---|---|
| "Oenanthic ether"—HCl | 31aX | 0.85968 | 1.01356 |
| Benzyl acetate—$H_2SO_4$ | 32aY | 1.04611 | 1.08033 |
| Methyl benzoate—Water | 33 | 1.07786 | 0.99570 |
| Isobutyl benzoate—$H_2SO_4$ | 34Y | 0.98958 | 1.07959 |
| " —NaOH | 34Z | 0.98954 | 1.03832 |
| Benzyl benzoate—Water | 35a | 1.10745 | 0.99565 |
| Amyl salicylate—Water | 37 | 1.04207 | 0.99561 |
| " —$H_2SO_4$ | 37Y | 1.04226 | 1.07959 |
| Ethyl phthalate—Water | 38 | 1.10929 | 0.99569 |
| " —HCl | 38X | 1.10935 | 1.01349 |
| " —NaOH | 38Z | 1.10906 | 1.03830 |
| Ethyl acetoacetate—Water | 39′ | 1.01840 | 0.99643 |
| " —$H_2SO_4$ | 39′Y | 1.01160 | 1.0803 (?) |

Densities of the Aqueous Solutions at 30°:—

| Solution | Density $\left(\frac{30°}{4°}\right)$ | Normality at 15° | % Solute approx. | Series |
|---|---|---|---|---|
| Water | 0.99567 | 0 | 0 | — |
| Hydrochloric acid | 1.01351 | 1.030 | 3.69 | X |
| Sulphuric acid | 1.07957 | 2.796 | 10.2 | Y |
| Sodium hydroxide | 1.03831 | 1.024 | 3.6 | Z |
| Sodium hydroxide | 1.05200 | 1.339 | 4.9 | Z′ |

several days these esters gave increasingly acid solutions, but the effect of this hydrolysis on the I.T. of the ester-water is slight and not to be distinguished, in general, from those of other disturbing causes such as solubilities and impurities. But with the HCl solution, which accelerates the saponification (as is well known), the effect of the latter is enhanced.

(12) The interfacial tension, y, of an oil against the 2.796 Normal sulphuric acid solution is greater than its I.T., I, against water, and excepting the benzaldehyde and the amyl salicylate, $y = 1.017 \cdot I$,—(3).

(13) With oils insoluble in and unacted on by both water and the sulphuric acid solution, the variations in the interfacial tensions will be the same in the both cases, e.g. with petrol. With the $H_2SO_4$ solution and acetophenone, benzaldehyde and ethyl acetoacetate the variation in the I.T. was large; in the last case chemical action was undoubted and in the former two cases most probable. With the esters and the $H_2SO_4$ solution there is, in general, a decrease in the I.T. with time, which is comparable to that occurring with the HCl solution.

(14) There is no simple relation between the I.T. of oil-water and that of the oil against the sodium hydroxide solutions. Taking the initial I.T. of petrol with the 1.024N NaOH solution as showing the normal rise of I.T.

with this solution compared with water, then the lower esters show a greater rise proportionately, and the higher esters—the last seven liquids in Table III, series Z—show not even a rise but a considerable lowering of I.T. from the oil-water I.T.

(15) With the sodium hydroxide solutions the variations in the interfacial tensions of the oil are large; here the I.Ts. usually decrease with time. In many cases the capillary meniscus lags behind on making a fresh setting and h is temporarily large; the meniscus behaves as if it were filmed, and contamination of the meniscus is evident with the last five esters of the series Z. Here, then, the variation of I.T. is larger with the higher than with the lower esters; also for the lower esters the I.T. variation with the normal alkali solution is less than that with the normal acid solution but greater than that with water. But for the higher esters the I.T. variation with the alkali solution is greater than that with the acid solution and much greater than that with water.

The case of petrol with the normal alkali solution may be taken to indicate that the merest traces of saponificable impurities in an oil greatly lower the I.T. from that with water after contact for some time; and possibly traces of soaps or similar substances (e.g. sodium silicate) in the alkali solution will be adsorbed at the interface and do likewise,—see the result with petrol and the 1.339 N solution of alkali. The higher esters give low I.Ts. with the alkali solutions, for any acids of high molecular weight, traces of which are present in them originally or are formed by their hydrolysis, will form soaps with the alkali and thus lower the I.T. Similarly with the benzaldehyde that contained some benzoic acid. The esters of lower molecular weight, e.g. the acetates, form (sodium) salts of little soap-like character; here the initial I.T. is higher than with water—the normal behaviour, and the decrease of the I.T. with time is less than with the higher esters. Under equal conditions, the higher esters are the less rapidly hydrolysed, but the products formed from them have the greater power of decreasing the I.T. and in extreme cases the contamination of the menisci is quite evident. Certainly the hydrolysis of esters by acid and alkali solutions, and to a much smaller extent by water, is one factor which causes their decreasing I.Ts. The large decrease of I.T. with the lower esters and the normal HCl solution is due to this cause supported by the added one of increased mutual solubility due to the products of the hydrolysis; and the large decrease of I.T. with the higher esters and alkali solutions is due to the hydrolysis and to the soaps formed thereby.

## Notes on the Organic Liquids used, Their Purity, Interfacial Tensions, etc.

In this section the facts will be condensed as much as possible, and standard abbreviations used often, e.g. b.p. for boiling point, S.T. and I.T. for surface and interfacial tension. After the organic liquids had been shaken with water at the ordinary temperature or merely kept in contact therewith at this temperature or at 30° (including the I.T. tests themselves), the acidity or alkalinity

of the water was frequently tested by litmus paper (and sometimes by methyl orange); these tests will be generally referred to later to indicate the purity or hydrolysis of the organic liquid. The numbering of the oils (organic liquids) and samples corresponds with that of the tables.

(1) "Plume Benzoline", from the Vacuum Oil Co., was divided into the distillate boiling between 40° and 70° and the residue; these fractions were of approximately equal bulk. They were then fractionated separately; the b.p. rose regularly throughout each fractionation. From the former, after discarding the more volatile fraction, was collected *petrol* 1*a*, in bulk about 3/10 ths of the original benzoline. From the latter, after discarding the first distillate, were collected *petrol* 1*b* and *petrol* 1*c*. These petrols, from Pennsylvanian petroleum, presumably consist of the paraffins,—hexane, heptane, etc. With these petrols and water h increased with time; the density changes did not account for the rise in h, and thus the I.T. increased. However it was found later that each of these petrols gave with water an acid solution. The cause of this acidity was not obvious. Then fresh samples of petrol were prepared. The samples 1a, 1b, and 1c, after use as above, were dried with $CaCl_2$ and bulked; this liquid was filtered on to $K_2CO_3$, and after 16 hours was filtered off and distilled. The first third was rejected and then one-half was collected as *petrol* 1*d*. Another sample of commercial petrol, which gave with water a solution practically neutral or very feebly acid, was distilled; one-fifth of it was rejected and then one-half was collected as *petrol* 1′. Petrols, 1d and 1′, gave with water neutral solutions, even after four days' contact with water in the I.T. apparatus. With water and the petrols, 1d and 1′, h was constant over 5 settings in the first two hours, but after 16 hours h had decreased. With sample 1d this decrease continued to the third day, after which h remained constant for another 24 hours. With sample 1′ h increased after 16 hours but very slowly after the third day. The final I.T. was a little greater than the initial I.T., but this might be within the limits of the experimental errors, so that this petrol might be considered to have a constant interfacial tension with water. With the NaCl, aq. the rise of I.T. was more pronounced; after the test the solution was neutral. With this petrol and the NaOH, aq. h was variable; it was constant in the first set over half an hour; in each succeeding setting the initial value of h increased, but during each setting h decreased. With the 1.339 N. NaOH, aq. the variations in h were still greater.

In a paper on I.T. between petroleum products and water, E. M. Johansen[1] states that the presence of small amounts of organic acids in the former affects their I.T. against water and dilute alkali solutions. Shoeter and Ellingsworth[2], state that Donnan showed that with a hydrocarbon oil to which a little fatty acid had been added, the I.T. of the oil-alkali solution was much lower than that of the oil-water, but with an ordinary hydrocarbon oil, i.e. free from fatty acid, the oil-water I.T. is little affected by addition of alkali. Judging from Harkins and Humphrey's work, the I.T. between a hydrocarbon

[1] J. Ind. Eng. Chem., 16, 132 (1924).
[2] Proc. Roy Soc., 92, 231 (1916).

oil and water is raised by addition of mineral acids and salts to the water, lowered by organic acids (the lowering increasing from formic to butyric acid), lowered by the first additions of alkali and then raised by further additions (above 1/100 or 1/10th normal) of alkali; also the I.T. is greatly lowered by small additions of soluble soaps (e.g. sodium oleate below 1/100 normal).

It might be concluded that petrol 1′ even after careful distillation contained traces of impurities, possibly volatile fatty acids, that caused the variable and, in general, diminishing I.T. against alkali solutions, and that with the 1.3 N NaOH, aq. there might be further impurities in this solution which were not present in the normal solution. Even the petrol 1d, which was twice distilled besides being treated with $K_2CO_3$, gave with water an I.T. much more variable than would be expected. The interfacial tensions of hydrocarbon oils against water or aqueous solutions seem to be extraordinarily sensitive to minute amounts of impurities.

(2) The *benzene* was that carefully purified in 1922. On shaking with water or after keeping with water for two years, it gave a solution neutral to litmus. Its density (Table I) was unchanged after keeping. The I.T. of this benzene-water could be considered constant over 20 hours; the value in Table I is somewhat higher than the I.T. found in 1922, and there was some tendency for this I.T. to decrease with time.

(3) Commercial toluene was treated with $P_2O_5$ for twelve hours and then fractionated. The first reaction made *toluene* 3*a*; the second fraction, *toluene* 3*b*, was the main one and in bulk was about one-half of the original liquid. These toluenes had similar b.ps. to the 1922 samples, but lower densities and lower I.Ts. with water, indicating that the present samples were the less pure. Toluene 3b after 17 hours' contact with water at 30° gave a slightly acid solution; sample 3a was probably similar.

(4) Xylene was shaken for a few minutes with $P_2O_5$ and then fractionated. The first fraction was neglected; *xylene* 4*a*, the next fraction, was the main lot; *xylene* 4*b*, the next fraction involved boiling nearly to dryness. The three isomers were doubtless present in both samples, 4b being the more homogeneous (m-xylene). Both samples gave neutral solutions with water, but the I.T. behaviour indicated that 4b was the purer or the more homogeneous.

(5) *Turpentine*, 5, was the distilled American turpentine of 1922 (b.p. = 160.6°). It had been kept for two years in a corked bottle but not secure from oxidation, which certainly had occurred. The liquid now had a deeper yellow colour, and the glass in contact with it had been attacked and permanently roughened. The density at 30° had increased from 0.85460 to 0.91207. The variations in h were fairly large; evidence was seen of solution and of density changes, and the apparent constancy of the I.T. was certainly the result of the balancing of several factors, e.g. the lowering of the I.T. due to contamination of (or adsorption at) the interface, the raising of the I.T. due to the water becoming acid, changes in (d—d′) etc. A minimum I.T. of 8.5 dy/cm was obtained after a long setting of 17 hours, and then the menisci were flat. These I.Ts. are less than one-half of the 1922 values. Reynolds also found that the

I.T. of turpentine-water decreased with the age of the turpentine, when the latter was kept exposed to air.

This turpentine was placed for an hour or so over $CaCl_2$, filtered and distilled. It frothed over at the start, probably due to decomposition, and then about two-fifths of the original liquid was collected as a slightly milky distillate, which however became clear on passing through filter paper,—preferential adsorption of water (?). The distillate was *turpentine* 5*a*; it gave a strongly acid solution with water. It like all the terpenes (oils 5 to 10) showed variable I.T. with water, but the I.T. was greater and its variability was less with this distilled and purer turpentine 5a than with the original turpentine 5.

*Turpentine*, 5′, was a colorless American turpentine, which was filtered only before testing. It had $D_4^{14^\circ} = 0.865$ and $[\alpha]_D^{14^\circ} = +\ 19.9^\circ$. It gave with water a neutral or very feebly acid solution, but the aqueous solution from the I.T. test after 18 hours was feebly acid and after 46 hours quite acid. The minimum I.T. observed was 9.5 dy/cm, after 18 hours.

*Terebene*, 6, from Howards and Sons, London, was used straight from the bottle. It was very pale straw-colored, gave a strongly acid solution with water, and had $D_4^{14^\circ} = 0.871$ and $[\alpha]_D^{14^\circ} = -\ 6.0^\circ$. The I.T. decreased slightly in each setting.

This was shaken with $CaCl_2$ for half an hour, filtered and fractionated. About one quarter came over as a milky liquid from 168.5° to 174°, then one-half collected as *terebene* 6*a*. This was made quite clear by filtering and standing; evidently some decomposition accompanies the distillation. It gave a strongly acid solution with water, and had $D_4^{14^\circ} = 0.866$ and $[\alpha_D^{14^\circ} = -\ 5.2^\circ$. Its I.T. behaviour was similar to that of the original terebene 6; compare experiments 6 and 6a with experiments 5 and 5a.

*Limonene*, 7, was prepared from Sicilian oil of lemon by distillation under reduced pressure. This sample probably contains about ten per cent of terpenes other than limonene. It was light straw brown in colour, and had $[\alpha]_D^{15^\circ} = +\ 65^\circ$. It gave with water an acid solution.

*Pine oil*, 8, was "standard A" oil from Georgia, U. S. A. It was a clear yellow, somewhat viscous oil, and gave with water an acid solution—the acidity being more pronounced after prolonged contact. It had $D_4^{13^\circ} = 0.937$ and $[\alpha]_D^{13} = +\ 2.00^\circ$. h increased with time rather more than (d—d′) decreased, so that the I.T. increased.

*Eucalyptus oil*, 9, was from Maryborough, Victoria. It was a colorless oil, containing 75% cineol, and had $D_4^{13^\circ} = 0.920$ and $[\alpha]_D^{13} = +\ 1.28^\circ$. The water from the I.T. test was feebly acid. This oil was similar to the (cineol) eucalyptus oil of 1922.

*Cineol*, 10, was separated from the above oil by phosphoric acid; the cineol-phosphate was pressed dry, washed with petrol, decomposed with water; the separated cineol was washed with water, dried over $CaCl_2$ and filtered before use. It was a yellowish oil; exposed to a temperature of $-8^\circ$ for one hour it did not freeze at all; thus it was not pure cineol, of which the accepted melting point is $-1^\circ$. In the I.T. test h was very variable; in each

setting h decreased for the first few minutes, then increased for about 20 minutes, and then in the last setting decreased over 18 hours. After a few minutes contact with water, the cineol became opalescent at the interface, and this finally spread throughout the whole of the cineol and little drops appeared at the outer meniscus. It might be supposed that as the cineol became saturated with water, it deposited some other component (petrol, phellandrene, etc.). In Table I the initial Y is the initial and minimum value in the first setting, which was also the mean of the minimum values in the first three settings over one hour; maximum recorded Y = 10.1, and the final value after 20 hours = 6.6 dy/cm. For giving the I.T. of pure cineol these figures are worthless but they illustrate the possible variations in I.T. of a complex mixture. Isobutyl alcohol,—from E. Merck, Germany, was placed with anhydrous $K_2CO_3$ for several days, then filtered and fractionated. The liquid boiled from 104° and about two-thirds was distilled off till the rate of increase in the b.p. slackened and then was collected the *isobutyl alcohol*, 11, in bulk about one-fifth of the original. This sample has constants agreeing with Perkin's isobutyl alcohol[1]. It gave a neutral solution with water and was optically inactive. It was too soluble in water for any I.T. therewith to be obtained directly with accuracy, the value (1.5 dy/cm) quoted in Table I being merely indicated,—h being very small and soon zero and the menisci flat and vanishing. Against concentrated salt solution it gave a constant I.T., from which the I.T. with water may be taken as 2.1 dy/cm.

(12) *Amyl alcohol*, from Merck, was treated with $K_2CO_3$ for 12 hours, then filtered and fractionated. After rejecting one-fifth, the rest was collected in two equal lots as samples 12a and 12b. These samples of amyl alcohol were slightly laevorotatory, $[\alpha]_D^{14} = -0.9°$; they were mainly inactive isobutyl carbinol with a little of the active variety and of other isomers. They gave with water solutions acid to litmus. Amyl alcohol and water are appreciably mutually soluble, and the density changes due to such are considerable (Table V). In the I.T. tests with water for the first hour h and (d—d′) both decreased, but afterwards h was nearly constant. The 1922 samples of amyl alcohol were from a different source to the above; the results for them were recalculated and put in Table I as for samples 12′a and 12′b ,and they were similar to the above. At 16° the S.T. of water is 73.45, and the S.T. of the original Merck's amyl alcohol was 23.35, and thus the maximum I.T. (of the liquids before mutual solubility) would be 73.45 − 24.35 = 49.1 dy/cm; the much smaller I.Ts. observed reflect the great mutual solubility.

(13) *Phenyl-ethyl alcohol*, from L. Givaudan, Geneva, was purified by distillation, collecting about three-quarters of the original liquid as sample 13. This is presumably the normal alcohol, $C_6H_5 . CH_2 . CH_2 . OH$, though the b.p. was higher than the accepted figure,—212° in Atack's Year Book, 1918. Sample 13 was a clear, colorless, slightly viscous liquid with a faint smell; it was practically optically inactive; it was somewhat soluble in water (Table V) and the solution was neutral to litmus even after 25 hours contact with the alcohol. The I.T. is practically constant with water or salt solution.

[1] J. Chem. Soc., 45, 421 (1884).

(14) Commercial *acetophenone*, from Givaudan, was a slightly straw-colored liquid. It was distilled, the first quarter rejected, and then sample 14 was collected—in bulk about one-half of the original liquid. This gave with water a solution neutral or very feebly acid, even after 24 hours contact in the I.T. apparatus. In the I.T. tests with the salt, acid and alkali solutions the variations in h were more irregular than might have been expected. With the $H_2SO_4$, aq. I.T. test some turbidity was noticeable and the menisci tended to flatten, and the I.T. decreased. Is there any chemical action here? With the alkali solution h and (d—d′) both increased with time, so the I.T. increased; here no turbidity was observed.

(15) A small amount of Merck's "purest furfurol", kept in sealed vessels filled with hydrogen, was distilled. All of the distillate was taken, and a trace of moisture in it was removed by filtering. This sample of *furfural*, 15, was of pale straw-yellow colour and gave with water a neutral solution. The I.T. was practically constant; h, which was always small, showed a tendency to increase with time, probably due to density changes as furfural is somewhat soluble in water.

(16) *Benzaldehyde*, from Schuchardt, was purified by distillation in air, and consequently the product certainly contained some benzoic acid due to oxidation. Samples 16 and 16′ were from different stocks; with water both gave solutions acid to litmus but probably sample 16 was the purer. However the I.Ts. of the two samples were more constant and closer than might have been expected, considering the benzoic acid as a variable impurity and the density changes which were considerable (Table V). The supply of this material was limited; otherwise it would be an interesting one to study.

The sample 16′ after keeping a couple of months in a stoppered bottle was found to contain some crystals of benzoic acid. The latter were filtered off, and the filtrate had $D_4^{30°} = 1.04855$,—a considerable increase over the density of the original sample. This filtrate, which must have been saturated with benzoic acid, was used in an I.T. experiment with the $H_2SO_4$ aq.. Here was turbidity, sticking of the capillary meniscus, and chemical action?

Other benzaldehyde that had been kept under water for two months, was separated therefrom and used in an I.T. experiment with the 1.339 N. NaOH, aq.. This water-saturated benzaldehyde had $D_4^{30°} = 1.03838$, and presumably contained less dissolved benzoic acid than the preceding lot. Here the I.T. (z) decreased continuously; the outer meniscus was at first flat and than concavè downwards (the reverse of the usual, when the organic liquid is introduced from the top of the apparatus). No turbidity was noticed, but the final alkali solution was yellow; in this case there was probably chemical action,—at least with the alkali and the benzoic acid impurity.

(17) *Acetic anhydride* was shaken for some minutes with $P_2O_5$, then filtered and fractionated. The original of sample 17 was from Merck, and that of sample 17′ from May and Baker, London. With acetic anhydride and water h and the I.T. were always small and fell rapidly to zero. At 8° the S.T. of sample 17 was 33.85, and of sample 17′ was 34.05; the S.T. of

water at 8° is 74.65, so that the maximum possible I.T. with water at 8° should be 40.8 dy/cm.. The observed low I.T. points to great mutual solubility. But the hydrolysis of acetic anhydride results in the formation of acetic acid, which is completely miscible with both the anhydride and water, and therefore certainly increases the mutual solubility of the latter liquids. The anhydride on shaking with an equal volume of water at 12° was completely miscible in an hour, but with equal volumes of water and acetic acid together it was immediately completely miscible. Thus the originally low I.T. decreases continuously on account of the increased mutual solubility due to the acetic acid produced by the hydrolysis. In a concentrated salt solution both the mutual solubility of the original liquids will be less and the rate of hydrolysis will also be less. In the I.T. experiments the lowering of h with time was faster with water at 30° than with water at 7.5°, and the lowering with concentrated salt solution at 30° was less than that with water at 7.5° (see Table IV). The I.Ts. given in the tables are the extrapolated values at time zero, i.e. at the time of first reaching the position or setting in the I.T. apparatus, but the liquids were of course in contact for some minutes before that. Slight irregularities occur for the first readings,—temperature and solution changes then; the final values of *h* also fall abnormally rapidly but many possible complications occur then. As no allowance was made for density changes due to the mutual solubility, the values of the I.Ts. must be only approximate.

(18) *Quinoline*, from the British Drug Houses Ltd., London, was distilled. It boiled at a constant temperature,—say 237.5° (Young), our thermometer being incorrect. About half of the original liquid was collected as *quinoline*, 18, a pale straw-colored liquid, which gave with water a neutral solution even after 5 months contact. When the organic liquid is heavier than water, it is introduced into the I.T. apparatus from the bottom upwards, and then the outer menuscus is higher than the capillary meniscus and both are convex upwards; this is the usual behaviour. Quinoline and water formed the only observed exception to that behaviour; in this case the menisci were concave upwards and nearly flat, and the capillary meniscus was the higher; when re-setting in the apparatus the outer meniscus might be raised momentarily above the capillary meniscus, but after the setting the latter soon rose up through the former and took up a position as before. Quinoline must have a great power of replacing water from glass surfaces; a study of such and of the contact angles would be interesting. Duplicate I.T. experiments were done with quinoline and water; in both h was small and its variations rather erratic; the general tendency was for h to rise with time,—a lag that obviously was related to the facts above. Quinoline and water, too, are somewhat mutually soluble, and the density changes (not determined) would also tend to make h rise. The initial I.T. given in Table I was the mean result of the two experiments. Over a longer period of time the results are less regular; in both experiments after 24 hours the Y approximated to 3.0 dy/cm. With salt solution the I.T. was constant over two days; here the quinoline was introduced from the top downwards and no irregularities (as with water) were observed.

The liquids, 19 to 22, were those prepared in 1922. The results in Table I for these liquids and water are taken from the writer's previous paper, the final I.Ts. being corrected for density changes and the boiling-points for thermometer errors. The *aniline* 19′, used with the salt and the soda solutions, was purified by distillation; it had $D_{4^\circ}^{30^\circ} = 1.01302$. With the NaOH, aq., h varied at first somewhat irregularly but then tended to decrease; there is noticeable solution of the aniline into the NaOH, aq., but the density changes were not determined.

(23) *Chlorobenzene*, from the British Drug Houses Ltd., was fractionated and the samples 23a and 23b were obtained. The latter was probably the purer; it was twice the bulk of sample 23a; both gave with water solutions very feebly acid, and after 20 hours contact with water at 30° sample 23b gave an acid solution. For both samples and water the rise of h with time rather more than counterbalanced the decrease of (d—d′). The rise of I.T. might be due to the increasing acidity of the solution next the capillary meniscus.

(24) *Benzyl chloride* was distilled and about half of the original liquid was obtained as samples 24a and 24b. These were nearly but not quite clear and colorless; on shaking with water for a minute these samples gave no decided acid solutions; after being in the I.T. apparatus for 4 days, the water therefrom was acid, containing HCl but in no great amount. In the I.T. experiments in the initial settings h was constant; thereafter h decreased with both samples, and approximately proportionately to the time and showing no signs of reaching a limit; the rate of decrease was somewhat greater for sample 24a. In both experiments the benzyl chloride became quite opalescent or turbid. The turbidity began a few minutes after the contact with water, was pronounced throughout the oil after one hour, was always most prominent at the outer meniscus, and was somewhat more marked with sample 24a than with 24b, and with the latter sample was not worse (perhaps better i.e. thinner) during the last two days than it had been during the first two days. This turbidity was therefore due to the solution of the water in the oil mainly, but hydrolysis had undoubtedly occurred to some extent and might have been partly responsible for the turbidity as for the decrease in the I.T. The benzyl chloride, after drying with $CaCl_2$ and filtering, had $D_{4^\circ}^{13^\circ} = 1.1050$ and at 13° its S.T. = 38.3 dy/cm; therefore the maximum I.T. against water at 13° would be 73.9 − 38.3 or 35.6 dynes/cm. As the initial I.T. at 30° was 30 dynes/cm, the mutual solubility was not large. On contact with a concentrated salt solution at 30° the benzyl chloride immediately gave such a turbidity that the menisci could not be seen and therefore the I.T. could not be determined.

(25) *Ethyl acetate, sample 25*, was that as supplied by Merck. The greater portion was washed several times with water and all of the water washes were acid. Then it was shaken for some minutes with $CaCl_2$, filtered on to $K_2CO_3$. After 40 hours it was filtered on to $P_2O_5$, shaken therewith for 1 hour, filtered off and then slowly fractionated. Rejecting the first quarter, there were collected the samples 25a and 25b, each in bulk about a third of

the original liquid. Sample 25b appeared to be very pure product (see previous paper); on shaking with water for a minute at the ordinary temperature it gave a neutral solution, but that from the I.T. test after 49 hours was acid. With ethyl acetate and water the solubility and density changes are too great to allow the study of the effect of the hydrolysis, if any, on the I.T. with water. With the sample 25a and a concentrated salt solution the I.T. was greater and its variations were less than with water; after the test the salt solution was neutral. With the sample 25b and the N. HCl, aq. the value of h decreased with time and became zero after 18 hours; as (d — d′) also decreased with time, the I.T. decreased faster than h did. With the NaOH, aq. h decreased more slowly, at any rate after the first few hours. With the acid and the alkali solutions it may be considered that the hydrolysis is affecting the I.Ts.

(26) *Butyl acetate*, from W. J. Bush and Co., London, was dried with $K_2CO_3$ for 18 hours and then fractionated. The first tenth, b.p. 118°-120°, was neglected; then samples 26 a, b, and c were collected, in bulk about one-eighth, one-half and one-fourth of the original liquid. With sample 26b the rate of increase of the b.p. was the least. These fractions are undoubtedly mixtures, probably of the normal primary and secondary butyl acetates. These samples with water gave slightly acid solutions. The water from the I.T. test with 26b, after 140 hours contact at 30°, was still feebly acid. On boiling for a minute or on keeping the ester and water together for a month at the ordinary temperature the acidity increased. Sample 26a would be the least pure; it probably contained a trace of alcohol, the smell of which was noticed in the preceding, discarded fraction; the variation in the I.T. was the greatest for this sample. With the N HCl, aq. the butyl acetate, 26b, gave h constant in the first three settings over four hours. The fourth setting was observed over 10 days, for the middle 7 days of which, however, the temperature was about 12° and not 30°. In this setting h decreased but the rate of decrease became very slow after the second day. The "final I.T." in Table III (Series X) was that obtaining after 24 hours, which will be more comparable with the final I.Ts. given for the other oils. After the 10 days the I.T. was 5.33 dy/cm, a reduction of 30% from the initial value. No turbidity or irregularity was noticed in this test. With the N NaOH and sample 26b, in the third setting h decreased continuously, the rate of decrease being just less than that with the N. HCl over the same period.

(27) The *amyl acetate* was that purified in 1922, but in the present experiments two fractions of the material were worked with; the sample used in 1922 was the first fraction, 27a, and the next fraction was sample 27b. Sample 27b gave with water a feebly acid solution and the water after the I.T. test was definitely acid; probably sample 27a would be similar. Sample 27b was optically inactive, while 27a was slightly dextro-rotatory. For 27a and water the I.T. was recalculated from the 1922 data. The density of sample 27a was re-determined at 30° and found to have increased from 0.8545 in 1922 to 0.8554 in 1924. With this substance and the acid and alkali solutions h and (d-d′)

decreased together and thus the I.Ts. decreased. With the NaOH, aq. the first setting gave the initial I.T. given in Table III; for the next hour the I.T. was constant at 11.80, and then decreased.

(28) *Ethyl butyrate*, from W. J. Bush and Co., was treated with $K_2CO_3$ for 17 hours, then filtered and fractionated. The first fraction, b.p. 81.5°-112.5°, about five-ninths of the original, was further purified; the second fraction was used as sample 28c and the third fraction as sample 28d. 28c was two-ninths and 28c was one-ninth of the original. The above first fraction was washed with water, dried for 5 days over $K_2CO_3$ and again fractionated, when it gave one quarter of b.p. 101°-104.5°, which was neglected, one quarter as sample 28a and the third quarter as sample 28b. Perkin (loc. cit) gives for ethyl n.-butyrate the b.p. = 121.2° and $D_4^{30°}$ = 0.8680 and for ethyl iso-butyrate the b.p. 110.2° and $D_4^{30°}$ = 0.8588. Our samples 28a-d had decreasing densities and increasing boiling points, and they must be somewhat complex mixtures containing probably methyl and ethyl normal and iso-butyrates. (The original ethyl butyrate, and butyl acetate were optically inactive.) Samples 28c and 28d with water gave feebly acid solutions, and the waters from the I.T. tests with 28a and 28b were feebly acid but after keeping for a month with the ester became definitely acid. With this substance and water the I.T. was constant, but with the N. HCl, aq. the I.T. decreased continuously—the two experiments agreeing well. With the N. NaOH the I.T. decreased rapidly at first, and then slowly; the initial I.T. may be as high as 13.7 dy/cm.

(29) *Amyl butyrate*, from W. J. Bush and Co., a slightly yellowish liquid, was used as sample 29; it had $D_4^{13°}$ = 0.8725 and $[\alpha]_D^{13°}$ = + 0.80°. The greater part was distilled, giving one-sixth of b.p. 152°-166°, which was neglected, and then samples 29a, 29b and 29c, in bulk about one-third, one-fourth and one-sixth respectively of the original liquid. The distillates were colorless; they gave with water neutral solutions, becoming feebly acid after standing awhile and after a month's contact definitely acid. After the I.T. tests the waters were feebly acid. All of these liquids are, of course, mixtures of various isomers. With the N NaOH, aq. h tended to increase in successive settings, diminishing in each setting, and behaving as if there was a film hindering the motion of the capillary meniscus; no film was visible. This behaviour was also given in liquid 30b; with liquids 33, 34, 35, 37, 38 and 39 the filming or turbidity was visible and contamination of the meniscus was quite evident.

(30) *Amyl valerianate*, from W. J. Bush and Co., was a yellow liquid; it had $D_4^{13°}$ = 0.8772 and $[\alpha]_D^{13°}$ = + 0.67°. Part was filtered and used as sample 30. The greater part was distilled; the first distillate boiled from 100° to 171.5°, formed about 6 per cent of the original and was neglected; then were collected the samples 30a, 30b and 30c, in bulk about 24, 30 and 18 per cent respectively of the original liquid. These liquids, too, are obviously mixtures of isomers and related compounds. The boiling point of iso-amyl iso-valerate is given as 189°-190° in Atack's Year Book. These samples gave with water acid solutions. With the N NaOH, aq. this substance behaved similarly to the amyl butyrate (q.v.); after these tests the NaOH, aq. was yellow colored.

(31) *"Oenanthic ether"*, from Merck, was shaken for a short time with $CaCl_2$,—long contact resulted in some combination, as is the case with several esters, e.g. ethyl, butyl and amyl acetates. The liquid was then filtered off and distilled; a little came off at about 80° and then the temperature rose rapidly to above 200°. After discarding a small amount, the samples 31a and 31b were collected. This material, according to Roscoe and Schorlemmer, is a mixture of the ethyl esters of several fatty acids, especially caprylic, pelargonic and capric acids; it would not contain much, if any, of ethyl oenanthate. Both samples 31a and 31b gave with water acid solutions. With NaOH, aq. they gave immediately a thick white solid or soap, so that this I.T. could not be determined.

(32) *Benzyl acetate*, from W. J. Bush and Co., was distilled; the first fraction, about 15 per cent of the original, b.p. = 212.5°-214°, was discarded, and then were collected the samples 32a and 32b, about 35 and 28 per cent respectively of the original liquid. These with water gave feebly acid solutions, sample 32a giving the greater acidity.

(33) *Methyl benzoate*, from L. Givaudan and Co., was distilled; the first distillate, one quarter, was discarded, and then was collected sample 33,—in bulk one-half of the original. Sample 33 gave with water a very feebly acid solution, and after the I.T. test of 65 hours the water was no more acid. With this sample and the N NaOH, aq. h decreased continuously, so that the initial and final I.Ts. were taken from the h—time graph. Here turbidity was noticed at the interfaces and in the ester.

(34) *Isobutyl benzoate*, from L. Givaudan and Co., was distilled; the first sixth was discarded and then was collected sample 34, about two-thirds of the original bulk. The sample gave with water a feebly acid solution and was probably a little worse in this respect than the original liquid. This liquid is heavier than water at room temperature (about 12°), but the liquid at 30° is lighter than water at 30°. The value of (d—d′) at 30° is so small that in our apparatus the I.T. with water could not be determined as a large enough value of h could not be accommodated. This substance was optically inactive. From the I.T. against salt solution the I.T. against water was reckoned as 24.1 dynes/cm (maximum value) at 30°. There was marked turbidity with the NaOH, aq.

(35) The purest *benzyl benzoate*, from W. J. Bush and Co., was a colorless, odorless, viscous liquid. Part was filtered only and formed the sample 35. Part was distilled; the first fraction, one-ninth, was discarded, and then was collected sample 35a, about two-thirds of the original bulk. The liquid during distillation developed a yellow colour and a slight odour (of benzaldehyde ?); sample 35a was very slightly yellowish and practically odorless. The sample 35 with water gave a slightly acid solution and sample 35a a distinctly acid solution. Evidently therefore there was a little decomposition during the distillation. The waters from the I.T. tests were feebly acid to litmus. With water the I.T. decreased with time and faster with sample 35 than with sample 35a; turbidity in the apparatus was marked with 35 and very slight with 35a. With the NaOH, aq. there was turbidity etc.

(36) *Methyl salicylate* was shaken with a little anhydrous $K_2CO_3$, filtered and distilled; after discarding the first distillate, the sample 36 was collected. (Atack's Year Book gives the b.p. as 224°). With water it gave a feebly acid solution.

(37) *Amyl salicylate*, from L. Givaudan and Co., was a colorless, somewhat viscous, fragrant liquid. It boiled at a high temperature with a little decomposition. This liquid therefore was used as supplied; it had $D_4^{13^\circ} = 1.0569$ and $[\alpha]_D^{13^\circ} = +1.82^\circ$; with water it gave a neutral solution. After the I.T. test of 48 hours the water was very feebly acid. With the $H_2SO_4$, aq. h decreased rapidly and continuously. With the N NaOH, aq. a milky soapy mass was formed in a few seconds and the I.T. could not be determined.

(38) *Ethyl phthalate* was supplied by L. Givaudan and Co., as "Neantine"; it was a clear colorless viscous liquid. It was not certain whether this material is the acid ester (mono-ethyl phthalate) or the neutral ester (di-ethyl phthalate). It was distilled under reduced pressure and the first third was collected as sample 38, the b.p. being constant. This sample was not appreciably soluble in water, though the solution became acid in a few minutes. With the N NaOH, aq. turbidity and contamination of the meniscus were marked.

(39) *Ethyl acetoacetate*, from Kahlbaum, a straw-colored liquid, was distilled. After rejecting about one-fifth, there was collected over one-half of the original liquid as sample 39. This sample was used with water, a salt solution and the N NaOH, aq. The used material was separated, dried with $CaCl_2$ and re-distilled giving sample 39′. This was slightly straw-colored, the distillation being carried rather far. Sample 39′ was used with water and the $H_2SO_4$, aq. With water the two samples gave an acid solution, the acidity increasing with the time of contact; also the mutual solubility was considerable and the density changes were marked. Our samples were not of the highest purity, but only a limited supply of material was available. Perkin gives for ethyl acetoacetate the b.p. = 180°-182° and $D_4^{30^\circ} = 1.01501$. The density given in Table I for sample 39 may be low; a second determination a fortnight later gave $D_4^{39^\circ} = 1.01474$. The value 1.01460 was taken in the tests with sample 39 and the salt and soda solutions. But perhaps the density of this substance increases with time, owing to changes (v. Table V). In the I.T. tests with water the value of h decreased continuously; considering the variations possible, the two tests agreed quite well. After 12 hours h did not decrease much, giving then a minimum I.T. of about 3 dynes/cm. With the salt solution the I.T. decreased very slowly; solubility differences might explain the differences between the latter test and the I.T. tests with water, but decreased hydrolysis probably helps the explanation. With the $H_2SO_4$, aq. h decreased rapidly for 20 hours, then less rapidly for the next 20 hours, and then more rapidly than ever. After 20 hours bubbles of gas were noticed rising from the acid solution, and after 40 hours they were continuously rising and passing up through the acid solution, the outer meniscus and the ethyl acetoacetate; the gas was carbon dioxide. The density of the acid solution from this I.T. test could not be determined by the S.G. bottle on account of

the gas evolution, and the approximate value thereof was assumed from the experiment with water. Evidently ketonic hydrolysis (the products being acetone, alcohol and $CO_2$) was proceeding with the ethyl acetoacetate dissolved in the sulphuric acid solution. The presence of the first two products of the hydrolysis would undoubtedly cause a lowering of the I.T. With the NaOH, aq. turbidity developed immediately after contact and made it impossible to obtain readings of h after 40 minutes; during this time the I.T. was constant (but no corrections were made for mutual solubility etc.).

(40) *Maize oil, sample 40*, is that of 1922, which was used as supplied; see the previous paper, from which the results are quoted. In 1924 it was filtered and re-investigated as *sample* 40 *a*; here too with water the menisci became flatter and turbidity developed in the oil with time,—after half an hour the outer meniscus was appreciably flatter and after several hours it was contaminated and crinkled. Sample 40a had lighter I.Ts. with water than sample 40 at corresponding times and perhaps a somewhat lower rate of decrease of I.T.

*Maize oil, sample 40'*, was from a different source. It filtered hot to a clear yellow liquid—lighter than samples 40 and 40a. In the I.T. test with water turbidity was noticeable at the outer meniscus only after some 6 hours. The low I.T. and rapid decrease of I.T. of oils like 40, 40a and the 1922 fatty oils might be due partly to colloidal impurities therein, as well as to hydrolysis by water.

(41) *Cotton Seed oil* after filtering was an orange yellow liquid, sample 41. With water turbidity was noticed after 5 hours, and the menisci behaved as if contaminated.

(42) *Sperm oil* was filtered cold (at 10°) from some dark and whitish sediment and gave *sample 42*, a clear light brown oil with a slight greenish fluorescence. After keeping at room temperatures, 10° and less, for a month, the sample had deposited more yellowish solid, stearin or spermaceti. *Sample* 42*a* was thus prepared by placing sample 42 in a freezing mixture at −8° for an hour and then putting the semi-solid mass on a filter-paper and letting it drain at about +8° for 5 hours; the filtrate, sample 42a was a little over half the bulk of the original oil, which it closely resembled. The I.Ts. of these samples with water decreased with time; no turbidity was noticed with sample 42 and very little with sample 42a; in both cases the outer meniscus became flatter with time. The final water from the I.T. test with 42a was neutral. A short first setting with sample 42 gave the I.T. of 4.48 dy/cm, constant over half an hour; this value was neglected in Tables I and IV.

## Summary

There have been measured the interfacial tensions of organic liquids against water and aqueous solutions at 30°, and also the densities of the mutually saturated solutions. In addition, the variations of these interfacial tensions with time were observed over long periods. When two partially miscible liquids saturate each other, their densities usually change in the normal manner, i.e. the lighter liquid becomes denser and the heavier liquid less dense.

Making allowance for such density changes, there has been shown the constancy of the interfacial tension over several days between many pairs of liquids. Purification of an organic liquid tends to make its interfacial tension against water (etc.) higher and less variable with time. But many mixtures of organic liquids have with water (etc.) interfacial tensions constant over a long period; certain impurities, however, may greatly influence the interfacial tension, usually causing it to decrease continuously with the time of contact.

The greater the mutual solubility between two liquids, the lower is the interfacial tension between them, i.e. between their saturated solutions. With certain esters and dilute acid and alkali solutions in water the interfacial tensions decrease largely with the time. Here the varying interfacial tension is due to the hydrolysis of the esters, when the products of the hydrolysis increase the mutual solubility of the two liquids or give a contaminated interface between them. The detailed summary is in §§ (1) to (15), pp. 7 to 11.

In conclusion the writer desires to thank Messrs. N. Brelaz, G. Cornwell, W. Davies and G. Harker, and also Jas. Hardie and Co., Melbourne, for donations of organic liquids and oils.

*The School of Mines,*
*Ballarat.*
*December, 1925.*

# HEATS OF ADSORPTION AND THE PROBLEM OF PROMOTER ACTION*

BY CHARLES FREDERICK FRYLING[1]

The heat of adsorption of hydrogen on catalytic nickel has recently been measured by Foresti[2], who obtained values at variance with those of Beebe and Taylor[3]. Both of the methods employed were apparently of the same order of accuracy, and the fact that neither of the above results agreed with those obtained in this investigation, shows that the problem is less simple than it was first thought to be.

Recent work has thrown considerable light on the role of promoters in the surface of contact agents. Thus, Russell and Taylor[4] have shown that thoria in a nickel catalyst prevents coalescence of the unsaturated nickel surface atoms. Wyckoff and Crittenden[5] have confirmed this conception by a thorough X-ray examination of promoted ammonia catalysts. Since adsorption has been shown to be so intimately connected with catalytic activity,[6] it was thought that a study of the (probably enhanced) thermal effects occurring with adsorption on promoted catalysts might reveal the nature of the change produced in the adsorbed gas whereby its chemical activity is increased.

*Measurement of the Heat of Adsorption.*—The method of Beebe and Taylor (q.v.) was used. These authors found a troublesome adsorption drift with nickel catalysts. The effects of this were largely overcome by taking the temperature readings for ten minutes instead of three minutes. This necessitated an accurate knowledge of the cooling curve. It was found that the calorimeter cooled according to Newton's cooling law. The linear relationship between the rate of cooling and the temperature facilitated this correction. Consequently, temperature readings were taken every half minute, and the total cooling correction was the sum of the half-minute corrections. The accuracy of this procedure was about two per cent. Furthermore, it was found that the rate of cooling was not influenced by the amount of catalyst within the calorimeter, nor by the volume or nature of gas present so long as 2 c.c. of nitrogen were present.

The temperature of evacuation of the catalyst was 300°C. for all cases, with the exception of those presented in Table IV, which were evacuated at 0°C. All of the heats of adsorption were measured at 0°C.

It was important to determine the heats of adsorption at low pressures. Small amounts of gas were admitted into the calorimeter, and the heats of

---

* Contribution from the Laboratory of Physical Chemistry, Princeton University.

[1] National Research Fellow in Chemistry.

[2] B. Foresti: Gazz. 53, 487 (1923); 55, 185 (1925).

[3] Beebe and Taylor: J. Am. Chem. Soc., 46, 43 (1924).

[4] Russell and Taylor: J. Phys. Chem., 29, 1325 (1925).

[5] Wyckoff and Crittenden: J. Am. Chem. Soc., 47, 2866 (1925).

[6] Hugh S. Taylor: "Colloid Symposium Monograph", (1923).

adsorption at constant volume ($Q_v$) were measured. When values for the heats of adsorption of the total amount of gas adsorbed were obtained, since the pressure was kept constant, they were designated as ($Q_p$). Following the procedure of Foresti, this value was diminished by 0.5 kg.-cal. to make it comparable with the measurements at low pressures.

The method of Beebe and Taylor has been found to give measurements with an a.d. of 3% for total adsorption. From this it has been calculated that the a.d. rises to about 20% for 0.6 c.c. of gas adsorbed, 10% for 1 c.c., 6% for 2 c.c., and 4% for 4 c.c. However, for values obtained in sequence, the deviations were not so marked as these figures indicate. But little value was accorded to the absolute values recorded, the variation of the heat of adsorption with amount adsorbed being deemed of greater significance. A source of error was introduced by a slight adsorption (ca. 0.6 c.c.) of nitrogen on the promoted catalysts. It was considered a possibility that this was responsible for the interesting variation obtained in these cases; but, several determinations made on the promoted catalysts without nitrogen present, showed that such could not be the explanation.

*Preparation and Purification of Gases.*—The gases were prepared and purified by the same methods used by Russell and Taylor. It was found, however, that carbon dioxide prepared from marble contained a small residue (ca. 1%) of gas which would not dissolve in sodium hydroxide solution. This may explain the poor results obtained with this gas, since it was determined that a small amount of air admitted with hydrogen gave an abnormally high heat effect. Such being the case, extreme precautions were necessary relative to the purity of the nitrogen and hydrogen employed.

*Preparation and Catalysts.*—Recrystallized C.P. nickel nitrate was used for catalysts I, II, and III. Pure metallic nickel, dissolved in C.P. nitric acid, was the basis of catalysts IV, V, and VII. Merck's commercial nickel carbonate was used for catalyst VI. At first the catalysts were ignited in a porcelain casserole to expel the oxides of nitrogen; but it was later found that better results could be obtained if the nitric acid solution of nickel was ignited in a large Pyrex test tube in a tubular electric furnace. A glass tube was inserted into the upper part of the test tube, and suction from a water pump removed the gases and steam evolved. As the solution evaporated, the temperature of the furnace was raised slowly enough to prevent foaming and excess spattering until 300°C. was reached. This procedure seemed to incorporate the promoter more thoroughly with the nickel oxide. The oxide was then transferred to a Pyrex glass furnace of the type described by Rideal and Taylor[1] and reduced at 300°C. with hydrogen. C.P. cerium nitrate and thorium nitrate were employed as promoters. These reagents were tested and found to be free from sulphates.

Table I gives the necessary data relative to the various catalysts employed. It was deemed significant that no highly adsorptive catalysts of the type pre-

[1] Rideal and Taylor: "Catalysis in Theory and Practice", 72 (1919).

pared by Foresti or Schmidt[1] were obtained. Catalyst III was prepared according to Foresti's directions. A very pronounced shrinkage was observed when the oxide, obtained from nickel carbonate, was reduced. Indeed, it occurred even after the catalyst had been transferred to the calorimeter, and it eventually rendered it impossible to obtain concordant values for the heat effect. It is believed possible that both Schmidt and Foresti had some impurity in their nickel carbonate which acted as a promoter and prevented coalescence of the nickel particles, for catalyst VII, which contained thoria to the amount of 13.5% of the nickel present, underwent no appreciable shrinkage when reduced from the oxide.

The amount of promoter in Table I is calculated as per cent of nickel present in the nickel nitrate. Catalyst I, although promoted, did not act as such. The promoter was evidently not incorporated well enough with the nickel. The fact that the best catalysts were jet-black, as noted by previous investigators, was confirmed in all cases with the exception of catalyst VII. An excess of promoter was used in the preparation of this catalyst and it is thought that finely divided thoria, on the surface of the nickel, was the cause of this exception.

*Results.*—Table II presents the values of the integral heat of adsorption for varying amounts of hydrogen adsorbed. The Roman numerals designate the catalyst employed. The heats of adsorption are given in kg.-cal. per g. mol of hydrogen adsorbed.

Table III presents the values obtained for the integral heats of adsorption of carbon dioxide on nickel catalysts. It seemed evident that the values ob-

TABLE I

| Catalyst number | weight g. | Cc. of $H_2$ adsorbed at 760 mm. by 100 g. Ni | Preparation |
|---|---|---|---|
| I | 21.5 | 97.3 | 4% $Ce_2O_3$ Reduced from oxide at 300-320° for 260 hours. |
| II-a | 27.0 | 32.6 | Reduced from oxide at 300-320° for 260 hours. |
| II-b | " | 30.7 | Accidentally poisoned. |
| II-c | " | 11.6 | Sintered for 14 hours at 450°. |
| III | 25.6 | 77.4 | Reduced from nickel carbonate according to Foresti, for 72 hours at 300-320°. |
| IV-a | 20.4 | 71.1 | 6.4% $ThO_2$. Reduced for 72 hours at 300-320°. |
| IV-b | " | 20.5 | Sintered at 400° for 20 hours. |
| V | 21.9 | ? | Identical with IV-a. |
| VI | 33.3 | 90 | Reduced from com. nickel carbonate at 300-320° for 120 hours. |
| VII | 23.2 | 71.9 | 13.5% $ThO_2$. Reduced at 300-320° for 60 hours. |

[1] Schmidt: Z. physik. Chem., 118, 193 (1925).

TABLE II

Integral Heats of Adsorptions of Hydrogen on Nickel Catalysts

| I | | II-a | | II-b | | II-c | | III | |
|---|---|---|---|---|---|---|---|---|---|
| Cc. ads. | $Q_v$ | Cc. ads. | $Q_v$ | Cc. ads. | $Q_v$ | Cc. ads. | $Q_v$ | Cc. ads. | $Q_v$ |
| 0.21 | 19.7? | 2.17 | 18.1 | 0.42 | 28.7 | 1.29 | 12.2 | 1.08 | 25.6 |
| 1.83 | 29.2 | 2.48 | 15.6 | 0.84 | 24.8 | 2.28 | 9.1 | 1.27 | 38.8? |
| 1.85 | 28.8 | 2.74 | 14.3 | 2.01 | 16.4 | 3.14 | 7.4 | 7.12 | 14.5 |
| 2.02 | 24.5 | 3.12 | 12.4 | 4.43 | 12.5 | | | 18.4 | 10.0 |
| 2.99 | 22.4 | 4.35 | 10.6 | 5.09 | 12.0 | | | 19.8 | 9.4 |
| 4.04 | 16.9 | 8.03 | 11.0 | 7.80 | 10.1 | | | | |
| 6.23 | 14.6 | 8.21 | 10.5 | 8.29 | 10.2 | | | | |
| 16.7 | 10.2 | 8.81 | 10.1 | | | | | | |
| 18.2 | 9.9 | | | | | | | | |
| 19.3 | 10.8 | | | | | | | | |
| 19.6 | 10.0 | | | | | | | | |
| 20.3 | 9.9 | | | | | | | | |
| 20.6 | 9.8 | | | | | | | | |
| 20.9 | 9.4 | | | | | | | | |

TABLE II (continued)

| IV-a | | IV-b | | V | | VI | | VII | |
|---|---|---|---|---|---|---|---|---|---|
| Cc. ads. | $Q_v$ | Cc. ads. | $Q_v$ | Cc. ads. | $Q_v$ | Cc. ads. | $Q_v$ | Cc. ads. | $Q_v$ |
| 0.61 | 11.3 | 0.76 | 27.6 | 0.83 | 17.5 | 1.32 | 25.6 | 0.72 | ca 15 |
| 1.40 | 18.7 | 1.38 | 22.1 | 1.75 | 25.0 | 2.57 | 21.4 | 0.73 | 13.5 |
| 1.71 | 21.1 | 1.98 | 16.3 | 2.41 | 27.2 | 3.81 | 19.6 | 1.42 | 20.3 |
| 2.08 | 23.2 | 2.98 | 16.9 | | | 6.00 | 17.7 | 1.48 | ca 22 |
| 2.45 | 25.8 | 4.18 | 15.1 | | | 8.66 | 16.3 | 2.13 | 24.4 |
| 2.65 | 25.5 | | | | | 26.5 | 13.6 | 2.81 | 25.8 |
| 3.62 | 22.6 | | | | | | | 4.83 | 26.1 |
| 5.21 | 19.0 | | | | | | | 5.69 | 25.4 |
| 10.9 | 16.0 | | | | | | | 7.70 | 21.9 |
| 11.6 | 15.5 | | | | | | | 16.7 | 16.3 |
| 14.0 | 16.2 | | | | | | | | |
| 14.5 | 15.7 | | | | | | | | |

TABLE III

Integral Heats of Adsorption of Carbon Dioxide on Nickel Catalysts

| I | | | | II-b | | | |
|---|---|---|---|---|---|---|---|
| Cc. ads. | $Q_v$ | Cc. ads. | $Q_v$ | Cc. ads. | $Q_v$ | Cc. ads. | $Q_v$ |
| 1.77 | 17.6 | 15.6 | 6.6 | 0.43 | 9.3 | 3.78 | 7.3 |
| 13.3 | 9.0 | 18.8 | 7.6 | 2.63 | 7.1 | 4.00 | 5.4 |

TABLE IV

Integral Heats of Adsorption of Hydrogen on Catalyst II-a evacuated at 0°C.

| Cc. ads. | $Q_v$ | Cc. ads. | $Q_v$ |
|---|---|---|---|
| 1.93 | 8.9 | 2.43 | 8.8 |
| 4.91 | 9.6 | 4.51 | 8.7 |

Av. = 9.0 a.d. = 0.3

TABLE V

Differential Heats of Adsorption of Hydrogen on Nickel

| Cc. previously adsorbed | Cc. ads. | Value plotted | Catalyst VI Corrected temp. rise | Calibration = 10.4 cal/°C. calories evolved | cal./Cc. adsorbed | kg.—cal./g. mol adsorbed |
|---|---|---|---|---|---|---|
| 0 | 1.32 | 0.66 | 0.145 | 1.508 | 1.14 | 25.6 |
| 1.32 | 1.25 | 1.95 | 0.091 | 0.947 | 0.76 | 17.0 |
| 2.57 | 1.24 | 3.19 | 0.084 | 0.874 | 0.70 | 15.8 |
| 3.81 | 2.19 | 4.91 | 0.135 | 1.404 | 0.641 | 14.4 |
| 6.00 | 2.66 | 7.33 | 0.152 | 1.581 | 0.595 | 13.3 |
| 8.66 | 17.8 | 17.56 | 0.944 | 9.82 | 0.559 | 12.4 |
| | | | Catalyst VII | Calibration = 9.92 cal./°C. | | |
| 0 | 0.73 | 0.37 | 0.045 | 0.446 | 0.611 | 13.7 |
| 0.73 | 0.69 | 1.08 | 0.085 | 0.843 | 1.222 | 27.3 |
| 1.42 | 0.71 | 1.78 | 0.104 | 1.032 | 1.453 | 32.5 |
| 2.13 | 0.68 | 2.47 | 0.092 | 0.912 | 1.331 | 29.8 |
| 2.81 | 2.02 | 3.92 | 0.241 | 2.390 | 1.183 | 26.5 |
| 4.83 | 0.86 | 5.26 | 0.084 | 0.833 | 0.959 | 21.5 |
| 5.69 | 2.01 | 6.70 | 0.108 | 1.072 | 0.533 | 11.9 |
| 7.70 | 9.04 | 12.22 | 0.467 | 4.63 | 0.512 | 11.5 |

tained for hydrogen were of greater importance, so the work on carbon dioxide was discontinued.

In Table IV are a few values of the integral heats of adsorption on catalyst II-a when evacuated at 0°C.

Table V presents the values of the differential heats of adsorption of hydrogen on two typical catalysts, VI and VII.

### Discussion of the Results

H. S. Taylor[1] has proposed a theory of the catalytic surface based on the results of modern X-ray methods of analysis of crystal structure. In the "Fourth Report of the Committee on Contact Catalysis",[2] he has successfully treated the whole subject with the aid of this conception. Briefly stated atoms of varying degrees of saturation are to be found in the catalytic surface. To the most unsaturated of these atoms is to be ascribed catalytic activity. The following quotation from the latter report, with reference to catalytic nickel, is most apt. "There will be a certain variability in the surface fields of attraction with variation in the exposed faces. The fields will be weakest in the closest packed faces, i.e. the 111 faces, stronger in the 100 faces and strongest in the 110 faces. Atoms in the edges of such a crystal will be one degree less saturated than the atoms in the surfaces". An atom within the crystal may be considered as having six bonds, analogous to valence bonds.

[1] H. S. Taylor: Proc. Roy. Soc., 108A, 105 (1925).
[2] Taylor: J. Phys. Chem., 30, 145 (1926).

Varying degrees of unsaturation are exhibited according to the number of free bonds. Thus a singly attached nickel atom is the most unsaturated and, according to this theory, exhibits the greatest catalytic activity.

Before it is possible to treat the measurements made in this investigation in terms of this theory, it is necessary to make one additional assumption, namely, that active nickel atoms dissociate hydrogen molecules. This assumption, however, can be logically deduced from the probable properties of the most unsaturated surface atoms. These atoms are in an almost gaseous condition, in short, they are in a state corresponding to a higher temperature than are the rest of the nickel atoms. They are analogous to Christiansen's "hot molecules" in that they possess large amounts of potential energy. To deduce this assumption, it is only necessary to consider the influence of hot metals on hydrogen.

Langmuir[1] found that tungsten, at high temperatures, dissociates hydrogen. Sieverts[2] found that nickel dissolves hydrogen at temperatures above 300°C., and from the fact that the solubility of hydrogen varies as the square root of the pressure, he concluded that the dissolved hydrogen is in the atomic condition. This same relationship holds for other combinations of gases and metals, and McKeehan[3] has shown by X-ray analysis that hydrogen probably exists as atoms in palladium.

Further evidence in favor of the existence of atomic hydrogen on the surface of catalytic nickel is furnished by the studies of the critical potentials of hydrogen in the presence of nickel catalysts by Gauger[4] and by Wolfenden[5]. It is believed that these considerations, together with the evidence found in this investigation, constitute sufficient proof for the validity of the assumption that un-ionized atomic hydrogen, of the type produced by Langmuir, Wood[6] and Bonhoeffer[7] exists on the surface of hydrogenating catalysts.

*Total Adsorption.*—In agreement with Russell and Taylor, it may be seen from Table I that the total adsorption is not an absolute criterion of catalytic activity. The promoter may not change the adsorptive capacities of the catalysts to any great extent; although it is conceivable that, by the proper choice of promoter and method of preparation, nickel catalysts, possessing adsorptive capacities in excess of any hitherto recorded, may be prepared. Kubota and Yoshikawa[8] in an interesting study of selective poisoning of nickel catalysts, present results which tend to show that 62% of the nickel atoms are in the surface. From the data of Table I, it can be calculated that not more than 0.2% of the nickel atoms are capable of adsorbing hydrogen. Thus, it would seem that only a small fraction of the surface is covered with

[1] Langmuir: J. Am. Chem. Soc., **37**, 417 (1915); **38**, 1145 (1916).
[2] Sieverts: Z. Elektrochem., **16**, 707 (1910).
[3] McKeehan: Phys. Rev. **21**, 334 (1923).
[4] Gauger: J. Am. Chem. Soc., **46**, 674 (1924).
[5] Wolfenden: Proc. Roy. Soc., **110A**, 464 (1926).
[6] Wood: Proc. Roy. Soc., **97A**, 455 (1921).
[7] Bonhoeffer: Z. physik. Chem., **113**, 199 (1924).
[8] Kubota and Yoshikawa: Sci. Papers Inst. Phys. Chem. Research, **3**, 223 (1925).

hydrogen. However, it is very improbable that so high a percentage of the nickel atoms exist in the surface. It is likely that the reagent (hydrogen sulphide) employed reacted with more than surface atoms. An infallible criterion whereby the total percentage of molecules in the surface of a catalyst might be determined, would be of great advantage. The experimental results obtained by the above authors are in complete agreement with the requirements of Taylor's theory, although they do not so interpret them.

*Effect of Heat Treatment of Catalysts.*—Taylor and Beebe found that heating a nickel catalyst for 21 hours at 450°C. reduced its adsorptive capacity

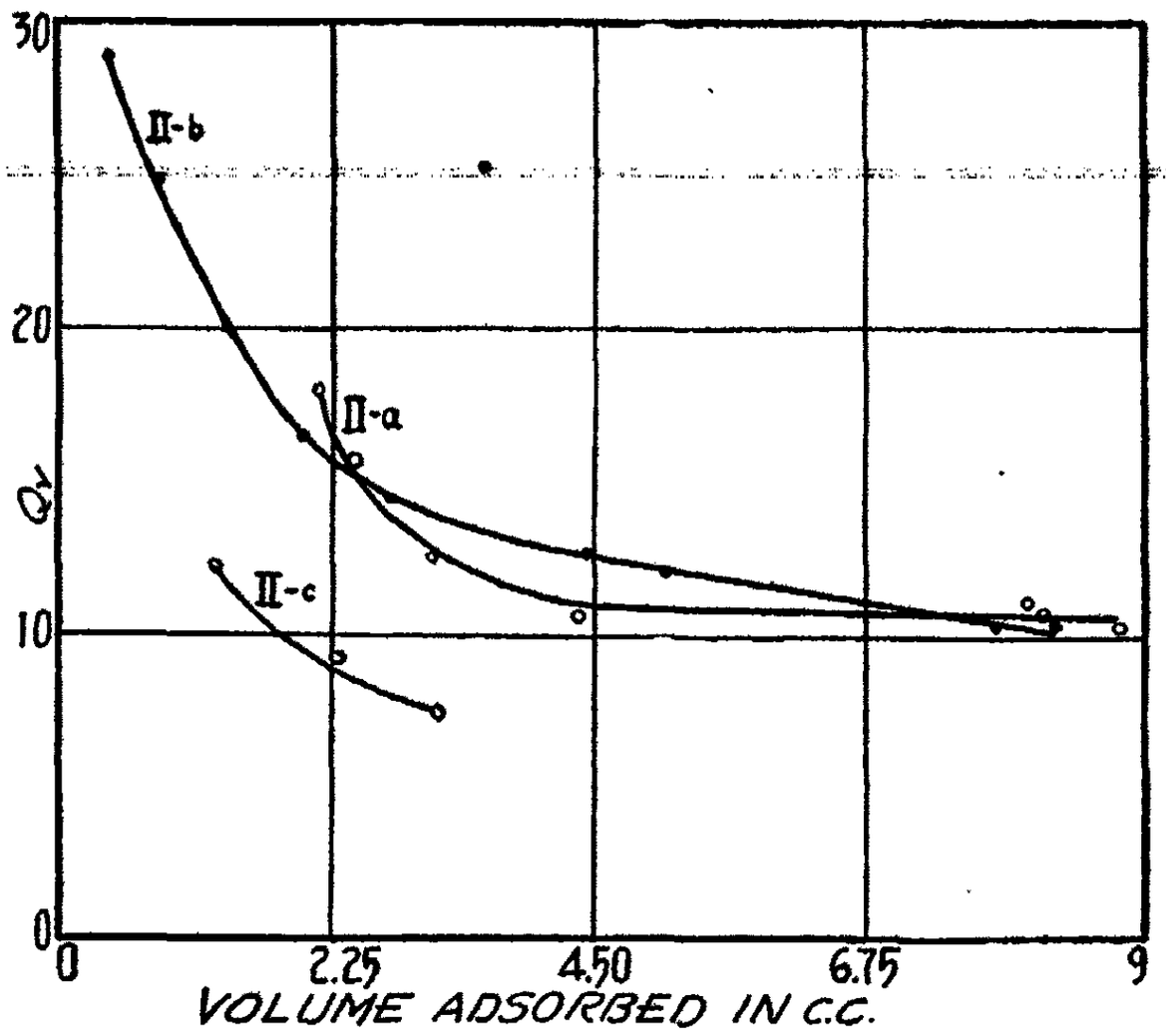



FIG. 1

Integral Heats of Adsorption of $H_2$ on Ni in kg.-cal. on Catalyst II

from 17 cc. to 8 c.. and increased the total integral heat of adsorption from 14.2 kg.-cal. to 20.7 kg.-cal. In another case, these authors, by heating a nickel catalyst for 4 hours at 450°C. reduced its adsorptive capacity from 35 cc. to 16 cc. and increased the heat of adsorption from 13.5 kg.-cal. to 15.5 kg.-cal. Foresti thought these results to be contrary to the theory of active centers and, upon duplicating the heat treatment of the above authors, he found a decrease in the integral heat of adsorption from 15.2 kg.-cal. to 14.5 kg.-cal.

From Table II and Fig. 1 it may be seen that the heat treatment of catalyst II-a reduces the values of both the adsorptive capacity and the total integral heat of adsorption, the former from 8.81 cc. to 3.14 cc. (the saturation capacity of II-c) and the latter from 10.1 kg.-cal. to 7.4 kg.-cal. In the case of the

promoted catalyst IV-a, heat treatment reduced the adsorptive capacity from 14.5 cc. to 4.18 cc. and only a slight decrease (from 15.7 to 15.1) in the value of $Q_v$ resulted.

Taylor's theory requires that heat treatment of the catalyst should lower the heat of adsorption, since the more active centers on the catalyst are destroyed by sintering. It is evident that Beebe and Taylor's results do not agree with this theory, and unless some other effect is found to explain their values, the theory will require modification. However, from the description of their catalysts, and from the values obtained for the total integral heats of adsorption, it seems likely that these authors made their measurements on accidentally promoted catalysts. The evidence in favor of dissociation of hydrogen on active nickel surface atoms permits of a formulation of these phenomena which is in complete accord with Taylor's theory. The heat of dissociation of hydrogen has been shown by Langmuir to have a value of about 90 kg.-cal. The effect of destroying the active spots, which cause this strongly endothermic reaction to take place, naturally results in an increase in the net heat of adsorption. Had their heat treatment been of a more intense nature, the heat of adsorption would have been lowered again. Foresti's results, and the results recorded in Table II are in agreement with the requirements of Taylor's theory, since there were but few active centers present in the catalysts before heat treatment. Thus, by assuming that unsaturated nickel atoms dissociate hydrogen molecules, all of the data relative to the heats of adsorption on sintered nickel catalysts are in agreement with Taylor's theory.

When the dissociation theory was advanced to explain the apparent discrepancy of these results, the possibility of obtaining a $Q_v$-volume curve with a maximum was foreseen. This is because the first portion of the hydrogen adsorbed goes to the active centers which cause dissociation. The complete verification of this prediction will be discussed under promoter action.

*Catalytic Poisoning.*—Air was accidentally admitted to catalyst II-a and V. In the case of catalyst V the ability to exhibit a maximum in the $Q_v$-volume curve was destroyed. Values for the poisoned II-a are listed in Table II under II-b and their curves are given in Fig. 1. This case is analogous to one observed by Beebe[1] for a copper catalyst, and the poisoning is attributed to a change in the relative numbers of different surface atoms.

*Promoter Action.*—The $Q_v$-volume curves of IV-a, V and VII exhibit maxima. Fig. 2 shows this phenomenon. It is the function of the promoter to shift the maximum to the right, and it does so by increasing the number of unsaturated nickel atoms which, in turn, dissociate hydrogen. It is believed that all of the cases investigated for both simple and promoted catalysts would exhibit a maximum in the $Q_v$-volume curve if the method of measurement for small quantities of hydrogen adsorbed were sufficiently exact.

These results are in agreement with the ideas recently expressed by Taylor, Russell and Taylor, and Wyckoff and Crittenden. In addition they furnish

[1] R. A. Beebe: Unpublished research.

vigorous support to the validity of the dissociation theory. The deformation of adsorbed molecules, advanced by numerous investigators to account for catalytic activity, is intense enough to cause complete rupture of the molecular structure.

*Differential Heats of Adsorption.*—Volmer[1], from thermodynamic considerations, came to the conclusion that the heat of adsorption upon a uniform surface is independent of the amount of gas previously adsorbed. He correctly attributed experimental divergences to the different surfaces exhibited by adsorbents. Table IV presents the values obtained for the heats of adsorption on catalyst II-a when evacuated at o°C., and, within the limits of accuracy of

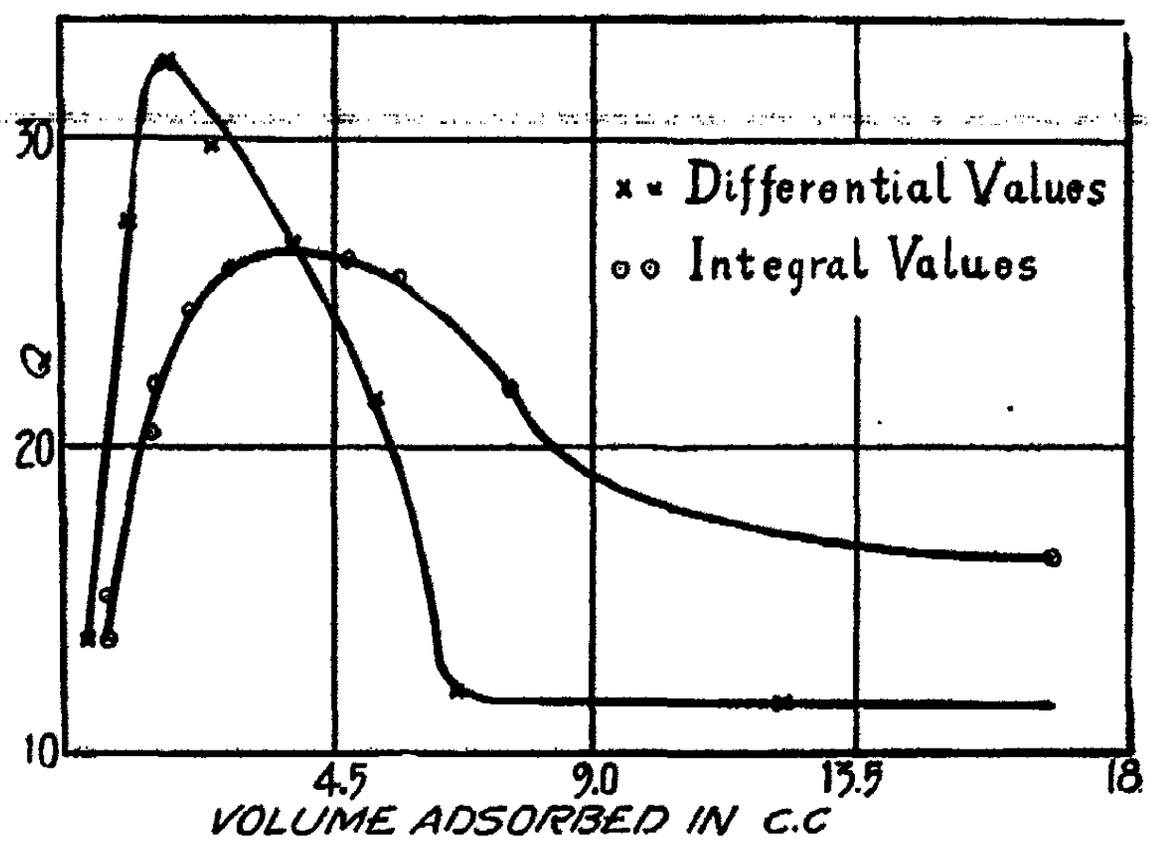



FIG. 2

Heats of Adsorption of $H_2$ on Ni in kg.-cal on Catalyst VII

the method, they agree with the above deductions. The curve so obtained is parallel to the volume axis and asymptotic to the $Q_v$-volume curve obtained by evacuation at 300°C. The differential heat of adsorption is the heat evolved per unit volume of gas adsorbed for an infinitesimal increase in total adsorption. It may be expressed in calories per mol or in calories per cc. of gas adsorbed, and it is only possible to measure this value approximately. By allowing sufficiently small quantities of gas to adsorb at a time, however, concordant values can be obtained. Table V contains values for the differential heats of adsorption on catalysts VI and VII. All the values obtained become constant considerably before total adsorption has been attained. The values are those actually measured in obtaining a sequence of integral heats of adsorption, and they vary more widely than do the latter values.

[1] Volmer: Z. physik. Chem., 115, 253 (1925).

Fig. 3 is a schematic representation of the energy relationships revealed by this investigation. The ordinate represents calories evolved per cc. of hydrogen adsorbed or differential heats of adsorption. The abscissa represents the volume of gas adsorbed. Therefore the area under the curve represents heat evolved, i.e., the integral heat of adsorption. The energy levels $Q_1$, $Q_2$, etc. represent the calories evolved when hydrogen is adsorbed on surfaces of nickel atoms of increasingly varying degrees of unsaturation. The experimental differential curve should likewise be stepwise, but an overlapping effect caused

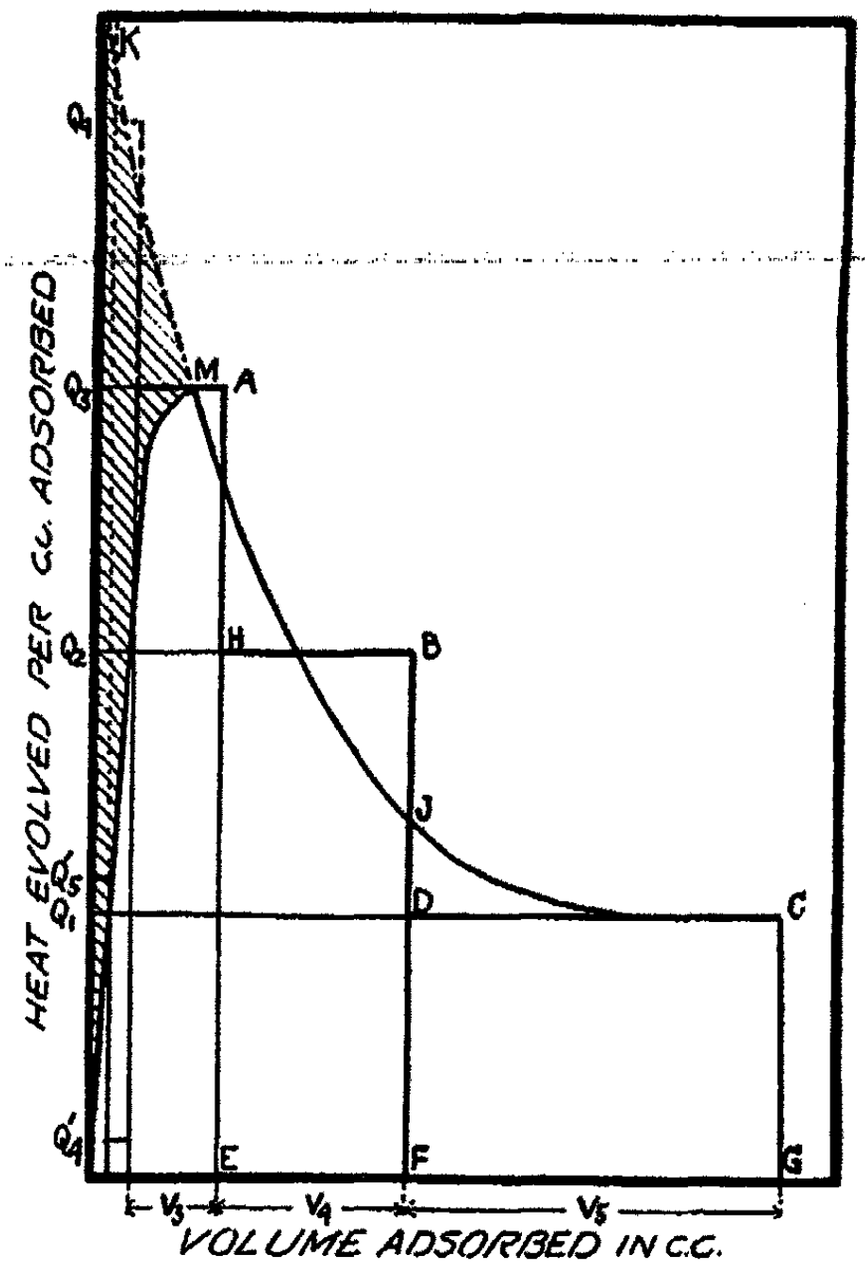



FIG. 3

by the gas adsorbing on the atoms of lower activity before those of higher activity are fully saturated, and, in part, by impurities on the catalytic surfaces, have thus far prevented the realization of this result experimentally. The volumes $V_1$, $V_2$,—$V_5$ represent the number of cc. of gas adsorbed by the various types of surface atoms, and the sum of these volumes represents the adsorptive capacity of the catalyst. $V_1$ and $V_2$ are not marked on the abscissa because of lack of space. These volumes also represent the relative numbers of the different kinds of unsaturated atoms present in the catalytic surfaces. The areas FDCG, EHBF, etc. represent the integral heats of total adsorption of molecular hydrogen upon their respective types of nickel surface atom s

In some cases the more unsaturated of these areas may be practically absent for the purpose of calorimetric determinations; consequently, curves of the type given in Fig. 1 for unpromoted catalysts will be obtained, i.e., there will be no maximum. From the discussion of total adsorption it is evident that it is not known what degree of unsaturation is required to cause adsorption. Nor is it known whether the various Q levels are even multiples of some primary value. The properties of different catalysts will be determined by the relative numbers of different types of unsaturated surface atoms present.

If no dissociation took place, the curve would follow the course K, M, J, C. Hence the shaded area represents the heat used in dissociating the gas. If this be divided by the unknown heat of dissociation of hydrogen adsorbed on nickel, the amount of dissociated gas is obtained. It is this value which is of importance in the study of reaction kinetics. Thus, by introducing a small amount of promoter into their catalyst, Russell and Taylor (q.v.) increased the reaction velocity of hydrogenation of carbon dioxide to a far greater extent than the adsorptive capaci' . of the catalyst. By shifting the maximum M to the right, a relatively large increase in the shaded area is produced. This area is directly proportional to the amount of dissociated hydrogen.

$Q_v$-$Q_4'$ represents the unknown heat of dissociation of hydrogen adsorbed on nickel. Polanyi[1], from a study of the adsorption potential, came to the conclusion that the heat of dissociation is lowered by adsorption. Because of this uncertainty it is not known whether the Q′ levels, which represent the net heat of adsorption on the most unsaturated centers are positive or negative in value.

The value of K, the intersection of the theoretical curve with the Q axis, is of interest. If that portion of the differential curve of Fig. 2 which has the negative slope be extrapolated to the $Q_v$ axis, values from 40 to 58 kg.-cal. are obtained. It so happens that this latter value is 5/6 of the energy estimated to be necessary to gasify metallic nickel. Therefore it is possible that the most unsaturated nickel atoms are attached to the surface by but one crystal structure bond.

Beebe and Taylor discussed the "anomalous" heat of adsorption of hydrogen on nickel when they found that there was no variation in the differential heat of adsorption. They did not extend their measurements to low enough hydrogen pressures to determine the complete nature of their integral heat of adsorption curve.

Foresti obtained values for the integral heats of adsorption of hydrogen on nickel which had been evacuated at varying temperatures up to 300°C. This procedure is equivalent to measuring the area under the curve of Fig. 3 from G to points such as F and E which are determined by the temperature of evacuation. Thus, the Q axis of Fig. 3 represents evacuation at 300°. This diagram is not drawn to scale. The area FDCG is large enough to prevent the appearance of a maximum in an integral heat of adsorption curve so obtained. From his data, Foresti calculated differential values and found that one of his

[1] Polanyi: Z. Electrochem., 27, 142 (1921).

samples exhibited a maximum, although he did not attribute any particular importance to the phenomenon. Thus, for evacuation within the temperature interval of 0-90°, the value of 12.2 kg.-cal. was obtained; from 120 to 145°, 19.6 kg.-cal.; and from 240 to 304°, 16.4 kg.-cal.

## Conclusion

Bancroft[1] has said: "Any action between so-called saturated compounds involves either a preliminary dissociation which means the breaking of a regular bond, or a preliminary association which means the opening of a contravalence. . . . To simplify matters this problem will be discussed solely on the assumption that adsorption involves dissociation". It is evident that, in any case of hydrogenation, the hydrogen, because it is univalent, requires dissociation; although one must be careful not to consider this the sole prerequisite. In an interesting survey of the field of reactions on solid surfaces, Armstrong and Hilditch[2] in reference to this point say: "Hence, it appears that the intervention of the hydrogen is probably secondary to that of the organic compounds present, but there is still room for considerable investigation upon the precise mechanism whereby the hydrogen is brought into chemical combination". Suffice it to say, Taylor and Marshall[3] have produced a number of reactions, similar to catalytic reactions, with the aid of atomic hydrogen generated according to the method of Cario and Franck.

A number of dissociation and ionization theories[4] have been proposed, but their general application has been hindered by lack of evidence of the existence of atomic hydrogen on catalysts at ordinary temperatures and by the arbitrary assumptions regarding the dielectric constants of metals which were necessary in order to account for the energy of ionization. The present investigation has disclosed a source of energy sufficient for the purpose.

The author wishes to acknowledge his indebtedness to Professor Hugh S. Taylor for his advice, enthusiasm and criticism, and to Princeton University for its generous provision of materials, equipment and laboratory.

## Summary

The heats of adsorption of hydrogen on simple and promoted nickel catalysts have been measured.

A maximum which has been attributed to the production of atomic hydrogen has been found to occur in the heat of adsorption-volume adsorbed curve for promoted catalysts.

Promoter action and the various phenomena encountered in the study of heats of adsorption have been discussed in the light of this theory and Taylor's theory of the catalytic surface.

*Princeton,*
*New Jersey.*
*March, 1926*

[1] Bancroft: Ind. Eng. Chem., **10**, 270 (1924).
[2] Armstrong and Hilditch: Chem. and Ind., **44**, 701 (1925).
[3] Taylor and Marshall: J. Phys. Chem., **29**, 1140 (1925).
[4] W. C. McC. Lewis: J. Chem. Soc., **117**, 623 (1920); Sieverts (q.v.); Polanyi (q.v.); Schmidt: Z. physik. Chem., **118**, 193 (1925).

# STUDIES IN ADSORPTION. XIV

## Influence of Hydrogen Ions on the Stability of Sols

BY S. GHOSH AND N. R. DHAR

In previous papers[1] we have studied the influence of hydrogen ion concentration on the coagulation of prussian blue and of arsenious sulphide sols. It has been observed that the previous addition of such acids as HCl, $HNO_3$ etc. makes the sols unstable towards electrolytes and quantities of KCl or $KNO_3$ smaller than the calculated amounts are required to coagulate the sols. On the other hand, practically additive amounts are required when the sols are coagulated with a mixture of KCl and $KNO_3$ or HCl and $HNO_3$. This marked influence of hydrogen ions on the coagulation of such hydrolysable sols as prussian blue, cupric ferrocyanide, arsenious sulphide etc. has been carefully investigated in this laboratory and an explanation of this behaviour based on the general principles of hydrolysis has been advanced.

It has already been shown in a former paper[2] that sols of the type of arsenious sulphide are hydrolysed according to the equation:—

$$As_2S_3 + 3H_2O \rightleftarrows As_2O_3 + 3H_2S$$

This hydrolysis stabilises the sol as has been observed experimentally. Now the checking of the hydrolysis by the presence of H' ions will certainly render the sol unstable. The presence of OH' ions in small quantities will help the hydrolysis and make the sol more stable towards electrolytes. The results, obtained by us in a previous paper on the coagulation of arsenious sulphide sol with mixtures as KCl and $KHCO_3$, KCl and $C_6H_5COONa$, KCl and $NaNO_2$ and $BaCl_2$ and $NaNO_2$ etc. are of interest from this point of view because in all these cases, OH' ions are present in the mixture due to the hydrolysis of one of the electrolytes (e.g. sodium benzoate, potassium bicarbonate etc.). In Table I one set of the results is reproduced:—

TABLE I

Concentration of the sol = 0.100 grm $As_2S_3$ per litre. Volume = 10 c.c. Time = 1 hour. Maximum turbidity is observed.

| 2NKHCO₃ added cc. | N/2 KCl added cc. | N/2 KCl calculated cc. | Difference cc. | Percentage Difference |
|---|---|---|---|---|
| 0 | 1.6 | — | — | |
| 1.9 | 0 | — | — | |
| 0.4 | 2.8 | 1.35 | +1.45 | 107 |
| 0.8 | 1.9 | 0.90 | +1.00 | 111 |
| 1.2 | 1.3 | 0.70 | +0.60 | 86 |

[1] J. Phys. Chem., 29, 659 (1925); Kolloid-Z., 36, 129 (1925).
[2] Kolloid-Z., 36, 129 (1925).

From the results of Linder and Picton it will be seen that larger quantities of such electrolytes as potassium tartrate, potassium oxalate, potassium citrate, etc., are necessary to coagulate a sol of arsenious sulphide than that required to coagulate the same amount of the sol with KCl. Exactly similar results were obtained by us[1] in the coagulation of negatively charged ferric hydroxide, chromium hydroxide, antimony sulphide etc., when coagulated by potassium oxalate, potassium citrate, etc. This is due more to the hydrolysis of the salts of the weak organic acids than to the adsorption of the organic anions. The presence of OH′ ions due to the hydrolysis of the added electrolytes certainly stabilises the sulphide and negatively charged ferric hydroxide and chromium hydroxide sols and it is, therefore, apparent that the electrolytes, which give out OH′ ions due to their hydrolysis, are required in larger amounts than those which are not hydrolysed appreciably. We have made further experiments on this line with sols of ferric and chromic hydroxides on their coagulation by mixutres of easily hydrolysable salts and strong acids. The results are as follows:—

### Ferric Hydroxide Sol

The sol was prepared according to the method of Krecke and was dialysed for a week to free it from electrolytes. The sample of sol used in these experiments was three and half months old. The experimental results are given in Tables II-IV.

TABLE II

Concentration of the sol = 1.43 gram. $Fe_2O_3$ per litre. Amount of sol taken each time = 2 c.c. Total volume = 6 c.c. Immediate turbidity is observed.

Coagulation with a mixture of KCl and HCl

| Amount of N/100 HCl | Amount of KCl to congulate |
|---|---|
| c.c. | c.c. |
| 0.0 | 0.90 N/5 KCl |
| 0.1 | 0.80 N KCl |
| 0.2 | 1.20 " |
| 0.4 | 1.35 " |
| 0.6 | 1.30 " |
| 0.8 | 1.30 " |

TABLE III

Coagulation with a mixture of sodium acetate and HCl

| Amount of N/100 HCl | Amount of N/20 $CH_3CooNa$ |
|---|---|
| c.c. | c.c. |
| 0.0 | 0.75 |
| 0.1 | 1.35 |
| 0.2 | 1.90 |
| 0.4 | 2.30 |
| 0.6 | 2.70 |
| 0.8 | 3.05 |

[1] Kolloid-Z., 34, 262 (1924); 36, 129 (1925).

TABLE IV

Coagulation with $K_2SO_4$ and HCl, or $K_2C_2O_4$ and HCl

| Amount of N/500 HCl | Amount of N/500 $K_2C_2O_4$ | Amount of N/500 $K_2SO_4$ |
|---|---|---|
| c.c. | c.c. | c.c. |
| 0.0 | 0.70 | 0.60 |
| 0.1 | 0.80 | 0.90 |
| 0.2 | 0.90 | 1.00 |
| 0.3 | 0.95 | 1.05 |
| 0.4 | 1.00 | 1.05 |
| 0.5 | 1.10 | 1.05 |

## Chromium Hydroxide Sol

This sol was prepared by adding ammonium hydroxide to a solution of $CrCl_3$ till the precipitate of $Cr(OH)_3$ just appeared. The sol was first dialysed for a week and then hot dialysis was continued for another week. The sol was free from acid but on dissolving the sol with $HNO_3$, a precipitate was obtained with $AgNO_3$ showing that chloride ion was not completely removed even by hot dialysis. The experimental results are given in Tables V-VIII.

TABLE V

Concentration of the sol = 3.91 gms of $Cr_2O_3$ per litre. Amount of sol taken each time = 4 c.c. Total volume = 10 c.c. Time = 1 hour.

Coagulation with $K_2SO_4$ or $K_2C_2O_4$ in the presence of $H_2SO_4$

| Amount of N/100 $H_2SO_4$ | Amount of N/500 $K_2SO_4$ | Amount of N/500 $K_2C_2O_4$ |
|---|---|---|
| c.c. | c.c. | c.c. |
| 0.0 | 2.5 | 3.0 |
| 0.2 | 2.6 | 3.0 |
| 0.4 | 2.65 | 2.9 |
| 0.6 | 2.6 | 2.6 |
| 1.0 | 1.75 | 1.8 |

TABLE VI

Coagulation with $K_2SO_4$ or sodium potassium tartrate in the presence of HCl.

| Amount of N/100 HCl | Amount of N/500 sodium potassium tartrate | Amount of N/500 $K_2SO_4$ |
|---|---|---|
| c.c. | c.c. | c.c. |
| 0.0 | 2.4 | 2.5 |
| 0.1 | 3.00 | 2.9 |
| 0.2 | 3.5 | 3.6 |
| 0.3 | 4.2 | 4.2 |

TABLE VII

Coagulation with NaCl in presence of HCl

| Amount of N/100 HCl c.c. | Amount of N/10 NaCl c.c. |
|---|---|
| 0.0 | 1.55 |
| 0.1 | 2.20 |
| 0.2 | 3.25 |
| 0.3 | >4.60 |

TABLE VIII

Coagulation with sodium acetate in presence of HCl

| Amount of N/100 HCl c.c. | Amount of N/20 $CH_3COONa$ c.c. |
|---|---|
| 0.0 | 0.55 |
| 0.1 | 0.65 |
| 0.2 | 0.80 |
| 0.3 | 0.90 |
| 0.4 | 1.00 |
| 0.5 | 1.05 |
| 0.6 | 1.10 |

## Discussion

Our experimental results with ferric hydroxide and chromium hydroxide sols show clearly that the peptising influence of $H^{\cdot}$ ions is not so marked when these sols are coagulated with sodium acetate as that observed when these sols are coagulated with KCl or NaCl. Thus in the presence of 0.2 c.c. of N/100 HCl the amounts of KCl or NaCl required to bring about coagulation of ferric hydroxide sol is seven times greater than that required to coagulate the sol when no acid is present. On the other hand, in presence of 0.2 c.c. of N/100 HCl, the amount of sodium acetate required to coagulate the same sol is about 2.5 times greater than the amount necessary to coagulate the sol in the absence of acid.

In presence of 0.3 c.c. N/100 HCl with chromium hydroxide sol, the amount of NaCl necessary to coagulate the sol is three times the quantity required to coagulate the sol in the absence of the acid; whilst in presence of the same amount of acid the quantity of sodium acetate required to coagulate the same sol is 1.5 times the quantity necessary to coagulate the sol, when no acid is present.

The precipitation values of $K_2C_2O_4$ and $K_2SO_4$ with ferric hydroxide sol is 0.12 and 0.10 millimole per litre respectively when no acid is present. In presence of 0.1 c.c. N/500 HCl, the precipitation values of $K_2C_2O_4$ become 0.13 and 0.15 millimole respectively. Hence $K_2C_2O_4$ becomes a more effective coagulant than $K_2SO_4$ in presence of an acid. On further increasing the concentration of acid, it is found that the precipitation value of $K_2SO_4$ remains constant

when 0.3 or 0.4, or 0.5 c.c. of N/500 HCl is added. On the other hand the precipitation value of $K_2C_2O_4$ goes on increasing with the increase in concentration of HCl.

When chromium hydroxide sol is coagulated by mixtures of $H_2SO_4$ and $K_2SO_4$ or $H_2SO_4$ and $K_2C_2O_4$ we obtain some interesting results. Our experiments show that, in absence of acid, $K_2SO_4$ is a better coagulant than $K_2C_2O_4$ for both the hydroxide sols. This fact is difficult to explain because experimental results show under identical conditions $C_2O_4''$ ion is more adsorbed than $SO_4''$ ion. Moreover, potassium oxalate is more hydrolysed than potassium sulphate; consequently the coagulating power of an oxalate ion should be greater than that of a sulphate ion. The probable explanation of this abnormal behaviour of $K_2C_2O_4$ seems to be that $K_2C_2O_4$ is adsorbed also in the molecular condition by the sols because of the tendency of forming complex ferric oxalates or chromic oxalates.

In presence of increasing amounts of sulphuric acid the coagulating power of potassium sulphate on chromium hydroxide sol at first remains practically constant, then it increases as the concentration of sulphuric acid is increased. On the other hand the coagulating power of $K_2C_2O_4$ increases as the concentration of sulphuric acid is increased. Though the coagulating power of $K_2SO_4$ is greater than that of $K_2C_2O_4$ in the absence of sulphuric acid, in presence of 0.6 c.c. N/100 sulphuric acid the coagulating power of $K_2SO_4$ and $K_2C_2O_4$ become equal.

It will be observed from our results on chromium hydroxide sol that, in absence of acid, sodium potassium tartrate is a slightly better coagulant than potassium sulphate, but in presence of 0.1 c.c. N/100 HCl, potassium sulphate becomes a slightly better coagulant than sodium potassium tartrate.

The foregoing results can be explained from the accepted views on the dissociation of weak acids.

It is well known that sols like $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, etc., highly adsorb $H^{\cdot}$ ions. Consequently in presence of hydrochloric acid, the positive charge on the sol will increase and much larger quantities of KCl, NaCl, etc., will be necessary to coagulate the sol. When, however, the precipitation is effected by a mixture of sodium acetate and hydrochloric acid, the stabilisation of the sol is not as marked as that obtained when they are coagulated by NaCl and HCl or KCl and HCl, because in presence of sodium acetate the free $H^{\cdot}$ ions from hydrochloric acid are more or less completely removed due to the formation of undissociated acetic acid, as acetic acid is a weak acid. Consequently a mixture of sodium acetate and hydrochloric acid behaves as undissociated acetic acid and sodium chloride and the few $H^{\cdot}$ ions that are available for adsorption by the hydroxides slightly stabilise the sols as will be seen from the experiments.

In the coagulation of chromium hydroxide sol by a mixture N/100 HC and N/500 sodium potassium tartrate we find that as the concentration of the acid is increased the concentration of sodium potassium tartrate necessary for coagulation is also increased. When HCl is added to sodium potassium tart-

rate the H· ions immediately combine with the tartrate ion forming the acid tartrate ion because the second dissociation constant[1] of tartaric acid is $5.8 \times 10^{-5}$. Hence the H· ions are removed more or less completely from the solution. In presence of 0.1 c.c. N/100 HCl, the amount of N/500 sodium potassium tartrate required for coagulation is 3 c.c. Now 0.1 c.c. of N/100 HCl is equivalent to 0.5 c.c. N/500 hydrogen tartrate ion, so this amount must be subtracted from the actual concentration of sodium potassium tartrate necessary for coagulation. Thus we find that really 2.5 c.c. of sodium potassium tartrate exist as such in the solution in presence of 0.1 c.c. of N/100 HCl. The amount required in coagulating the sol in the absence of the acid is only 2.4 c.c. Hence there is only a slight stabilisation when chromium hydroxide sol is coagulated with a mixture of sodium potassium tartrate and hydrochloric acid. Exactly similar results were obtained with other concentrations of acid and tartrate.

When ferric hydroxide sol is coagulated with a mixture HCl and $K_2C_2O_4$, the results show that there is hardly any stabilisation due to the adsorption of H· ions, because the H· ions are practically removed from the solution due to the formation of hydrogen oxalate ions, the second dissociation constant of oxalic acid being $3.1 \times 10^{-5}$. In other words, a mixture of HCl and $K_2C_2O_4$ behaves in a manner exactly similar to that of HCl and sodium potassium tartrate. On the other hand, when ferric hydroxide sol is coagulated by HCl and $K_2SO_4$ appreciable stabilisation takes place because of the adsorption of H· ions. When chromium hydroxide is coagulated by a mixture of $H_2SO_4$ and $K_2C_2O_4$, as the oxalate ion is replaced by the sulphate ion and as both these divalent ions exert similar coagulating influence, the sol is not at all appreciably stabilised, because the H· ions are removed as hydrogen oxalate ions.

The foregoing considerations can readily explain the results obtained in Table IX by Sen and Mehrotra[2] with chromium hydroxide sol:—

TABLE IX

| Amount of N/100 HCl | Amount of N/100 $K_2SO_4$ | Amount of N/100 $K_2C_2O_4$ |
|---|---|---|
| 0.0 | 2.4 | 3.0 |
| 0.1 | 2.9 | 3.2 |
| 0.2 | 3.0 | 3.3 |
| 0.3 | 3.3 | 3.32 |
| 0.4 | 3.5 | 3.34 |
| 0.5 | 3.7 | 3.34 |

There is more of stabilisation of the sol in presence of $K_2SO_4$ and HCl than in presence of HCl and $K_2C_2O_4$ because there are more of hydrogen ions in the first mixture than in the second.

[1] Compare Datta and Dhar: J. Chem. Soc., 107, 824 (1915).
[2] Z. anorg. Chem., 142, 345 (1925).

Linder and Picton[1] have shown that $K_2C_2O_4$ is a better coagulant for ferric hydroxide sol than $K_2SO_4$, whilst the results obtained by Weiser[2] and by us show that $K_2SO_4$ is a slightly better coagulant than $K_2C_2O_4$. It seems likely that Linder and Picton's sol was slightly acid.

From a critical consideration of the experimental results of other workers in this field we shall show in the subsequent pages that along with the hydrogen ion concentration of the medium, the adsorption of ions carrying the same charge as the sol and the degree of hydrolysis of the sols are very important factors in their stability.

In Table X the results obtained by Tartar and Gailey[3] with mastic sol are reproduced:—

TABLE X

| Electrolyte | Precipitation value in milliequivalents | Amount of the acid added in milliequivalents | Hydrogen ion concentration. pH value |
|---|---|---|---|
| KCl | 75 | — | 4.3 |
| $KCH_3COO$ | 400 | — | 8.0 |
| " | 75 | 62.5 | 4.5 |
| $K_2SO_4$ | 225 | — | 4.4 |
| " | 75 | 0.15 | 4.0 |
| $K_2C_2O_4$ | 275 | — | 5.9 |
| " | 75 | 7.5 | 4.4 |
| $K_2HPO_4$ | 100 | — | 4.8 |
| " | 75 | 13.6 | 4.3 |

From the above table the order of the precipitation values of various potassium salts is as follows:—

$$KCH_3COO > K_2C_2O_4 > K_2SO_4 > K_2HPO_4 > KCl.$$

In a previous paper[4] we have observed that a sol of mastic appreciably adsorbs an ion carrying the same charge as the sol. The great difference in the precipitation values of different electrolytes is due to two causes (1) the adsorption of anions to a different degree, and (2) the partial hydrolysis of some of these salts viz $CH_3COOK$, $K_2C_2O_4$ and $K_2HPO_4$, with the liberation of $OH'$ ions, which certainly peptise the sol. The first cause of stabilisation has been completely overlooked by Tartar and Gailey and the influence of $H^{\cdot}$ ions has been over-emphasised. From their data it is obvious that there is practically no difference in PH value when the sol is coagulated by either KCl(pH = 4.3) or $K_2SO_4$(pH = 4.4) though the precipitation value of $K_2SO_4$ is 3 times that of KCl.

On the other hand the pH value in the case of $K_2HPO_4$ is 4.8 and the precipitation value is 100, whilst with $K_2SO_4$ these values are 4.4. and 225. If Tartar and Gailey's contention that no appreciable adsorption of ions carrying

[1] J. Chem. Soc., 87, 1926 (1905).
[2] J. Phys. Chem., 24, 30 (1920).
[3] J. Am. Chem. Soc., 44, 2212 (1922).
[4] J. Phys. Chem., 29, 435 (1925).

the same charge as the sol takes place, then the precipitation value of $K_2SO_4$ should have been smaller than that of $K_2HPO_4$. These results of Tartar and Gailey show that $SO_4''$ ion is very likely more adsorbed than $HPO_4''$ ion.

In a recent paper Michaelis and Hirabayashi[1] have also determined the coagulating powers of HCl, $HNO_3$, $H_2SO_4$ and sulphosalicylic acid on mastic sol and their pH values at precipitating concentrations have been measured. The effect of adding LiCl, NaCl, RbCl, $K_2SO_4$, $Na_2CO_3$, $CaCl_2$ and sodium citrate in the presence of a definite amount of H· ion has also been investigated. The authors have shown that the anions are not entirely without effect, as has been concluded by Tartar and Gailey.

Moreover Bradfield[2] has determined the coagulating powers of HCl, $H_2SO_4$, $H_3PO_4$, acetic acid and citric acid and also of mixtures like KCl and HCl, KCl and KOH, $K_2HPO_4$ and KOH on colloidal clay. His results show that at the precipitating concentration of the different acids the H· ion concentration are in the order:—

Citric > phosphoric > acetic > sulphuric, hydrochloric.

Consequently coagulation of the clay is effected by the largest quantities of H· ions in the case of citric acid, then comes in order phosphoric acid. The results conclusively prove that citrate and phosphate ions are appreciably adsorbed by colloidal clay in its coagulation. Moreover, much larger quantities of dipotassium hydrogen phosphate are necessary than potassium chloride to coagulate the clay at the same H· ion concentration, proving that $HPO_4''$ ions are more adsorbed than Cl′ ions. These results are in agreement with the observation of Briggs[3] that a positively charged surface of aluminium hydroxide becomes negative in presence of citric acid due to the preferential adsorption of citrate ions.

Very recently Weir[4] has investigated the coagulation of prussian blue sol with hydrochloric, sulphuric, acetic, citric and oxalic acids, and pH values after coagulation have also been determined. From Weir's results we conclude that the order of the anions are as follows:—

$$C_2O_4'' > SO_4'' > Cl' > \text{citrate} > \text{acetate}.$$

There is no reason to expect that the order of adsorption of different anions by prussian blue will be the same as with other colloids like clay, mastic gamboge etc.

In this connection it will be interesting to discuss certain results obtained by Bender[5] on the coagulation of mastic sol with a mixture of electrolytes. The following obtained by Bender are given in Tables XI-XIV.

---

[1] Kolloid-Z., 30, 209 (1922).
[2] J. Am. Chem. Soc., 45, 1243 (1923).
[3] J. Phys. Chem., 21, 198 (1917).
[4] J. Chem. Soc., 127, 2245 (1925).
[5] Kolloid-Z., 14, 255 (1914).

TABLE XI

Coagulation by KCl and HCl

| HCl $10^{-4}$ mole per litre | KCl $10^{-4}$ mole per litre observed | calculated |
|---|---|---|
| 0.W | 1045 | — |
| 7.2 | 0.0 | — |
| 0.91 | 21.75 | 903.05 |
| 2.05 | 8.7 | 746.5 |
| 4.10 | 4.35 | 449.5 |

TABLE XII

Coagulation by $MgCl_2$ and HCl

| HCl $10^{-4}$ mole per litre | $MgCl_2$ $10^{-4}$ mole per litre observed | calculated |
|---|---|---|
| 0.0 | 87 | — |
| 4.5 | 0.0 | — |
| 0.28 | 45.5 | 80.45 |
| 0.56 | 22.75 | 76.04 |
| 1.70 | 4.55 | 54.05 |
| 2.80 | 2.27 | 32.85 |

TABLE XIII

Coagulation by NaCl and $Al_2(SO_4)_3$

| NaCl $10^{-4}$ mole per litre | $Al_2(SO_4)_3$ $10^{-4}$ mole per litre observed | calculated |
|---|---|---|
| 1300 | 0.0 | — |
| 0 | 0.180 | — |
| 1000 | 0.045 | 0.0415 |
| 660 | 0.090 | 0.0883 |

TABLE XIV

Coagulation by HCl and $Al_2(SO_4)_3$

| HCl $10^{-4}$ mole per litre | $Al_2(SO_4)_3$ $10^{-4}$ mole per litre observed |
|---|---|
| 0.0 | 0.184 |
| 0.34 | 0.184 |
| 0.91 | 0.455 |
| 1.80 | 0.455 |
| 3.60 | 0.276 |

It will be seen from Tables XI and XII that far smaller quantities of KCl or $MgCl_2$ are required to coagulate a sol of mastic in the presence of an acid like HCl, but the deviation from the calculated values is far more marked when the sol is coagulated by a mixture of KCl and HCl than that observed when the sol is coagulated by a mixture of $MgCl_2$ and HCl. Exactly similar results have been obtained by Bender when the same sol is coagulated with a mixture of LiCl and HCl, NaCl and HCl, $MgSO_4$ and HCl, $BaCl_2$ and HCl, $FeSO_4$ and HCl etc. In all cases the deviations are more marked when the sol is coagulated by mixtures of two monovalent ions than with mixtures of a monovalent and a bivalent ion. Table XIII shows appreciable ionic antagonism when coagulation is effected by NaCl and $Al_2(SO_4)_3$, but the ionic antagonism is more marked with mixture of HCl and $Al_2(SO_4)_3$ as shown in Table XIV. Similar high ionic antagonism is observed when the sol is coagulated with mixtures of $AuCl_3$ and HCl, and $HgCl_2$ and HCl. Slight ionic antagonism is also observed with a mixture of HCl and $Ce(NO_3)_3$. All these results of Bender are highly interesting and can be satisfactorily explained from our views already advanced in the case of the coagulation of arsenious sulphide and prussian blue sols by such mixtures as KCl and HCl, and $KNO_3$ and $HNO_3$.

It is well known that mastic is weakly acidic in water due to the partial hydrolysis of the resin into masticin resene ($C_{20}H_{32}O$) and the acid $C_{20}H_{32}O_2$, which yields a very complex anion. From our researches on adsorption we have shown that an ion of high molecular weight is generally highly adsorbed. It is, therefore, expected that the anion of the organic acid is preferentially adsorbed by the mastic sol and this adsorption renders the sol more stable. Consequently, as observed in the case of $A_2S_3$ and prussian blue sols, the checking of this hydrolysis by an added acid will render the sol unstable and far smaller quantities of an electrolyte will be required to coagulate a sol of mastic than the calculated amounts in presence of acids. The deviations between observed and calculated values are, however, more marked with mastic sol when coagulated with a mixture of KCl and HCl than that observed with $As_2S_3$ sol when coagulated with the same pair of electrolytes. The results with $As_2S_3$ sol as obtained by us are reproduced in Table XV.

TABLE XV

Coagulation of $As_2S_3$ sol with a mixture of KCl and HCl.

Concentration of the sol = 0.162 grm $As_2S_3$ per litre. Volume = 10 c.c. Time = 1 hour.

| HCl N/2 added c.c. | KCl N/2 observed c.c. | KCl N/2 calculated c.c. |
|---|---|---|
| c.c. | c.c. | c.c. |
| 0 | 1.40 | — |
| 0.8 | 0 | — |
| 0.1 | 1.20 | 1.23 |
| 0.2 | 0.80 | 1.05 |
| 0.3 | 0.55 | 0.88 |
| 0.6 | 0.20 | 0.35 |

From these results it is apparent that HCl can suppress the hydrolysis of mastic to a greater extent than that of $As_2S_3$ and hence HCl acts as a better coagulating agent towards mastic sol than for $As_2S_3$ sol. Table XVI will show that it is actually so:—

TABLE XVI

Coagulation of mastic sol

| Electrolyte | Precipitation value |
|---|---|
| NaCl | 1.00 |
| HCl | 0.010 |
| $BaCl_2$ | 0.025 |
| $1/2\ Al_2(SO_4)_3$ | 0.0004 |

From Table XV we find for arsenious sulphide sol that the coagulating power of HCl is about double of that of KCl whilst from Table XVI we observe that the coagulating power of HCl is 100 times greater than that for NaCl with mastic sol and HCl is a better coagulant for mastic sol than bivalent Ba ion.

From the foregoing considerations we find that there are two important factors in the coagulation of sols like $As_2S_3$, mastic, etc. In presence of hydrochloric acid, the hydrolysis of the sols is checked and they are rendered unstable. This effect is far more pronounced with mastic than with arsenious sulphide. Moreover, due to the adsorption of an ion carrying the same charge as the sol, both the sols behave abnormally when coagulated by mixtures like KCl and $BaCl_2$ and LiCl and $BaCl_2$. In other words, when small quantities of KCl, LiCl etc. are added to the sols they are stabilised towards bivalent or trivalent electrolytes as shown by our experimental results on mastic and arsenious sulphide sols. Now when the above sols are coagulated by mixtures like HCl and $BaCl_2$, HCl and $MgCl_2$ etc. appreciable ionic antagonism is observed with arsenious sulphide but this antagonism is less than that observed with KCl and $BaCl_2$ or KCl and $MgCl_2$, because in presence of hydrochloric acid, arsenious sulphide sol is rendered slightly unstable due to the checking of hydrolysis and also because the ratio of the coagulating powers of $Ba^{\cdot\cdot}$ and $H^{\cdot}$ ions towards $As_2S_3$ is appreciably smaller than that of $Ba^{\cdot\cdot}$ and $K^{\cdot}$.

With mastic, the presence of hydrochloric acid makes the sol far more unstable towards electrolytes due to the marked checking of hydrolysis. Moreover, the ratio of the coagulating powers of $Ba^{\cdot\cdot}$ and $Na^{\cdot}$ is about 40, whilst this ratio for $Ba^{\cdot\cdot}$ and $H^{\cdot}$ is only 0.25; because of these two factors, we actually find that far smaller quantities of divalent ions like $Ba^{\cdot\cdot}$, $Mg^{\cdot\cdot}$. etc. are necessary for the coagulation of this sol in presence of HCl, though appreciable ionic antagonism is observed when mastic is coagulated by such mixtures as $BaCl_2$ and KCl, $MgCl_2$ and KCl.

When mastic sol is coagulated by mixtures like NaCl and $Al_2(SO_4)_3$, NaCl and $Ce(NO_3)_3$ etc. the sol is rendered appreciably unstable due to the presence

of $H^{\cdot}$ obtained from the hydrolysis of salts like $Al_2(SO_4)_3$, $Ce(NO_3)_3$ etc. Hence the ionic antagonism cannot be highly developed. On the other hand, when the sol is coagulated by mixtures like HCl and $Al_2(SO_4)_3$, HCl and $AuCl_3$, HCl and $Ce(NO_3)_3$ etc. because of the presence of hydrogen ion from the acid, the hydrolysis of the sol has already been checked, consequently the comparatively few hydrogen ions obtained from the reduced hydrolysis of the salts due to the presence of HCl, cannot interfere with the hydrolysis of the sol. Hence well marked ionic antagonism should be observed with HCl and $Al_2(SO_4)_3$ as the ratio of the coagulating powers of Al and H is about 35. These conclusions are supported by the experimental results of Bender on mastic sol. In Tables XVII-XIX the experimental results with $As_2S_3$ and prussian blue sols obtained in this laboratory are also in support of the foregoing conclusions:—

TABLE XVII

Coagulation of $As_2S_3$ sol with $KNO_3$ and $Al(NO_3)_3$. Concentration of the sol = 0.1538 gram per litre. Volume = 10 c.c. Time = 1 hour. 4 c.c. of the sol is taken each time.

| N/2 $KNO_3$ | N/1000 observed c.c. | $Al(NO_3)_3$ calculated c.c. | Percentage difference |
|---|---|---|---|
| c.c. | c.c. | c.c. | c.c. |
| 1.4 | 0 | — | — |
| 0 | 1.65 | — | — |
| 0.1 | 1.25 | 1.53 | −18.3 |
| 0.4 | 1.4 | 1.18 | +18.6 |
| 0.7 | 1.4 | 0.825 | +68.4 |
| 1.0 | 0.9 | 0.45 | +100 |

TABLE XVIII

Concentration of the sol = 0.1426 gram per litre. Coagulation by a mixture of $HNO_3$ and $Al(NO_3)_3$.

| N/4 $HNO_3$ | N/1000 $Al(NO_3)_3$ observed | calculated | Percentage difference |
|---|---|---|---|
| 1.6 | 0 | — | — |
| 0 | 1.65 | — | — |
| 0.4 | 1.20 | 1.25 | −4 |
| 0.8 | 1.10 | 0.825 | + 33.3 |
| 1.2 | 1.15 | 0.41 | +180.5 |
| 1.4 | 0.40 | 0.20 | +100.0 |

With prussian blue sol only a slight ionic antagonism is observed when it is coagulated by a mixture of KCl and $Al(NO_3)_3$ as shown in Table XIX.

TABLE XIX

Concentration of the sol = 2.88 grms prussian blue per litre. Amount of sol taken each time = 1 c.c. Volume = 10 c.c. Time = 2 hours.

| N/4 KCl | N/400 $Al(NO_3)_3$ observed | calculated |
|---|---|---|
| 1.8 | 0 | — |
| 0 | 0.9 | — |
| 0.2 | 0.85 | 0.80 |
| 0.4 | 0.80 | 0.70 |
| 0.6 | 0.70 | 0.60 |
| 0.8 | 0.55 | 0.50 |

Bender has obtained well-marked ionic antagonism when mastic is coagulated by a mixture of HCl and $HgCl_2$. We believe that this is due to the marked adsorption of the complex $HgCl_4''$ ion by mastic.

We have already proved in a foregoing paper that $As_2S_3$ sol is highly stabilised by the adsorption of OH′ ions from NaOH or from a sodium or potassium salt of a weak acid. Hence marked ionic antagonism was observed when $As_2S_3$ sol was coagulated by mixtures like KCl and $KHCO_3$, KCl and $NaNO_2$, KCl and $CH_3COOK$ etc. Exactly similar well-marked ionic antagonism has been observed by Bender in the coagulation of mastic sol by such mixtures as KCN and NaCl, NaOH and NaCl.

From our experiments[1] on the coagulation of mastic sol we find that greater quantities of both KCl and $BaCl_2$ are necessary to coagulate a dilute sol than a concentrated one. Similar results have been obtained by Burton and Bishop[2] with KCl and $CaCl_2$ towards the same sol. In Tables XX-XXI the results obtained by Tartar and Gailey on the influence of concentration on the coagulation of sols of mastic and gamboge by different acids are given:—

TABLE XX

Coagulation of mastic sol

| Acid | milliequivalents per litre for colloid 100% | milliequivalents per litre for colloid 75% | milliequivalents per litre for colloid 50% |
|---|---|---|---|
| HCl | 3.04 | 2.88 | 2.84 |
| $CH_3COOH$ | 350.0 | 200.0 | 300.0 |
| $H_2SO_4$ | 3.12 | 2.96 | 2.96 |
| $H_2C_2O_4$ | 6.50 | 4.75 | 6.50 |
| $H_3PO_4$ | 5.33 | 5.33 | 5.33 |

[1] J. Phys. Chem., 29, 435 (1925).
[2] J. Phys. Chem., 24, 701 (1920).

TABLE XXI

Coagulation of gamboge sol

| Acid | millieqivalents per litre for 100% colloid | millieqivalents per litre for 75% colloid | millieqivalents per litre for 50% colloid |
|---|---|---|---|
| HCl | 4.0 | 3.90 | 3.90 |
| $CH_3COOH$ | 550.0 | 600.0 | 750.0 |
| $H_2SO_4$ | 3.6 | 3.68 | 3.6 |
| $H_2C_2O_4$ | 9.5 | 9.00 | 9.5 |
| $H_3PO_4$ | 7.5 | 7.40 | 7.2 |

From the above tables we find that both mastic and gamboge have a tendency to behave normally towards dilution when coagulated by acids. These results can be explained from the following considerations:—

We have already emphasised that substances like mastic and gamboge are appreciably hydrolysed in water, and this hydrolysis renders the sols more stable towards electrolytes. On the addition of an acid this hydrolysis will be checked and the sols will be rendered unstable. The checking of hydrolysis will be more pronounced with a dilute sol than a concentrated one, when the same amount of an acid is added. Hence it is expected that a dilute sol of mastic or of gamboge will require smaller quantities of acids like HCl, $H_2SO_4$ etc. In other words, when these sols are coagulated by $H^{\cdot}$ ions they are expected to behave normally on dilution. On the other hand, the adsorption of anions by these sols will make them stable on dilution. Consequently, when these two opposing forces are counteracting each other, change in concentration of a sol should not affect the coagulating power of an acid. Moreover, it is expected that when the checking of the hydrolysis is more pronounced than the effect of the adsorption of ions carrying the same charge as the sol, it should behave normally on dilution towards $H^{\cdot}$ ions.

In a previous paper we have shown that prussian blue sol behaves abnormally towards dilution when coagulated by KCl, NaCl etc. We are making further experiments with prussian blue, cupric ferrocyanide, arsenious sulphide, antimony sulphide and other easily hydrolysable sols to find out whether they behave normally when coagulated by acids.

In this connection, it will be interesting to note that Tartar and Gailey have shown that in presence of small quantities of acids like $H_2SO_4$, $H_3PO_4$, $H_2C_2O_4$ etc., far smaller quantities of the corresponding salts than the calculated amounts are necessary for coagulating sols of mastic and gamboge. These results are certainly caused by the checking of the hydrolysis of mastic and gamboge and rendering them unstable towards electrolytes in presence of hydrogen ions from the added acids.

In a recent communication Kruyt and Tendeloo[1] have shown that $H^{\cdot}$ ions do not play such an important role as was suggested by Loeb in the coagulation of gelatine.

[1] J. Phys. Chem., 29, 1303 (1925).

## Summary

From the foregoing considerations it will be seen that all the existing work on the coagulation of sols in presence of varying concentrations of H'' ions can be satisfactorily explained from the following facts which are emphasised in this paper:—

(1) Adsorption of ions carrying the same charge as the sol.

(2) Hydrolysis of the sols and generation of acids, which stabilise the sols. Addition of acids renders the sols unstable by checking the hydrolysis of the sols. Alkalies make the sols stable by helping such sols to be hydrolysed to a greater extent.

(3) Hydrolysis of the coagulating electrolytes.

We are at present investigating the effect of concentration of easily hydrolysable sols on their coagulation by acids.


*Chemical Laboratory,*
*University of Allahabad,*
*Allahabad, India.*
*December, 1926.*

26-98

# GRAIN SIZE AND THE QUANTUM THEORY OF PHOTOGRAPHIC EXPOSURE

BY MALCOLM C. HYLAN

## Introduction

In a paper[1] entitled "Dispersity of Silver Halides in Relation to their Photographic Behavior" published by the author and Dr. F. E. E. Germann it is shown that theoretically we should expect fine-grained photographic emulsions to be faster than coarse-grained ones, altho in practice the order of sensitivity seems usually the reverse. This discrepancy between theory and fact is explained on the basis of adsorption of retarding soluble halide, the fine-grained emulsions adsorbing relatively more than the coarse-grained ones, and thus reversing the purely dimensional effect. They back up their theoretical conclusions by experimental evidence, actually preparing emulsions of large and of small grains, and comparing their speeds both before and after sensitization. The sensitization was by a process calculated to remove adsorbed retarding halide. Before sensitization they found the large-grained emulsion the faster, but after sensitization, the small-grained one the faster.

Their assumption that their sensitizing process removed the adsorbed retarding halide was based on evidence described in a previous article[2] on the "Photographic Sensitiveness of Silver Iodide". That the sensitizing process does remove adsorbed retarding halide is not to be doubted, but the increase of sensitivity of the small grains over the large ones might be due, not to their size alone, but to the fact that the sensitizer, which consists of a solution of metol, pyrogallol, hydroquinone and sodium sulfite, may itself be adsorbed relatively more by the small than by the large grains, and thus produce an unequal accelerating effect. We might say, then, that the evidence by which they support their theoretical conclusions is merely "circumstantial". That is, their results are a necessary but not sufficient condition of proof of their theory. The "direct" evidence in support of their theory could be obtained only by the comparison of speeds of emulsions of different grain size, known to be free of either adsorbed retarder or adsorbed sensitizer. Such results would depend purely upon the dimensional effects of the grains.

In their discussion Germann and Hylan showed that the "effective area" of a given amount of silver halide is greater with greater dispersity, and argued that from either the continuous wave theory of light, or from the light-dart-quantum theory, a larger portion of the light incident upon the plate would be absorbed by the silver halide in small-grained emulsions than in large-grained ones, hence the speed of emulsions should be increased with increased dispersity. In a criticism of their theoretical conclusions S. O. Rawling[3]

[1] J. Phys. Chem., 28, 1924, 450-456 (1924).
[2] J. Am. Chem. Soc., 45, 2486-2493 (1923).
[3] Brit. J. Phot., 71, 401 (1924).

points out that Silberstein[1], in an article on the "Quantum Theory of Photographic Exposure", has shown that the number of grains hit and affected by exposure to these light quanta is given by the equation

$$k = N(1 - e^{-na})$$

where k = number of grains hit, N = number of grains per unit area of plate, n = number of light quanta impinging, and a = average area of grains. Rawling goes on to show that on the basis of this equation the total "effective area" of grains hit, in emulsions containing equal amounts of silver halide, will be greater for large-grained emulsions than for small-grained ones.

Both Rawling and Silberstein proceed on the assumption that every grain hit by a light quantum is rendered developable, that its developability is unaffected by absorption of further light quanta, that the amount of silver deposited by any grain is proportional to its effective area, and therefore that the total amount of silver deposited is proportional to the total effective area of grains hit, regardless of how many or how few times they have been hit. Germann and Hylan, on the other hand, assume that the developability of a grain is proportional to the amount of light it absorbs, and that the amount of silver deposited is proportional to the total amount of light incident upon the silver halide grains.

To the author, the latter view seems the more reasonable. It is a well known law of photo-chemistry that only the light absorbed has any photochemical effect. The converse, that the photochemical effect is proportional to the light absorbed, seems reasonable. If this be true, a silver halide grain absorbing two light quanta should be twice as developable as one of the same size having absorbed but one. Perhaps even, it requires the absorption of a certain minimum number of light quanta per unit mass of silver halide in the grain to render that grain developable. There is experimental evidence in support of this last assumption.

If the view of Rawling and of Silberstein is correct, we should expect the density-exposure curve to pass thru the origin, or at least come infinitely close to it, for the absorption of a single quantum by any grain should cause some silver deposit. It is well known, however, that there is a certain finite minimum value of exposure up to which the density of the silver deposit on development is zero. This can only mean that a certain finite amount of light must be absorbed by the silver halide to render it developable. Also, in certain "ripening" processes the emulsions are exposed to a subdued light, especially in the case where an emulsion is being rendered sensitive to light of some definite color, where it is exposed to light of that color. Now if the absorption of a single quantum of light rendered a grain developable, some of these grains should absorb a quantum of light during ripening and should be developable without further exposure.

The present investigation was undertaken with a view to seeing if "direct evidence" in support of the theoretical conclusions of Germann and Hylan

[1] Phil. Mag., 44, 257-273 (1922).

could not be obtained, and also to see if the behavior of emulsions free of adsorbed impurities would not furnish evidence as to which of these two views, that of Germann and Hylan, or that of Rawling and of Silberstein, was more nearly correct.

## Experimental

Equimolar quantities of potassium iodide and of silver nitrate were accurately weighed on an analytical balance, and emulsions of silver iodide prepared as follows:

### Emulsion I

| *Solution A* | | *Solution B* | |
|---|---|---|---|
| potassium iodide | 2.767 gms | silver nitrate | 2.830 gms |
| gelatin | 0.5 gms | water | 15 cc |
| water | 15 cc | | |

Warmed A to dissolve the gelatin, added B with stirring and added the mixture to a solution of 40 gms of gelatin in 220 cc of water.

### Emulsion II

| | |
|---|---|
| potassium iodide | 2.767 gms |
| gelatin | 40 gms |
| water | 25 cc |

Warmed to dissolve the gelatin then added
silver nitrate (crystals) 2.830 gms

Slides of these emulsions were prepared and examined under the microscope. Emulsion I was found to have the larger grains, being on the average 50% to 100% larger in diameter than those in Emulsion II. This result is the reverse of that obtained by Germann and Hylan in their work, and the discrepancy will be explained in the discussion.

Cards were painted with these emulsions, and after drying, were exposed and developed. Emulsion II was the faster.

Fifty cc from each of Emulsions I and II were decanted into clean beakers and 5 gms of gelatin added to each, and these modified emulsions labelled I-G and II-G respectively. Cards painted with these, exposed and developed showed them faster than I and II but II-G faster than I-G.

Forty eight cc of 20% ammonia was added to each of Emulsions I and II, and 12 cc to each of Emulsions I-G and II-G, and the resulting emulsions labelled I-A, II-A, I-G-A, and II-G-A respectively. Cards painted with these showed them to be faster than I, II, I-G, and II-G, but II-A faster than I-A, and II-G-A faster than I-G-A.

In order to approximate as closely as possible the conditions in an emulsion as usually prepared with an excess of soluble halide, cards from these emulsions were soaked five minutes in a 1% solution of potassium iodide. After drying, exposing, and developing, Emulsions I and I-G were now the faster.

## Discussion

In every case, the emulsions free of adsorbed impurities showed the fine-grained emulsion faster than the coarse-grained one. On soaking in 1% potassium iodide the order of sensitivity was reversed, as was to be expected, for the fine-grained emulsion should adsorb more retarder and be slowed down more than the coarse-grained one.

These results offer direct evidence in favor of the theory of Germann and Hylan, and against the theory of Rawling and of Silberstein.

Germann and Hylan in their work found that the emulsion prepared by adding silver nitrate crystals to a solution of potassium iodide gave them much larger crystals of silver iodide than by mixing solutions of the two salts, while the author found in this investigation the reverse to be true. The key to the difference in the two cases is found in the ratio between the speed of reaction between potassium iodide and silver nitrate, and the speed of solution of silver nitrate. Germann and Hylan used large crystals of silver nitrate, some being as much as one centimeter in diameter and a millimeter thick. In this case the speed of reaction was greater than the speed of solution, leaving consequently, always a very low concentration of silver nitrate in solution. The author this time used finely ground silver nitrate in order to facilitate accurate weighing on the analytical balance. In this case the speed of solution was much greater, probably producing in the neighborhood of the crystals a fairly high concentration of silver nitrate in solution, with a corresponding decrease in size of silver iodide grains.

## Summary

1. The experimental evidence offered by Germann and Hylan in support of their theoretical conclusions as to the relation between grain size and sensitivity in photographic emulsions might be regarded as merely "circumstantial".

2. Direct evidence in support of their conclusions can be obtained only by a comparison of emulsions known to be free of all adsorbed "impurities", either retarding or accelerating.

3. The quantum theory of photographic exposure as expounded by Silberstein, combined with the assumption that a silver halide grain is rendered developable by the absorption of a single light quantum, was shown by Rawling to lead to conclusions directly opposed to those of Germann and Hylan.

4. The theory of Germann and Hylan is shown to be more in accord with known facts and principles of photo-chemistry than is that of Rawling and of Silberstein.

5. Emulsions free of adsorbed "impurities" have been prepared and their speeds compared, with results which support the theoretical conclusions of Germann and Hylan.

*Hale Physical Laboratory,*
*University of Colorado,*
*Boulder, Colorado.*

# IONIC ACTIVITY VS. CONCENTRATION IN THE INTERPRETATION OF EQUILIBRIA BETWEEN AMALGAMS AND AQUEOUS SODIUM AND POTASSIUM HALIDE MIXTURES

BY GEORGE McPHAIL SMITH

In a recent examination by Bjerrum and Ebert[1] of a series of investigations carried out during a number of years by the writer and his students,[2] the former advocate the use of ionic activities rather than concentrations, for the interpretation of equilibrium data. This affords the writer an occasion for the presentation of his own views on this subject. To him it has long seemed that so-called activities have too often been made use of merely as quantities with which to force constant values from tentative equilibrium expressions; that while the conception of activity might perhaps be a very useful one in connection with the application of thermodynamics to certain chemical processes, its usefulness would seem often to be very questionable in connection with the interpretation of chemical reactions from the kinetic molecular point of view.

It is the object of Bjerrum and Ebert to show that the data contained in the papers cited are in harmony with a recent hypothesis of the complete ionization of the strong electrolytes. They present their examination under the headings: "Transference Numbers and Conductivity," "Amalgam Equilibria," and "Some Other Properties of Mixed Salt Solutions"; but the last they dispose of in the space of less than a page. The present paper will be limited to a consideration of Bjerrum and Ebert's interpretation of the data on amalgam equilibria.

With the discussion confined to data obtained by Wells and Smith in experiments with sodium and potassium alone, and numbered into sections in order to facilitate the critical examination that is to follow, Bjerrum and Ebert's argument is as follows.[3]

## A. Bjerrum and Ebert's Argument

1. "In a series of papers Smith with various co-workers has carried out a number of excellent experimental investigations of the heterogeneous equilibria between amalgams containing two light metals (Na, K) and aqueous solutions of salts of these metals.

[1] On Some Recent Investigations concerning Mixtures of Strong Electrolytes (Transference Numbers and Amalgam Equilibria): Kgl. Danske Videnskab. Selskab, Math.-fys. Medd., 6, No. 9, pp. 3-20 (1925).

[2] G. McP. Smith: J. Am. Chem. Soc., 35, 39 (1913); Smith and Ball: 39, 179 (1917); Smith and Braley: 39, 1545 (1917); 40, 197 (1918); Smith and Rees: 40, 1802 (1918); Stearn and Smith: 42, 18 (1920); Smith, Stearn and Schneider: 42, 32 (1920); Wells and Smith: 42, 185 (1920); Braley and Hall: 42, 770 (1920); Stearn: 44, 670 (1922); Schneider and Braley: 45, 1121 (1923).

[3] The numbering of tables and equations corresponds to that employed in Bjerrum and Ebert's paper.

"The results of these experiments are conveniently expressed in tables containing the values of the following equilibrium constant:

$$K = \frac{[K_{Hg}]\,[NaX]}{[Na_{Hg}]\,[KX]} \qquad (10)$$

where $[K_{Hg}]$, $[Na_{Hg}]$ denote molal concentrations in the amalgams and [KX], [NaX] molal salt concentrations in the aqueous phase.

2. "From the many experiments made by Smith and his co-workers we are able to see how $K$ varies with the amalgam concentration, with the ratio between the salt concentrations, and with the total salt concentration.

"The variations of $K$ caused by changes in the amalgam concentration do not here concern us. The values for $K$ given in Table VI correspond to very nearly the same amalgam concentration. The salt-concentration ratio alters $K$ to no great extent. The values for $K$ given in the table always correspond to solutions in which the two metal salts possess the same normality.

"From Table VI it may be seen how $K$ changes with the total salt concentration for the different salt pairs. These changes in $K$ Smith ascribes to the existence of complexes in the salt solutions.

TABLE VI[1]

The Equilibrium Constant $K$ at 25°
K and Na possess the same normality inthe solution.
0.15-0.20 Milliequiv. of metals per 10 g. Hg.

| Ion Normality | NaCl-KCl | NaCl-KBr | NaCl-KI | NaBr-KBr | NaBr-KI | NaI-KI |
|---|---|---|---|---|---|---|
| 0.1 | 0.453 | 0.461 | 0.457 | 0.456 | —— | —— |
| 0.2 | 0.454 | 0.453 | 0.452 | 0.449 | 0.448 | 0.448 |
| 0.5 | 0.439 | 0.445 | 0.430 | 0.437 | 0.433 | 0.430 |
| 1.0 | 0.427 | 0.425 | 0.409 | 0.412 | 0.406 | 0.398 |
| 2.0 | 0.402 | 0.395 | 0.365 | 0.367 | 0.360 | 0.350 |
| 4.0 | 0.342 | 0.330 | 0.295 | 0.299 | 0.276 | 0.262 |

3. "In the following we shall show how the changes in the $K$ values can be explained by the hypothesis of the complete ionization of the strong electrolytes without assuming the existence of complexes.

"The lack of constancy in $K$ is due to the use of concentration instead of activity. In applying activity in the mass-action expression we get a true constant, designated $K_o$.

"We have $$K_o = K.\ F_{Na}/F_K. \qquad (13)$$

Here $F_s$ denotes the apparent activity coefficient for the ion $S$, *i. e.*, the ratio between the activity of the non-aqueous ion ($a_s$) and the concentration in the solution ($c_s$): $$F_s = a_s/c_s. \qquad (16)$$

4. "If we suppose complete dissociation we can assume that the deviation of the activity coefficient from 1 is due partly to the electric forces between

[1] Wells and Smith: Loc. cit., Cf. Tables V-X, incl.

the electric charges of the ions and partly to the hydration of the ions. Then the following relation will hold good:

$$F_s = f_s\left(\frac{p_o}{p}\right)^{m_s}. \qquad (17)$$

Here $f_s$ denotes the decrease in the activity of the ion $S$, due to the electric forces, $m_s$ the hydration number of the same ion, $p_o$ the vapor pressure of water and p the vapor pressure of the solution.

"By introducing in (13) expressions from formula (17) and by logarithmic transformation we obtain:

$$\log K_o/K = \log f_{Na} - \log f_K + (m_{Na} - m_K) \log (p_o/p). \quad (18)$$

5. "In order to explain the experimental data of Table VI by means of (18), we may put $f_{Na} = f_K$, since the electric forces show approximately the same effect on the activity of ions of the same valency. For $K_o$ we may put the value to which $K$ approaches with decreasing salt concentration ($\log K_o = -0.34$) and for $\log (p_o/p)$ the value from

$$\log (p_o/p) = 0.00421.t = 0.00421\ (3.4.c_{ion}) = 0.0143.c_{ion}. \qquad (21)$$

Here t denotes the lowering of the freezing point of the solution, $c_{ion}$ is the salt normality of the solution, and 3.4 is a value for the molecular lowering of the freezing point which can be employed with sufficient accuracy both for the sodium and potassium salts within the range of concentrations here employed. We thus obtain:

$$\log (K_o/K) = (m_{Na} - m_K)\ 0.0143\ c_{ion}. \qquad (22)$$

"In Table VIII are given the values of $m_{Na} - m_K$, *i. e.*, the difference in the sodium- and potassium-ion hydration, obtained from equation (22), for the salt pairs: KCl-NaCl and KI-NaI.

TABLE VIII

| | NaCl-KCl | | | NaI-KI | | |
|---|---|---|---|---|---|---|
| Salt Normality | $-\log K$ | $\log (K_o/K)$ | $m_{Na}-m_K$ | $-\log K$ | $\log (K_o/K)$ | $m_{Na}-m_K$ |
| 0.1 | 0.344 | 0.004 | — | —— | —— | — |
| 0.2 | 0.343 | 0.003 | — | 0.349 | 0.009 | — |
| 0.5 | 0.357 | 0.017 | 2.4 | 0.366 | 0.026 | 3.5 |
| 1.0 | 0.370 | 0.030 | 2.1 | 0.400 | 0.060 | 4.2 |
| 2.0 | 0.396 | 0.056 | 2.0 | 0.450 | 0.110 | 3.8 |
| 4.0 | 0.466 | 0.126 | 2.2 | 0.582 | 0.242 | 4.2 |
| | $\log K_o = -0.34$ | | | $\log K_o = -0.34$ | | |

"For each salt pair the hydration-numbers found are sufficiently constant, but whilst the experiments with the chloride pair can be explained by the fact that sodium-ion combines with 2.2 more than potassium-ion, the experiments demand a difference of 3.9 in the hydration of the ions in the case of the iodide pair. For the other salt pairs in Table VI the changes in $\log K$ correspond to hydration differences varying between 2.2 and 3.9. Since, according to our hypothesis the hydration difference should have been the same in all

cases, the variation in the hydration numbers found for the various salt pairs shows that the change of $K$ with salt concentration cannot be ascribed exclusively to hydration. In order to explain the results of the experiments, we must assume that the various anions have specific effects on the activity of the sodium and potassium ions.

6. "From investigations on non-electrolytes we know something about the effect of such forces and hence may draw certain conclusions as to their effect on electrolytes.

"Solubility experiments with non-electrolytes have shown that the activity of these substances in solution is affected by the presence of foreign substances, both ions and non-electrolytes. These effects which have been called the salting-out effects ordinarily vary linearly with the concentration of the foreign substances. They may be explained partly by the hydration and partly by the dipole and quadrupole forces between the molecules.

"Whilst the hydration effect only depends on the depressing effect of the foreign substances on the vapor pressure of the solvent (hence mainly on the number of their molecules), the effect of the dipole and quadrupole forces is specific for the different foreign substances.

"When dealing with the activity of the ions we may, besides the effects of the hydration of the ion and of its gross charge, also expect to find effects from possible dipole or quadrupole forces. From the experience gained from the salting out of non-electrolytes we may expect that these effects will be proportional to the concentration of the reacting substance. For any definite salt pair these effects will then be proportional to the concentration, like the hydration effect. If then, as above, the hydration numbers are calculated without taking into account the effect of these forces, we get constant hydration numbers for each salt pair, but on account of the specificness of the forces, the hydration numbers calculated for the various salt pairs may differ. In order to explain the experimental results of Smith and his co-workers we must assume that the dipole and quadrupole forces between halogen-ion and alkali metal-ion vary in such a degree with the nature of the halogen that activity differences corresponding to a hydration of one or two molecules of water may appear. This is what might be expected from experiments on the salting out of non-electrolytes.

"To complete the discussion we may add that the typical ion forces, *i. e.*, the forces between the gross charge of the ions, may also lead to specific activity differences between the ions when we take into account the non-negligible dimensions of the ions."

7. According to Bjerrum and Ebert, in their summary, it has thus been shown "how the careful experiments of Smith and his co-workers, on equilibria between amalgams and aqueous solutions of salt mixtures, might likewise be interpreted without the necessity of assuming complex formation when taking into account the more recent views on the nature of electrolytes."

## B. Critical Examination of Bjerrum and Ebert's Argument

The following critical discussion of Bjerrum and Ebert's study of the data obtained by the writer and his co-workers, on equilibria between amalgams and mixed sodium and potassium salt solutions, will, it is believed, suffice to show that Bjerrum and Ebert have not been fortunate in their attempt to interpret the experimental data.

1. The expression $\frac{[K_{Hg}]\,[NaX]}{[Na_{Hg}]\,[KX]} = K$ is not, as Bjerrum and Ebert designate it, an equilibrium constant; although in the case of the equivalently mixed salt pair NaCl-KCl, for example, its value should no doubt remain very nearly constant with increasing total salt concentration, if the salts really were completely ionized into simple and hydrated ions, as Bjerrum and Ebert suppose, and if in reality the excess hydration of sodium-ion over the hydration of potassium-ion remained constant, in accordance with their calculations. In the case of a specific salt pair, they have in no way accounted for a change in value of the ratio between the activities of the two cations with increasing salt concentration, so that it is hard to see how they can consider themselves to have explained the steady decrease in the value of $K$ with increasing salt concentration.

Wells and Smith,[1] on the other hand, developed the formula $(K_{Hg})(Na^+)/(Na_{Hg})(K^+) = k$, in which $(Me_{Hg})$ are mol-fractions and $(Me^+)$ are ion-fractions, as a theoretical equilibrium constant for the system, and pointed out that, since in any individual case $(NaX)/(KX) = n(Na^+)/(K^+)$, therefore $(K_{Hg})(NaX)/(Na_{Hg})(KX) = n \cdot k = C_c$, — *i. e.*, that $C_c = n \cdot k$ under specific experimental conditions, and that if $C_c$ is found to vary with the conditions, so must $n$ also vary. $C_c$ was referred to in this paper as an "equilibrium expression"; since it (or B. and E's. $K$) varies in value with the changing total salt concentration, under otherwise identical conditions, reference to it as an equilibrium constant cannot be justified.[2]

2. The first column in Table VI, headed "ion concentration" by Bjerrum and Ebert, should be headed "total salt concentration", since the table is an assemblage of experimental data; its contents should be confined to experimental facts and not involve any theoretical views whatsoever. Neither should the table itself be headed "The Equilibrium Constant $K$ at 25°"; the $K$ values in the table are not constant for the different salt concentrations.

3. In the opinion of the writer, activities are too often made use of as quantities with which to force tentative equilibrium expressions to give constant values, regardless of whether anything is to be gained thereby or not.

Bjerrum and Ebert, for example, state that the lack of constancy in the $K$ values is due to the use of concentration instead of activity, and that the

---

[1] Loc. cit., p. 185 f.

[2] In numerical value, our $C_c$ is identical with B. and E's. $K$ in the case of equilibria involving only univalent metals.

application of activity in the mass-law expression yields a true constant, $K_o$[1]:

$$K_o = K\ F_{Na}/F_K;$$

Cf. our expression $n \cdot k = C_c$ (or, in their terms, $n \cdot K_o = K$).

They are more concerned at this point than we were with the nature of the variable $n$; not satisfied with $n$ in its simple, non-committal form, they substitute for it the ratio of two unknown activities, $F_K/F_{Na}$, which they then proceed to analyze further into $\frac{a_K/c_K}{a_{Na}/c_{Na}}$, etc. Even if correct they would still have nothing but a more complex expression for $n$ itself. They do later, under 5, have to assume a value for $K_o$, just as we had to assume a tentative value for our $k$.

4. Next, they assume complete dissociation and ascribe the deviation of the activity coefficient from 1 partly to the electric forces between the electric charges of the ions and partly to the hydration of the ions. On the other hand, but without any idea of complete ionization, we ascribed the deviation of $n$ from unity in value to the existence in the solutions of hydrated or *other* complex ions, or both (see under 6).

We are therefore agreed, concerning the possible existence and influence of hydrates.

5. Finally, they attempt to explain the data of Table VI on the basis of complete ionization and some other very questionable assumptions. For example, they set $f_{Na} = f_K$, the validity of which they themselves later seem to question in their concluding remarks, under 6; and they assume 3.4 as a value for the molecular lowering of the freezing point which can be employed with sufficient accuracy both for the sodium and potassium salts within the range of concentrations employed (*namely*, 0.1-4.0 *total normality*.) Thus they develop a formula for obtaining the excess hydration of sodium-ion over the hydration of potassium-ion for the various salt pairs.

The excess hydration values calculated for sodium-ion, while probably without any significance in fact, as Bjerrum and Ebert themselves tacitly admit later under 6, are fairly constant for different concentrations in the case of a given salt pair, but they differ from one salt pair to another. Therefore Bjerrum and Ebert conclude that in addition to the hydration differences between the cations, the various anions must also have specific effects upon the activities of the sodium and potassium ions.

Since Bjerrum and Ebert assume complete ionization, since they also assume $f_{Na} = f_K$, and since in the case of a given salt pair their calculated excess hydration values for sodium-ion are the same at all concentrations, it is hard to understand the basis of their claim that they have accounted for the steady decrease in value of $K$, in the case of a given salt pair, with the increasing total salt concentration. Complete ionization, together with equal changes in the activities of the cations ($f_{Na} = f_K$; see 4, under A), and a constant difference

[1] How could anybody apply the individual cation activities, though, without actually knowing their values?

in the hydration of the cations, would rather point to a more nearly constant activity ratio of the cations in the case of a given sodium and potassium halide pair, and therefore to a more nearly constant value of $K$.

6. A very indefinite, hypothetical discussion of the specific effects of the anions upon the activities of the cations follows, in which, in their statement that certain effects on the cations vary linearly with the concentration of the foreign substances (in this case, the anions), Bjerrum and Ebert seem to have overlooked the fact that the anions increase in concentration, as well as the cations, with increasing total salt concentration. The impression produced upon the writer at this point is that of "anything rather than admit the existence of complexes (other than hydrates) in the solutions,"—an admission, of course, which would at once concede the inadequacy of the hypothesis of complete ionization.[1]

7. At this point it will perhaps not be out of place to give a short résumé of our own interpretation of the data which Bjerrum and Ebert have assembled in their Table VI.

Smith and Wells,[2] for example, have pointed out that if, in the expression $\frac{(K_{Hg})\ (Na^+)}{(Na_{Hg})\ (K^+)} = k$, the value of $k$ were known, the ion fractions of the metals in the individual mixtures might then be calculated by means of the formulas,

$$(K^+) = \frac{(K_{Hg})}{(K_{Hg}) + k\ (Na_{Hg})} \text{ and } (Na^+) = 1 - (K^+);$$

and that, although we are unable to ascertain the actual value of $k$, if we assume for $k$ a value equal to that of $C_0$ (or $K$) at $0.2N$ concentration, we can then with the use of this tentative value at least determine the direction and relative degree of the ion-fraction changes which accompany salt-concentration changes in the aqueous phase.[3]

This was done, and it was found that the $K^+$-ion fraction decreases while the $Na^+$-ion fraction correspondingly increases, with increasing total salt concentration; and that these changes take place the more rapidly, the higher the average atomic weight of the halogens in the salt pair. These results are shown in Table XII, which is here reproduced.

---

[1] Bjerrum and Ebert in their discussion have disregarded certain solubility determinations which were made in this connection by Smith and Ball (*Loc. cit.*, p. 217 f.), who, in a discussion of the effects of concentration changes upon the value of $C_0$ (or $K$) in the case of equivalent mixtures of sodium and potassium sulfates, pointed out that the experimental data seemed to indicate the existence in such solutions of equilibria of the following nature,

$$Na_2SO_4 + K_2SO_4 = 2NaKSO_4 = 2\ (Me')^+ + 2\ (Me''SO_4)^-,$$

in which the intermediate ion $KSO_4^-$, being more stable, exists at a higher concentration than the intermediate ion $NaSO_4^-$; and that upon this basis $K_2SO_4$ should be more soluble in $Na_2SO_4$ solutions than in pure water, and that its solubility should increase with increasing concentration of the $Na_2SO_4$ solution. Upon investigation, this predicted behavior was definitely observed.

[2] Loc. cit., pp. 185-7.

[3] If there were any advantage to be gained by so doing, we might even claim this as a means of determining the changes in the "activity ratio" of the cations with increasing total salt concentration in solutions of the various salt pairs.

## TABLE XII[1]

Ion Fraction Changes which accompany Salt-Concentration Changes in Equivalent Aqueous Mixtures of Sodium and Potassium Chlorides, Bromides and Iodides, at 25°.

| | | Total Normal Concentration of Equivalent Salt Mixture | | | | | |
|---|---|---|---|---|---|---|---|
| | | 0.1000 | 0.2000 | 0.5000 | 1.000 | 2.000 | 4.000 |
| Potassium-ion Fractions Calculated at 0.2 milliequivs. of metals per 10 g. Hg, upon the assumption that $n$ is here equal to unity. | NaCl-KCl | 0.499 | 0.500 | 0.493 | 0.485 | 0.470 | 0.430 |
| | NaCl-KBr | 0.504 | 0.500 | 0.495 | 0.484 | 0.466 | 0.421 |
| | NaCl-KI | 0.503 | 0.500 | 0.487 | 0.475 | 0.447 | 0.395 |
| | NaBr-KBr | 0.504 | 0.500 | 0.493 | 0.479 | 0.450 | 0.400 |
| | NaBr-KI | —— | 0.500 | 0.491 | 0.474 | 0.445 | 0.381 |
| | NaI-KI | —— | 0.500 | 0.490 | 0.470 | 0.439 | 0.370 |

These ion-fraction changes we have ascribed in our paper to the existence of hydrated, intermediate and or other complex ions. We did this deliberately, on the basis of the known existence of such ions; for example, we may cite the analogous silver complexes, $[Ag(OH_2)_2]^+$, $[Ag(NH_3)_2]^+$, $[AgCl_2]^-$, $[Ag(CN)_2]^-$.

It is of course a well known fact that compounds such as $K_2[PtCl_6]$, $Na[AuCl_4]\cdot nH_2O$, $KMgCl_3\cdot 6\ H_2O$, etc. may readily be obtained from aqueous solutions; and even the alkali halides are capable of forming addition compounds with one another, as well as with other substances,[2] and these may ionize to give complex ions, especially in concentrated solutions. Certain alkali halides also show a tendency to polymerize,[3] and in recent years evidence (based upon absorption-spectra data) has been adduced to indicate that the alkali metals, through the agency of residual valency, are capable of effecting closed-ring structures, with the formation of inner-complex salts.[4] Through conductance studies of the alkali salts of certain organic acids, Lifschitz[5] has arrived at a similar conclusion.

Evidently, then, since we may have the possibility of hydrated ions and molecules, addition and polymerized compounds, and many complexes capable of furnishing ions of various species, speculation as to just what specific

---

[1] Wells and Smith: loc. cit. p. 203.

[2] Joannis: Compt. rend., 112, 338 (1891); Abegg and Riesenfeld: Z. physik. Chem., 40, 84 (1902).

[3] Zannovich-Tessarin: Z. physik. Chem., 19, 251 (1896); Andrews and Ende: 17, 136 (1895); E. W. Washburn: Trans. Am. Electrochem. Soc., 21, 137 (1912).

[4] Hantzsch: Ber., 43, 3049 (1910); Hantzsch and Voigt: 45, 85 (1912).

[5] Z. physik. Chem., 87, 567 (1914).

complex do exist in these solutions,[1] and how they behave, is more or less futile. Nevertheless, owing to the greater tendency of potassium than of sodium, and of iodine than bromine or chlorine to form complexes, we should not be surprised to find, as we do in the equivalent aqueous salt mixtures under discussion, that the potassium-ion fraction decreases with increasing total salt concentration, and the more rapidly the higher the average atomic weight of the halogens is in the mixture. And, as a matter of fact, in the case of changes in concentration, and of changes from one salt pair to another, does not this interpretation account in a most satisfactory manner for the variations in value of the so-called cation "activity ratio" of Bjerrum and Ebert? When an ion loses in concentration, as compared with another ion in the same solution, it naturally must lose in "activity" also.

In conclusion, we may again be permitted to point out that ionization is too often discussed as if it were a simple dissociation alone, and that perhaps too much faith is placed in the supposition that the mass-law (a law which applies even in atomic disintegrations) is non-applicable to the dissociation of strong electrolytes; that perhaps the mass-law is less at fault than we ourselves, in our inability to determine just what molecular species are present in such solutions, and their individual chemical properties and concentrations.

At appreciable concentrations, especially in the case of mixtures, it would seem that the possible existence of complexes in solutions of (strong) electrolytes could not, without a flagrant disregard of known facts,[2] be set aside in favor of any theory whatsoever,—not even with the help of activities.

*Seattle, Washington,*
*March, 1926.*

---

[1] We may however assume, as a simple case, the following:

$$NaCl + KCl = NaKCl_2 \rightleftharpoons Na^+ + [Cl\cdot KCl]^- \quad (a)$$
$$\rightleftharpoons [NaCl\cdot K]^+ + Cl^- \quad (b)$$

These addition compounds might ionize, as indicated, in either or both of two ways: (*a*) into metallic cations and complex anions, and (*b*) into chloride anions and complex cations; the complex ions may be regarded as alkali-metal or chloride ions, as the case may be, which carry alkali halide instead of (or in addition to) water. Both types of complexes are known to exist: *e.g.*, (*a*) $K_2[PtCl_6]$ and (*b*) $[(CsCl_3)_2\,Cr(OH_3)_4]Cl_3$. Concerning (*b*), see A. Werner: Ber., **34**, 1602 (1901); "Neuere Anschauungen," pp. 226, 208 (1913).

[2] For an interesting example of complex formation in the case of aqueous nitric acid, see Hantzsch: Ber., **58 B**, 941 (1924).

## NEW BOOKS

**A Survey of Physics.** *By Max Planck. Translated by R. Jones and D. H. Williams. 19×14 cm; pp. vii + 184. New York: E. P. Dutton and Company. Price: $2.40.* This is a collection of lectures and essays arranged in chronological order but without the dates being given. The titles of the lectures are: the unity of the physical universe; the place of modern physics in the mechanical view of nature; new paths of physical knowledge; dynamical laws and statistical laws; the principle of least action; the relation between physical theories; the nature of light; the origin and development of the quantum theory.

This is a wonderfully good book. One should read it as a whole; but one can dip into it almost anywhere and be certain of finding interesting paragraphs which can be read by themselves provided one can stop then.

"What modern physicist thinks of rubbed amber when considering electricity, or, when dealing with magnetism, thinks of the small Asiatic town where the first natural magnet was found? Further, the sense-perceptions have been definitely eliminated from physical acoustics, optics, and heat. The physical definitions of sound, colour, and temperature are to-day in no way associated with the immediate perceptions of the respective senses, but sound and colour are defined respectively by the frequency and wave-length of oscillations, and temperature is measured theoretically on an absolute temperature scale corresponding to the second law of thermo-dynamics, or, in the kinetic theory of gases, as the kinetic energy of molecular motion. In practice it is measured by the variation in volume of a thermometric substance, or by the deflection of a bolometer or thermocouple. It is in no way described as a feeling of warmth," p. 5.

"While the principle of energy stands before us as a complete self-contained picture, freed from and independent of the vicissitudes of its development, this is by no means the case, to the same extent, with that principle introduced into physics by R. Clausius as the Second Law of Thermo-dynamics. Indeed, the fact that this theorem has not yet been completely established gives it a particular interest in present-day discussions. The second law of thermo-dynamics still retains a particularly anthropomorphous character in current criticism. There are several distinguished physicists who connect the question of its validity with the inability of men to penetrate the molecule and make it similar to Maxwell's demon, which, without doing work, can separate the more rapid from the slower molecules of a gas merely by well-timed movements backwards or forwards on a small path. One need not be a prophet to be able to predict with certainty that the kernel of the second theorem has nothing to do with human ability, and that its final presentation must and will follow in a manner which bears no relation to the feasibility of performing any natural processes through human agency," p. 10.

"To complete the emancipation of the conception of entropy from human experimental methods, and thereby create a real principle of the second law, was the life-work of Ludwig Boltzmann. Briefly it consists in making the conception of entropy depend upon that of probability. Thus the meaning of the word I used above is explained, namely, the *predilection* of Nature for a certain state. Nature prefers more probable to less probable states, in that all natural processes tend to the formation of states of greater probability. Heat flows from a body of high temperature to a body of lower temperature, because the state of equal temperature is more probable than a state of unequal distribution of temperature.

"The calculation of a certain measure of probability for every state of a system of bodies has been rendered possible by the introduction of the atomic theory, and of statistical methods. To determine the mutual action of individual atoms the known laws of dynamics, mechanics, and electro-dynamics can be used unaltered.

"In view of these considerations the second law of thermo-dynamics is ousted immediately from its isolated position, the mystery of Nature's predilection vanishes, and the entropy principle, bound up with the introduction of the atom into physics, becomes a well-established theorem in probability," p. 23.

"For the laws of heat radiation in free space, it must be pointed out that the constants involved, analogous to the gravitation constant, are of a universal character, since they are independent of any special substance, or any special body. Thus they can be used to determine units of length, time, mass, and temperature, and these units must necessarily retain their meaning for all time and for all extra-terrestrial and superhuman *kulturs*. It is known that this does not, by any means, hold for our ordinary weight units. Though these are usually described as absolute units, it must be borne in mind that they bear special relation to our present terrestrial life. The centimetre is derived from the present circumference of our planet, the second from its time of rotation, the gramme from water as the principal constituent of the earth's surface, and temperature from the characteristic points of water. The former constants, however, are such that the inhabitants of Mars, and indeed all intelligent beings in our universe, must encounter at some time—if they have not already done so," p. 28.

"I do not think any serious objection will be raised in physical circles when I remark that the assumption of the complete validity of the simple Maxwell-Hertz differential equations excludes any possibility of explaining, on mechanical lines, electro-dynamic phenomena in the ether. This is not altered by the fact that Maxwell originally derived his equations with the help of the mechanical theories. It would not be the first time that a correct result has been obtained from ideas associated not quite correctly," p. 55.

"The measure of the value of a new hypothesis in physics is not its obviousness but its utility. If the hypothesis proves successful, one becomes used to it and it gradually becomes obvious of its own accord. When the exploration of electric-magnetic effects was yet incomplete, it was thought impossible to visualize galvanic streams, electro-motive force and magnetic lines of force without the aid of flow in liquids, hydraulic pumps, and stretched strings. Now, the majority of students of electro-technics scorn the use of these incomplete analogies and prefer to work directly with electro-magnetic conceptions which have become reliable through use. I have occasionally noticed that conversely, attempts have been made to illustrate complicated fluid motions, such as Helmholtz's vortex motion, by means of electro-magnetic analogies," p. 61.

"One must not imagine that advance is possible, even in the most exact of all natural sciences, without some view of the world, i. e. quite without some hypotheses not capable of proof. The theorem holds also in physics, that one cannot be happy without belief, at least belief in some sort of reality outside us. This undoubting belief points the way to the progressing creative power, it alone provides the necessary point of support in the aimless groping; and only it can uplift the spirit wearied by failure and urge it onwards to fresh efforts. A research worker who is not guided in his work by any hypothesis, however prudently and provisionally formed, renounces from the beginning a deep understanding of his own results. Whoever rejects the belief in the reality of the atom and the electron, or in the electro-magnetic nature of light waves, or in the identity of heat and motion, can most certainly never be convinced by a logical or empirical contradiction. But he must be careful how, from his point of view, he makes any advance in physical knowledge," p. 86.

"Among the more or less general laws, the discovery of which characterize the development of physical science during the last century, the principle of Least Action is at present certainly one which, by its form and comprehensiveness, may be said to have approached most closely to the ideal aim of theoretical inquiry. Its significance, properly understood, extends, not only to mechanical processes, but also to thermal and electro-dynamic problems. In all the branches of science to which it applies, it gives, not only an explanation of certain characteristics of phenomena at present encountered, but furnishes rules whereby their variations with time and space can be completely determined. It provides the answers to all questions relating to them, provided only that the necessary constants are known and the underlying external conditions appropriately chosen.

"This central position attained by the principle of least action is, however, not even today quite undisputed; for a long time the principle of conservation of energy has been a keen competitor. The latter governs in a similar manner the entire range of physics and

certainly possesses the advantage of being more easily explained. It is, therefore, advisable to examine briefly the relative positions of these two principles.

"The principle of conservation of energy can be derived from the principle of least action and is consequently contained in it. The converse is, however, not true. Accordingly, the former is the more particular, and the latter the more general principle," p. 110.

"The characteristic of a theorem in probability is that it permits exceptions, and the determination of such exceptions forms an important problem in atomic statistical conception. The investigation of the conditions of equilibrium provides the most delicate proof of this. For while in dynamics equilibrium represents a condition of absolute invariability, statistical equilibrium is continually varying, more or less significant deviations referred to the so-called equilibrium of motion and, indeed, the magnitude of the mean deviation can be derived quantitatively and exactly from the theorems of probability. In this the statistical theory has established itself most brilliantly," p. 136.

"Now, the nature of electro-magnetic phenomena is no more intelligible than that of optical phenomena. To belittle the electro-magnetic theory of light, on the ground that it simply replaces one riddle by another, is to misunderstand the meaning of the theory. For its importance rests on the fact that it unites two branches of physics, which previously had to be treated as independent, and that, therefore, all theorems which are valid for one branch, are applicable to the other—a result which the mechanical theory of light did not, and could not, give. Before the introduction of the electro-magnetic theory, physics was divided into three separate branches—mechanics, optics, and electro-dynamics, and the unification of these is the ultimate and greatest aim of physical research. Though optics cannot be associated with mechanics, it combines completely with electro-dynamics, and thus the number of independent branches has been reduced to two—the penultimate step towards the unification of the physical world picture. When and how the last step will be made, the linking up of mechanics and electro-dynamics, cannot be said, and though many clever physicists are at present occupied with this question, the times does not yet seem ripe for the solution," p. 145.

"The emission of light always takes place abruptly, by impulses, for it is not determined by the regular oscillations of the electrons themselves but is only emitted when these electron oscillations receive a sudden change and a certain disruption in themselves; a kind of internal catastrophe, which throws the electrons out of their original paths into others more stable but associated with less energy. It is the surplus amount of energy liberated by the atom which travels out into space as a light quantum. Indeed, the most remarkable thing about this phenomenon is that the period of the emitted light and therefore its colour, does not, in general, agree with the period of oscillation of the electrons, either in their original or in their final paths. It is definitely determined by the amount of energy emitted, since the more rapid the oscillations, the greater is the light quantum. It follows that a short wave-length corresponds to a large amount of energy, considered as a light quantum. If, therefore, for example, much energy is emitted, we get ultra-violet or even Röntgen rays; if, however, but little energy is emitted, red or infra-red rays result. It is at present a complete mystery why the oscillations of light produced in this way are, with the utmost regularity, strictly monochromatic," p. 156.

"A question, from the complete answer to which we may expect far-reaching explanations, is what becomes of the energy of a light quantum after perfect emission? Does it spread out, as it progresses, in all directions, as in Huyghens's wave theory, and while covering an ever-larger amount of space, diminish without limit? Or does it travel along as in Newton's emanation theory like a projectile in one direction? In the first case the quantum could never concentrate its energy in a particular spot to enable it to liberate an electron from the atomic influences; in the second case we would have the complete triumph of Maxwell's theory, and the continuity between static and dynamic fields must be sacrificed, and with it the present complete explanation of interference phenomena, which have been investigated in all details. Both these alternatives would have very unpleasant consequences for the modern physicist," p. 178.

*Wilder D. Bancroft*

**Colloid Symposium Monograph.** *Vol. III. Edited by Harry N. Holmes. 24×17 cm; pp. 323. New York: Chemical Catalog Company, 1925. Price: $5.00.* This volume contains the papers presented at the meeting in Minnesota last June. The authors and titles are Herbert Freundlich, On the Electrokinetic Potential; W. D. Bancroft, Molecular Weight and Solution; P. Lecomte du Noüy, Some New Aspects of the Surface Tension of Colloidal Solutions which have led tc the Determination of Molecular Dimensions; Irving Langmuir, The Distribution and Orientation of Molecules; S. E. Sheppard, Photographic Sensitivity; L. H. Reyerson and Kirk Thomas, Catalysis by Metallized Silica Gel; H. T. Barnes, Colloidal Water and Ice; L. S. Palmer and G. A. Richardson, The Colloid Chemistry of Rennet Coagulation; L. V. Heilbrunn, The Colloid Chemistry of Protoplasm; W. P. Larson, H. O. Halvorson, R. D. Evans, and R. G. Green, The Effect of Surface Tension Depressants upon Bacterial Tóxins; I. N. Kugelmass, Physico-chemical Studies of the Mechanism of Blood Clotting; L. B. Miller, The Effect of Anions upon the Physical, Colloidal, and Chemical Properties of Aluminum Hydroxide; P. L. Gile, Nature of the Colloidal Soil Material; Emil Truog, The Colloid Chemistry of Soils; F. J. Alway, The Power of Soils to absorb Water from Air; C. A. Mann, The Mechanism of Lithopone Formation; A. J. Stamm, An Experimental Study of Emulsification on the Basis of Distribution of Size of Particles; J. B. Nichols and H. B. Liebe, The Centrifugal Method for the Determination of Size of Particle of Suspended Material; William Seifriz, Elasticity and Some Structural Features of Soap Solutions; L. V. Foster, A Simplified Slit Ultramicroscope; W. J. Kelly, The Plasticity of Rubber and its Sols; W. G. France, A Motion Picture Study of the Influence of Gelatin on Rates of Crystal Growth and Solution of Copper Sulphate.

This is rather an impressive list of papers and they are a great deal better than they seemed to be at the Symposium where most of them were presented at much too great length. By the electrokinetic potential Freundlich means the single potential which we obtain in cataphoresis and electrical endosmosis cases. It is the potential difference between the solution and an adsorbed liquid film on the electrode and may therefore be quite different from the ordinary or thermodynamic potential. This gives a plausible explanation for the difference between the Ostwald zero and the Billitzer zero. The only difficulty with this is that one would suppose that the flowing mercury electrode should give the electrokinetic potential, whereas it actually gives the thermodynamic potential. Freundlich's experiments seem to show that adsorption plays a great part in the electrokinetic potential and only a slight part in the thermodynamic potential. This may be true but it is not clear why it should be. There is no apparent reason why one should not have marked adsorption at the surface of the metal.

Sheppard says that "it has long been known to emulsion makers that different varieties and batches of gelatin used to prepare the same emulsion could give quite different photographic qualities and notably different sensitivities." From special experiments he concluded that "the sensitivity substance is specifically afforded by the gelatin, and in greater degree by one gelatin than by another." A long and skilful study has proved that "the sensitizing body in photographic gelatin is primarily allyl isothiocyanate, which becomes partly converted to allyl thiocarbamide," which may react with the silver halide to form silver sulphide. "The sensitivity substance discussed in the first part of this paper is, therefore, silver sulphide $Ag_2S$, which can be replaced by $Ag_2Se$ or $Ag_2Te$ with equal or greater effect. This substance is consistent with the theory developed for the function of the sensitivity nuclei.

"Silver sulfide is known to be capable of acting as nucleus in silver reductions. Further, its presence in the silver halide lattice would correspond to a sphere of disorientation (and ionic deformation) of the silver halide about it. It has been pointed out by G. von Hevesy that the smaller the ratio of electrolytic conductivity just above and below the melting point, the easier the orientation of the atoms in a (heteropolar) crystal lattice. For example, with the halides, . . . this condition increases up to silver iodide. This disorientation tendency is further related to the electron affinity of the ions forming the crystal. The smaller the work necessary to convert the ions forming the crystal into the neutral state, the greater the disorientation tendency of the crystal. This principle is, moreover, rever-

sible, and is fully in harmony with the theory of the sensitizing function proposed. . . . Silver iodide not only shows the greatest disorientation tendency, but lowest electron affinity. But further, as von Hevesy points out, sulfur has an electron affinity of only 45 kg. cals., and solid $Ag_2S$ shows an even greater conductivity than solid AgI, being the best known electrolytic conductor."

Palmer and Richardson have controverted Alexander's theory of the clotting of cow's milk by rennin by showing that lactalbumin does not act as Alexander had assumed and that there is no warrant for Alexander's alleged assumption that the casein compound natural to cow's milk is an unstable, irreversible colloid. The reviewer does not know whether Alexander really made this assumption or not; but it is not essential to his theory. One can consider that casein is peptized by lime and yet admit that the so-called "calcium caseinate dispersion is itself a protective colloid of a high order, emulsifying fats, protecting gold sols, and exhibiting other properties of emulsoid sols." A case in point is an alkaline chromic oxide sol. The reviewer holds no brief for Alexander; but the paper would have been more satisfactory if the authors had been a little fairer in their discussion.

Heilbrunn conceives of protoplasm "as consisting of an interior mass of fluid surrounded by a precipitation membrane of the Traube type. The interior fluid is a protein sol and contains various granules and droplets suspended in it. . . . As soon as it became at all apparent that the living material was a fluid or a semi-fluid, as soon indeed as the biologists began to think of it in physical terms, they suggested that in its various activities it might suffer coagulations like those which had previously been observed in such animal fluids as blood and milk. But it is easier to demonstrate the coagulation of blood or milk than the coagulation of protoplasm. Only with the development of reliable methods for viscosity determination within the living cell has it been possible to show conclusively that at least one process is associated with a coagulative change or at any rate a change involving a great increase in viscosity. Thus it was found in 1915 that the early stages of cell division in seaurchin eggs were accompanied by a sharp increase in viscosity. This knowledge has now been confirmed for plant cells."

"Perhaps it may be worth our while to reason about the colloidal phenomena of muscle and other living structures in an indirect way. If the effects of chemicals on protoplasm are the same for various sorts of protoplasm, and we have reason to believe within fairly wide limits that they are, then we can apply our knowledge of such effects to the interpretation of biological processes, even in those instances where there are at present technical difficulties in the way of a direct determination of the protoplasmic viscosity. Thus for example if it is true, and I think it is, that a higher proportion of sodium ions in the medium surrounding a cell or group of cells tends to produce an increased viscosity and that an increase in the proportion of calcium ions tends to have the opposite effect, then if it is found that sodium ions stimulate a muscle to contraction and that calcium ions tend to prevent such a contraction, we have reason for assuming that the contraction process is in some way associated with increased viscosity of the protoplasm. Actually it has been shown for a long time that sodium ions do stimulate muscle cells to contract and that the addition of calcium ions tends to prevent this action."

Truog sums up his work on the colloid chemistry of soils by saying that "the question of soil acidity is intimately linked with the colloids of the soil. When the colloidal silicates, the acid silicates, and the alumino-silicic acids, are largely neutralized due to an ample supply of bases, the soil solution cannot become acid due to the ease with which bases are secured from these colloids. When the colloidal acids, just mentioned are less completely neutralized, bases are not secured so easily and as a result the nitric and sulfuric acids which are formed in the decomposition of organic matter may not become completely neutralized, giving rise to an acid solution. The relatively insoluble colloidal soil acids, as has been shown, have a sufficient solubility to cause an acid reaction of the soil solution."

Stamm reports a case in which "the emulsifying agent is soluble in both phases. Emulsions of amyl alcohol in water result regardless of which phase the soap is dissolved in, and from qualitative tests appear to give the same dispersity."

*Wilder D. Bancroft*

**Die Methoden der Organischen Chemie.** *Vol. II. By J. Houben (and collaborators) Third edition. 17×26 cm; pp. 1431. Leipzig: Georg Thieme, 1925. Price: paper 75 marks, cloth 84 marks.* The second volume of Houben's "Die Methoden der Organischen Chemie," 3rd Edition, is now available, and comprised within its 1431 pages is a mass of information of interest to the organic, the physical, and the technical chemist. Indeed no one carrying out practical research work, whether of a purely scientific or technical character can afford to be without this very valuable work of reference.

The bias throughout is practical, the previous tradition having been maintained. The book is a treatise on "Methods". There is an index consisting mainly of the names of substances, but even more useful is the carefully drawn up table of contents, a glance at which reveals the plan underlying the general arrangement and enables the description of any process or method to be located with facility.

The scope of the work may be gathered from the fact that the following subjects, amongst others, are treated in detail: catalysis, electro-chemical methods, reactions at high pressure, photochemical methods, oxidation, reduction, addition reactions and condensation, optical resolution and the Walden inversion, and enzyme action. Remarks on one or two of these sections may be appropriate.

The chapter on catalysis extends over 126 pages and includes detailed descriptions of the methods for preparing contact material in an active condition—nickel for the Sabatier-Senderens process, platinum black for Willstätter's method, colloidal palladium for Paal and Skita's, etc. Descriptions and diagrams are given of the special apparatus employed. Then, with the aid of many examples, some of which are described in detail, the methods and experimental conditions which have been found most suitable for bringing about various types of reactions are discussed. Considerable space is devoted to the technically important process of hydrogenation and dehydrogenation. The conditions under which high pressure, with and without high temperature, is necessary are discussed and the appropriate experimental procedures are described. Non-catalytic methods of hydrogenation and dehydrogenation are, of course, dealt with in the section on reduction and oxidation, and a more general treatment of the subject of high-pressure reactions is given in a special chapter under this title.

Similarly, the chapter on electro-chemistry deals, in the first place, with apparatus, and the methods of making the preliminary electrical measurement necessary in establishing a given set of experimental conditions. Then numerous illustrations are given of the types of conditions that have been found most suitable in certain classes of cases. It should be said that this chapter contains one or two rather conspicuous lacunae: thus no mention is made of Crum Brown and Walker's classical work on the electrolysis of the salts of carboxylic acids. The tendency manifest throughout the whole book to draw illustrations mainly from German sources, whilst it does not impair its general usefulness, seems to be responsible for some of the more obvious gaps in the subjects treated.

The section on photochemical reactions is one of the best, containing as it does not only a remarkably complete account of the action of light on organic compounds, but also a copiously illustrated description of various light sources and light filters, tables of limits of transparency, maps of spectra, and other useful data.

From the standpoint of ordinary organic chemistry it is impossible to speak too highly of the book, which, during the few weeks it has been in the reviewer's hands, has shown the exit from a difficulty on several occasions.

*C. K. Ingold*

**Der Wasserstoff.** *By Alfred Stavenhagen. No. 76 of Sammlung Vieweg. 14×21 cm; pp. 104. Braunchweig: F. Vieweg, 1925. Price: 5 marks.* The manufacture of hydrogen for industrial purposes is constantly increasing in economic importance. The stimulus given by the development of aerial navigation to work on the preparation of this gas was intensified some fifteen years ago by the application of hydrogenation to the liquid glycerides for their conversion into higher-priced solid fats. Hydrogen requirements have since grown to yet larger dimensions in connection with the synthesis of ammonia and the world's con-

sumption for this purpose is likely to increase considerably in the near future. Any addition to our knowledge of this common element, and its isolation from its compounds or from admixture with other gases must be welcome.

The brochure under review cannot be said to add much to the store of published information or to make the available material more valuable by critical discussion. It is mainly a brief compilation of the patent and other literature without an attempt being made at assessing the various processes at any but their face value. The physical chemist will be disappointed with the scant consideration given to their fundamentals.

The methods of hydrogen manufacture dealt with are, the decomposition of water by metals or metallic hydrides, the action of acids or alkalies upon metals, the decomposition of water by carbon, the scission of hydrocarbons, the electrolysis of water. A concise summary of the chemical and physical properties of hydrogen, its physiological action, its use, storage and transport is given.

Mis-spelling of names, such as Bode and Howard, instead of Bone and Coward,—Langner instead of Langer, and the bracketing of the first-named authors to other, independent workers by a single reference (page 54) is a blemish not usually associated with the proverbial thoroughness of German authors. Some of the illustrations taken from pre-war catalogues of German manufacturers are known to those interested in the subject. A chronological list of Patents, completed by the inclusion of some notable omissions, would add to the value of the book for ready reference.

*R. Lessing*

**Textile Chemistry.** *By F. G. Cooper. 23 × 16 cm, pp. ix+235. New York: E. P. Dutton and Company. Price: $5.00.* The book is written for the classes in the Union of Lancashire Institutes and in the City and Guilds of London Institute; but "it should appeal also to the young studious cotton operative who desires to increase his technical knowledge, and to those in positions of authority in mills who wish to know something of the nature, preparation, and properties of the materials used in the various processes through which cotton must pass in its journey from fibre to marketable cloth."

There are twelve chapters on general chemistry entitled: chemical diagrams; glass manipulation; simple processes; classification of matter; water; gases; oxygen; acids, alkalies, bases, salts; the elements of chemical theory; carbon; chlorine; aluminum, etc. This is followed by six chapters on the application of chemistry to textiles: the natural fibres; the machinery; sizing; bleaching; dyeing; mercerizing.

It is very difficult to judge a book of this sort, because we give much more chemistry in the high schools than is contained in this book. It might appeal to an ambitious mill hand who had had no chemistry.

The reviewer was a little startled to read, p. 105, that one of the uses of carbon dioxide is as an indicator of impurities in an atmosphere—*e.g.* in mills and schools. While it is true that Seidlitz powders, health salts, and fruit liberate carbon dioxide when mixed with water, it seems to be a little far-fetched to say that therefore one of the uses of carbon dioxide is for medicine. The reviewer had supposed that salts were made effervescent to make the medicine more appetizing and not to make it more effective.

It was new to the reviewer that "bottles of ether should be kept on the floor and never on a laboratory bench. Very disastrous consequences have occurred due to inattention to this simple precaution," p. 119. The author adopts the view of Gladstone on the theory of mercerization and writes a formula, p. 228, for the hypothetical salt of cellulose.

*Wilder D. Bancroft*

# FRICTIONAL ELECTRICITY

BY HERMANN F. VIEWEG

## Introductory

It was known to the ancients that substances like glass or amber acquire the peculiar property of attracting small pieces of other matter when rubbed with cloth or fur. The attraction between the loadstone and iron was also known. It was not realized that these phenomena were distinct, and the earlier writers did not differentiate between them.

Gilbert[1], in his interesting treatise on the magnet, pointed out that these attractions were of two kinds. The first was that between iron and the loadstone; this he called magnetic. The other was the attraction exerted by amber on small bodies. Gilbert discovered that a number of other substances could acquire this same property of attraction, and he devised a simple electrometer to study their action. Those bodies which like amber (ἤλεκτρον) would attract others when rubbed he called "electrics"; others which lacked this property he called "an-electrics". Gilbert may thus be said to have started the study of frictional electricity.

During the seventeenth and eighteenth centuries, numerous investigations were undertaken; these, however, were directed mainly towards a study of the properties and action of the frictional electricity, developed by rubbing a few standard substances, rather than towards the examination of new substances, or an explanation of the origin of the electricity. The accounts of many of these experiments are interesting, and often very amusing, but they are of little scientific value to us at present.

For a long time, a substance was thought of as being either distinctly positive, or distinctly negative, and it was believed that the sign of its charge would normally be the same whenever it was rubbed. Wilcke[2] was the first to bring out the idea that materials could be arranged in a series grading from those with the greatest tendency to become positively charged to those becoming most readily negative. Thus any member of the series might become either positively or negatively charged, depending on the substance with which it was rubbed. Wilcke arranged a few materials in order, thus establishing the first simple frictional electric series.

Various other investigators since then have worked along the same line, adding new substances, and re-arranging those already studied. Among these should be mentioned Faraday,[3] who established a series, more complete than the previous ones. He determined the fact that water must be at the positive end of the series since it charged everything else negatively.

---

[1] Guilielmi Gilberti Colcestrensis: "De Magnete," Book II, Chapter II, London (1600).
[2] Wilcke: Phil. Trans., 11, 401 (1759).
[3] Faraday: Exp. Res., 2, 2075-2145 (1843).

As the subject was studied more and more, it was found that arranging such series was not quite as simple as it seemed. Thus, although Riess[1] believed that every substance had its own definite position in a frictional electric series, he had difficulties in proving it, because of certain contradictory results he encountered. He explained these as being due to abnormal surface conditions, the effect obtained not being characteristic of the material itself. In spite of these troubles, Riess managed to arrange most of the things he studied in a series. His most valuable achievement was the determination of the fact that an equal amount of both kinds of electricity is generated by friction.

While some were working to arrange various materials in order, others were more interested in developing the laws governing the generation of frictional electricity. Peclet[2] made a thorough study of a few substances, and found that there was a definite maximum surface density of charge which one substance could acquire by friction on a specified second substance. This maximum he found was independent of the velocity of rubbing, the pressure applied, and of the area of surface involved. Riecke[3] derived the mathematical expressions showing the relations between the density of charge, the area of surface, and the rate of rubbing. His calculations, as he showed, agree quite satisfactorily with the results of Riess.

With all these data of many workers available, it was to be expected that efforts would be made to offer an explanation for the cause of frictional electricity. In 1879, Helmholtz[4] proposed the theory that the fundamental cause is a contact difference of potential which exists between any two materials. According to this theory, when two unlike surfaces are brought together, there is a concentration of positive charge on one surface and of negative on the other. It can be shown theoretically that on separating the two, if either be a non-conductor, the contact potential difference is greatly magnified, and the two surfaces will therefore be charged oppositely and at very high potentials. If both surfaces are conducting, the charges will neutralize each other on separation, at the last instant that the two substances are in contact at any point. Thus two insulators, or an insulator and a conductor, will remain charged after separation; in the case of two conductors no appreciable charge persists.

This view was supported by Hoorweg,[5] who measured the contact potential differences between various materials. He found that friction between two substances charged them the same way as one would expect from their difference of potential while in contact. The existence of a contact difference of potential between metals and insulators, as well as between insulators themselves, was shown experimentally. Hoorweg believed that the charges were due in part to a thermo-electric effect caused by local heating due to friction.

[1] Riess: Pogg. Ann., 236, 589 (1877).
[2] Peclet: Ann. Chim. Phys., 57, 337 (1834).
[3] Riecke: Wied. Ann., 3, 414 (1878).
[4] Helmholtz: Wied. Ann., 7, 337 (1879).
[5] Hoorweg: Wied. Ann., 11, 133 (1880).

Further study of contact difference of potential between various materials was made by Christiansen.[1]

The Helmholtz theory does not predict what the relative polarity of two substances should be. Attempts have been made to determine the relation between other physical properties and the position in a frictional electric series. After investigating quite a number of di-electrics, Coehn[2] postulated the following: The order of non-conductors is the same as that of their di-electric constants, the higher di-electric constants corresponding to a greater tendency to become positively charged. In a later investigation it[3] was also shown that the difference of potential is proportional to the difference in di-electric constant.

On the other hand, Hesehus[4] believed it was a question of the relative density of the surfaces, the more dense becoming positively charged, electrons flowing to the less dense, this being aided by a change in the surface tensions at the points of contact.

It has been shown by Melander[5] that the temperature of a substance affects radically the sign of charge that it acquires on being rubbed. The few materials investigated by him became more easily positively charged as their temperatures were increased. He proposed the idea of "electronic temperature" as distinct from the ordinary molecular temperature. Two substances at the same molecular temperature will in general have different electronic temperatures, the substance having the higher giving up its electrons more readily than the other. With an increase in heat content, the electronic temperature will also be raised, and the tendency to acquire a positive charge increased. Thus a reversal in the potential difference might be expected if the ordinarily negative substance were heated sufficiently.

Although the study of frictional electricity has not reached the point of being a quantitative science, a few researches of a quantitative nature have recently been carried out. Morris-Owen[6] has studied the relation between the frictional work done in rubbing and the magnitude of charge developed, varying the pressure exerted between the two surfaces. It was found that the maximum surface density of charge obtainable was independent of the pressure used in rubbing, but that the greater the pressure applied, the smaller was the work required to attain the maximum charge.

Similarly, Morris-Jones[7] measured quantitatively the maximum charge of several materials when rubbed with silk, flannel, and chamois leather; also of certain metals rubbed with silk. Assuming that the rate of charging was proportional to the rate of work, and that the charge leaked from a surface

---

[1] Christiansen: Wied. Ann., **53**, 401 (1894).

[2] Coehn: Wied., **64**, 217 (1898); **66**, 1191 (1898).

[3] Coehn: Ann. Physik, (4) **30**, 777 (1909).

[4] Heschus: Physik. Z., **2**, 750 (1901); J. Russ. Phys. Chem. Soc., **34**, 1 (1902); **35**, 575 (1903); **37**, 29 (1905).

[5] Melander: Physik. Z., **8**, 700 (1907).

[6] Morris-Owen: Phil. Mag., **17**, 457 (1909).

[7] Morris-Jones: Phil. Mag., **29**, 261 (1917).

at a rate proportional to its charge, an expression was derived showing how the charge varied with the work done. The maximum charge would be attained when the rate of charging just equalled the rate of leakage. The results obtained agree quite well with the values predicted.

The recent work of Shaw[1] is no doubt the most complete and thorough investigation that has yet been made of the generation of frictional electricity. A large number of substances were arranged in a "tribo-electric" series. The surfaces, in addition to being studied under normal conditions, were investigated under abnormal conditions, such as after and during heating; under great pressure; while flexed; and after polishing or grinding. The general effect of each of these abnormalities of surface was determined.

Shaw divided all his materials into two groups, "A" and "B", depending on how they acted under these abnormal conditions. He postulated that there were two oppositely charged layers near the surface of any substance; those in group "A" having the negative layer outside, while in group "B" the positive layer was outside. Abnormal conditions would cause a disarrangement of these layers and might even reverse their positions. No explanation was given to show why any particular substance should belong to the group in which its tribo-electric properties placed it.

All that has been done in this field up to the present may be summarized as follows:

Various frictional electric series have been established, and a considerable number of materials have been assigned their positions in them.

The relation between position in the series and other physical properties, especially the di-electric constant, has been pointed out.

A few quantitative researches have been undertaken.

The effects of certain abnormalities of surface have been studied.

The existence of contact differences of potential between different solids has been shown.

No satisfactory explanation of the causes and origin of frictional electric charges has been given.

## A Frictional Electric Series

The present investigation was undertaken with the following objects in view: (1) to arrange a frictional electric series of suitable materials, (2) to explain, if possible, from such a series how various factors determine the position a substance takes, (3) to learn what the effect of moisture is, and to what extent this may account for anomalies previously observed.

The first step, then, was to study a group of materials, chosen as adapted to the purpose, with reference to the charges produced when different surfaces are rubbed together; and from the results to arrange a frictional electric series. In selecting the materials to be used, it seemed best to use crystalline substances of definite composition, and to observe the effect of definite faces. Many of the materials usually employed by other investigators are of such

[1] Shaw: Proc. Roy. Soc., 94A, 16 (1917).

indefinite nature that it does not seem probable that results obtained with them can be interpreted; nor are they always reproducible. Such substances as furs, while they serve excellently in the generation of frictional electricity, are surely of quite variable properties. It does not seem reasonable to require all cats to have furs with identical electric characteristics. In fact, Shaw found in his experiments that one fur might vary from one part to another, being positive at one point and negative at another, with reference to the same substance. Nor is one impressed with the dielectric constant of bacon as being an accurately defined physical property. Similar objections apply to such indefinite substances as "filter-paper," "blotting-paper", "sealing-wax", "wood", et cetera. In using such things, one is merely adding unknown factors, without which the problem is already sufficiently complicated.

On the other hand, we are dealing with something absolutely definite when we use a specified face of a specified crystalline substance. While, of course, not all the crystalline structures of the materials studied are known, they nevertheless do have definite structures, the properties of specific faces are definite, and results can be duplicated. In many cases, the arrangements of the component atoms have been determined, and we know just how each face is constructed. Also, sufficient work has been done on the distribution of electricity in atoms, to give a good idea of how they are made up.

The attitude adopted in this part of the investigation has been that the ultimate solution of the problem lies in a consideration of the electrical structure of the surfaces in question, and that the bases for such a consideration are, first, the arrangement of the component atoms, for which one depends chiefly on the results of X-ray analysis,[1] and, secondly, the structure and electrical properties of the atoms themselves, as indicated by the theoretical and experimental results of the Bohr and Lewis theories.[2]

In accordance with this view, various crystals were used, these being mainly well-crystallized minerals, the choice of those to be used depending to some extent on what was readily available. In addition, a few of the standard materials were used, in order to correlate this series with others previously established.

In the experimental work itself, care was exercised to avoid as much as possible all effects that might cause anomalous and inconsistent results. In particular, attention was paid to having the surfaces clean and dry. Fresh surfaces were broken where possible, as with minerals having good cleavage, others were scraped, and metals, were cleaned either chemically or mechanically. All substances were dried over sulfuric acid before testing.

The specimen to be investigated was fastened with sealing-wax or glue to a glass rod about 10 cm. long. This served as an insulator and also allowed materials to be handled at sufficient distance to prevent loss of charge by induction. The other end of the rod was equipped with a wire hook, so that it might be hung up in a desiccator.

[1] See W. H. and W. L. Bragg: "X-Rays and Crystal Structure" (1924).

[2] See Andrade: "The Structure of the Atom" (1924).

In rubbing two surfaces together, a pressure was applied, and the rubbing done rather vigorously. It was found that successive results might be inconsistent unless this was done. This is no doubt due to the adsorbed films which exist on some surfaces, the properties of which, rather than those of the surfaces themselves, are tested by gentle rubbing. Such films may be removed or penetrated by proper application of force.

To measure the charges so obtained, use was made of a sensitive electrometer, of the Dolezalek quadrant type. One set of quadrants was grounded, the other connected to a simple condenser at about two metres distance. This consisted of two circular copper plates of 3 cm. radius, separated by a glass plate, 3 mm. thick. The needle of the electrometer could be charged to a negative potential of 55 volts, from the negative terminal of a direct-current line. A U-tube of water was put in series with the instrument, this high resistance protecting it in case of short-circuit inside the electrometer, and still allowing the potential difference of 55 volts to be maintained. All wiring from the electrometer was thoroughly insulated, a grounded copper tube enclosing the rubber tubing in which the wiring was contained. The instrument itself was surrounded by a grounded metal container. These grounded conducting shields were a protection from outside electrostatic effects. The image of a lamp, reflected from the mirror of the electrometer, was focussed by a lens on a scale, about three metres distant.

No attempt was made at quantitative measurements, although it was desired to have some idea of the magnitude of the charges. When the upper plate was charged to a potential of 15 volts, the electrometer deflection was 20 scale divisions. The capacity of the two plate condenser can be calculated to be .00005 microfarads. A charge of $4\times10^{-11}$ coulombs, or $2.5\times10^{-8}$ electrons, was therefore equivalent to one unit of the scale. On this basis, the charges were found to vary between $10^{-9}$ and $10^{-10}$ coulombs, and in each case equal and opposite on the two substances.

Using the method just described, the following series was established, each substance being charged positively on rubbing with any one below it, and negatively by any above it. The composition, crystallization, and crystal face used, is stated for each member of the series, except that where no crystal face is mentioned, massive or non-crystalline specimens were used.

## Discussion

Whenever two unlike surfaces are brought into contact, there is a tendency for electrons to pass from one surface to the other. As a result, that surface which possesses the greater attraction for electrons or the lesser power to emit them becomes charged negatively, while the other acquires an equal positive charge. We may think of each substance as having a characteristic electron pressure; or, as Melander calls it, an electron temperature.

That two metals have a definite contact potential difference, a function of the temperature, is well-known from the Peltier effect. In the case of two non-conductors or of a non-conductor and a conductor a contact potential

TABLE I

The Frictional Electric Series

*Positive End of Series*

| Substance | Composition | Crystallization. | Face |
|---|---|---|---|
| Serpentine | $H_4Mg_3Si_2O_9$ | Monocl. | |
| Asbestos | Silicate | | |
| Fur | Organic | | |
| Topaz | $(AlOH)_2SiO_4$ | Rhombic | 001 |
| " | " | " | $00\bar{1}$ |
| Mica | $KH_2Al_3(SiO_4)_3$ | Monocl. | 001 |
| Glass | Silicate | | |
| Calcite | $CaCO_3$ | Hex. | $(1\bar{1}00)$ |
| " | " | " | $(1\bar{1}01)$ |
| Aragonite | " | Rhombic | (001) |
| Cheesecloth | Organic | | |
| Barite | $BaSO_4$ | Rhombic | (110) |
| " | " | " | |
| " | " | " | (001) |
| Quartz | $SiO_2$ | Hex. | $(1\bar{1}00)$ |
| " | " | " | $(1\bar{1}01)$ |
| | | | or $(\bar{1}101)$ |
| Magnesium | Mg | | |
| Fluorite | $CaF_2$ | Isometric | (111) |
| Lead | Pb | " | |
| Fluorite | $CaF_2$ | " | (100) |
| Gypsum | $CaSO_4 2H_2O$ | Monocl. | 010 |
| " | " | " | $0\bar{1}0$ |
| Celestite | $SrSO_4$ | Rhombic | (001) |
| Zinc | Zn | Isometric | |
| Orthoclase | $KAlSi_3O_8$ | Monocl. | (001) |
| Anhydrite | $CaSO_4$ | Rhombic | |
| Beryl | $Be_3Al_2Si_6O_{18}$ | Hex. | $(1\bar{1}00)$ |
| Blotting paper | Organic | | |
| Sealing-wax | " | | |
| Sphalerite | ZnS | Isometric | (110) |
| Magnetite | $Fe_3O_4$ | " | (111) |
| Galena | PbS | " | (100) |
| Pyrite | $FeS_2$ | " | (210) |
| Molybdenite | $MoS_2$ | Hex. | (0001) |
| Copper | Cu | Isometric | |
| Antimony | Sb | Hexagonal | |
| Stibnite | $Sb_2S_3$ | Rhombic | |
| Silver | Ag | | |
| Silicon | Si | | |
| Sulfur | S | Rhombic | |
| Rubber | Organic | | |

*Negative End of Series*

difference has been found by Helmholtz, by Hoorweg, and by Christiansen. Melander's work indicates that this, too, varies with the temperature.

The existence of such a difference of potential is disputed by Morris-Owen, because he could obtain no frictional charge from mere contact of two dielectrics. The real reason for this is that mere touching does not bring any appreciable area of either substance into contact with the other. Even rubbing does not bring a large percentage of the total area into effective contact. This is indicated by the fact that when a crystal is pulled apart on a cleavage plane where opposite faces are unlike, the charges so developed are very much larger than those obtained by rubbing the same surfaces together. One cannot hope by rubbing the smoothest surfaces to bring a large portion of the total area into real contact. It is therefore reasonable to expect that mere touching has no great effect. On the other hand, the fact that the separation of two surfaces in actual contact at molecular distances, without any rubbing, causes such great charges, is strong evidence in favor of a contact potential difference.

Shaw has expressed the opinion that, if the charge is due to a transfer of electrons, the metals with all their "free" electrons ought to be at the positive end of the series. Since they are not, he doubts the explanation given here. There seems to be no basis for such an objection. The electrons of a metal may be "free" in the sense that they can readily move through the material when the proper potential difference is applied, but there is no excess of electrons ready to be given up, when a metal is at zero potential. Hence a metallic element will take its place in the series according to its electronic structure, and not at a special place due to its metallic nature.

Let us consider what happens when two unlike surfaces are in contact. Electrons from each substance will, in their rotations or oscillations, come within the sphere of activity of some atom of the other substance. Occasionally one of the electrons, being more strongly attracted by a positive nucleus with which it was not originally associated, will stay with it. There will be a mutual exchange of electrons; but that surface which loses electrons less readily will get more than it gives up. On separation it will have acquired a negative charge, the other a positive charge.

The direction in which the effective transfer of electrons takes place is dependent on the nature and structure of the atoms in each surface. Each atom is a definite aggregate of electricity; the atoms are arranged in a definite manner in crystalline matter, but in a random way in amorphous matter. Experimentally it is found that the nature of the atoms, that is, the chemical composition of the surface, is a more important factor than the arrangement of the atoms. This is shown by the fact that, although different faces of the same crystal have different positions in the series, the general position of a chemical compound is independent of the face used. In the case of $CaCO_3$, the two crystalline forms, calcite and aragonite, occupy adjacent positions. Theoretically one might find something intermediate between two faces of any crystal; however, in this work the only case of this kind observed was that

of lead, intermediate between fluorite (111) and (100). It is interesting to note, too, that in case massive material is used, its position is intermediate between the positions of the faces of the crystal. The differences between two compounds are greater than the differences between two faces of the same compound; but that the latter differences exist is certain. In no case was it possible to obtain any charge from two like faces of a crystal.

When we come to a consideration of any particular case, the problem becomes more difficult. The study of the arrangement of atoms in crystals, and that of the arrangement and motions of the electrons in these atoms, have not advanced far enough to be entirely sufficient. However, with the information at present available, it is possible to explain some of the less complicated cases.

The most simple substances to consider are the elements. Every element has a definite ionization potential, that is, the amount of energy required to remove an electron from an atom is characteristic of the element. This can be calculated on the basis of its structure under the Bohr theory. In many cases this has been determined experimentally and found to agree closely with theory. There are other phenomena such as thermionic effect, and photo-electric effect which may be used as a basis for determining the "electron affinity"[1] of an element. The relative order is the same by these different methods. Taking the data that are available,[1] we find the following relations for the elements in our frictional electric series:

| Element | Ion. Potential. | Electron Affinity |
|---|---|---|
| Ag | | 4.1 |
| Cu | | 4.0 |
| Zn | 9.5 | 3.4 |
| Pb | 8.0 | |
| Mg | 7.8 | 2.7 |

The order of the elements in the frictional electric series is thus seen to correspond to the affinity for electrons indicated by other phenomena.

The so-called normal electrode potentials are also a measure of the relative tendencies of metals to lose electrons. For example, the electrode potential of Mg is more negative than that of Ag. This means that the reaction

takes place more readily than $\begin{matrix} Mg \longrightarrow Mg^{++} + 2\,\Theta \\ Ag \longrightarrow Ag^{+} + \Theta \end{matrix}$

and that therefore a Mg electrode will give up electrons at a greater pressure than will a Ag electrode. It does not mean, as it might seem at first, that Mg has a greater attraction for electrons than Ag has. Those atoms which actually react in each case acquire a positive charge, this occurring more easily in the case of Mg. The fact that the Mg metal which has not reacted has a more negative potential than the inert mass of the silver, is due to the greater tendency of the Mg atom to lose electrons, the reaction of course taking place

[1] "Smithsonian Physical Tables," 404 (1920).

continuously only when the excess electrons are removed from the electrode. The electrode potentials are therefore in accord with other phenomena depending on electron affinity.

Since the conditions under which relative electron affinities are determined differ so greatly in the cases of measuring normal electrode potentials, and of arranging a frictional electric series, one should not expect that the order of a set of elements would be exactly the same in both cases. However, the agreement between the two methods is good.

In considering compounds we are dealing with atoms of more than one kind. The ease with which a surface gives up its electrons will depend on how the atoms are arranged with reference to that surface. Therefore different faces of a crystal will have differences of potential. Several examples of this fact are found in the series.

It will be interesting to consider a substance of which the crystal structure has been determined, such as fluorite,[1] $CaF_2$. In the (100) face the outer two layers of atoms are arranged like this:

Surface

F F F F F F F

Ca Ca Ca Ca Ca Ca

In the (111) face the arrangement has been found to be:

Surface

F F F F F F F F F

Ca Ca Ca Ca Ca Ca Ca Ca Ca

The distance between the layers is 1.73 times as great in the second case as in the first.[2] Since in the octahedron face the calcium layer is further from the surface, and also since the atoms are less exposed than in the cube face, it is to be expected that the properties of the Ca atom will be relatively more important in the (100) face than in (111).

In considering the properties of atoms in a crystal it must be remembered that the electrical structure of an atom is somewhat modified when it is part of a compound. That is, in $CaF_2$ the F atoms have each acquired one electron from some Ca atom, or at least are holding one in common with a Ca atom. Under such an arrangement the fluorine atom has no further tendency to take an electron from another atom; the Ca atom, having two of its electrons held by F atoms, has some tendency to take an electron if it can get one. Therefore that face, (100), in which the properties of Ca are relatively more predominant, should acquire the negative charge with reference to the other face. Experimentally, the octahedron is found to be positive with reference to the cube, as predicted.

[1] Bragg: "X-rays and Crystal Structure".

[2] $1.36 \times 10^{-8}$ cm., and $2.35 \times 10^{-8}$ cm., respectively.

Another interesting case to consider is that of a crystal in which two faces perpendicular to the same line are different. Thus in topaz, where other evidence has shown that 001 is different from $00\bar{1}$, it is found that the former charges the latter negatively. This is true either when the crystal is broken apart on its cleavage, without rubbing, or when the two faces are rubbed together. Probably when the internal structure of topaz is determined, it will be found that those atoms which more readily lose electrons are on the outside of the 001 surface, thus putting the atoms with greater attraction for electrons on the outside of $00\bar{1}$.

With two substances of different composition, the problem is more complex. If they are salts of different metals with the same acid radical, the differences are essentially those between the basic atoms themselves. Thus barite, $BaSO_4$, charges celestite, $SrSO_4$, negatively, and this charges anhydrite, $CaSO_4$, negatively. This means that the tendency to lose an electron is greatest for Ba, and least for Ca, and is, of course, in agreement with the fact that Ca is nearer the noble elements in the electrochemical series than Ba is

In case both the acid and base are different, it may be difficult to foresee how much the effect of each will count. In general the position of a compound will be a resultant of the electron affinities of the different atoms, but the determination of the relative importance of each atom may be complex.

A thorough study of this subject would involve a consideration of various series of similar compounds, in order to determine the effects of different atoms and radicals. Such a study has not been attempted in this investigation.

However, enough has been brought out here to show that this general method of attach leads to results in accord with facts familiar to us from other phenomena. No doubt as knowledge of the electrical structure of matter increases, further consideration from this same point of view will throw more light on the subject of frictional electricity.

## "Coehn's Rule"

Since Coehn's rule is perhaps the most valuable generalization of frictional electric effects that has yet been presented, it will be considered here. It states that a frictional electric series of non-conductors from positive to negative corresponds to a series from highest to lowest dielectric constant. This offers no explanation as to why the two series have the same order, why a high dielectric constant should make a substance more positive, or why good conductors occur in a frictional electric series between dielectrics. Perhaps from a consideration of the electronic theories here discussed, we can see what this rule means.

The dielectric constant of a medium is a measure of the force existing between two opposite charges in the medium. The greater the dielectric constant the less will be the force. Without attacking the problem quantitatively, we can see that, in the higher dielectric medium, an atom which is positively charged because it has lost an electron will exert a lower attractive force on

an electron at the surface than will a positively charged atom in the other medium, when two non-conductors are in contact. The resultant effect will be to give the medium of lower dielectric constant a better chance to regain any electrons it may have lost, and it is therefore to be expected that it would be negatively charged. This is in agreement with the rule.

To refer the sign of charge back to the dielectric constant is really not explaining anything. Let us consider what this constant actually represents.

The arrangement of the electrical components of any medium determines its electrical properties, one of which is the dielectric constant. To say that one medium has a higher dielectric constant than another means that in the first case positive and negative charges are so arranged in its structure that an electron is attracted by a unit positive charge with a smaller force than it would be under similar conditions in the second case. The dielectric constant is merely one physical property which measures the relative attraction between an electron and the positively charged mass of the substance. In the case of conductors the methods usually applied in the determination of dielectric constants fail. The reason for this is that, since opposite charges do not persist for any appreciable time in a conducting medium, the force between such charges cannot be directly measured. Conductors, however, occur in the frictional electric series, in positions determined by their relative attraction for electrons, independent of their conducting properties.

## Applications

A knowledge of the way different faces of the same crystal charge each other may be a means of giving us certain information which is more difficult to obtain by other methods.

A point brought out by this work is the possibility of using a frictional electric study to determine whether or not two faces of a crystal are alike. This method is apparently very sensitive.

For example, the two faces of gypsum parallel to the good cleavage are usually considered to be alike. However, the fact that 010 and $0\bar{1}0$ charge each other oppositely, either when a gypsum crystal is pulled apart on its cleavage plane or when the two faces are rubbed together, indicates that the two faces are different.

## The Effect of Moisture

So far we have considered only ideal cases, that is, the surfaces were assumed to be clean and perfectly dry. Under ordinary conditions this is usually not true. Films of adsorbed moisture and other impurities may be present. It is well known that on damp days it is difficult to generate frictional electricity. Results so obtained are often inconsistent. Many previous investigators have had peculiar results because of this. Some were not aware of the fact that they were having any trouble; others, knowing it, cheerfully ignored it; while a few, Hoorweg for example, tried to work in the absence of moisture when it became obvious that inconsistencies were due to it. No one, up to the present, has made a systematic study of the effect of moisture, although such a study is evidently of great importance.

As a preliminary experiment, the materials previously arranged in the series were moistened by allowing steam to condense on them. On rubbing any two together, it was found that both would acquire a positive charge. This however, was small compared with the charges developed on the dry substances.

Such a method is obviously crude, and it was therefore decided to make a more careful and systematic study of a few substances. Those selected were: quartz; glass; composition insulation (CI); sealing-wax; and silver. This is a representative set, distributed throughout the series.

Five large desiccators were arranged with glass stands so that these samples could be suspended in them. The solutions in the desiccators were: (1) $H_2SO_4$; (2) 56% $H_2SO_4$, 44% $H_2O$; (3) 43% $H_2SO_4$, 57% $H_2O$; (4) 30% $H_2SO_4$, 70% $H_2O$; (5) $H_2O$. In the temperature range 15° to 25°C. these solutions will maintain aqeous vapor pressures above them in the ratio of 0%, 25%, 50%, 75%, and 100%. The relative humidities of the atmospheres in these desiccators therefore had the same relations to each other as the vapor pressures.

Specimens were placed in a desiccator and allowed to remain there for at least 24 hours to reach equilibrium. They were then rubbed on one another, and the charge measured with the electrometer. After discharging the specimen, by holding it in the ionized region near a gas flame, it was returned to the desiccator to again come to equilibrium before another determination. In this manner every possible pair of the five substances was tested at each humidity.

The results brought out the interesting fact that in every case the effect of water was the same. The exact value of the charge varied with the conditions of rubbing, but the effect of the moisture was always to add a positive charge to each surface. The naturally negative substance might be negative, neutral, or positive; the other surface was always positive.

In the extreme case where the substances had come to equilibrium with an atmosphere saturated with water vapor, the general result was to charge any two substances positively.[1] However, the two charges were not equal; the substance which would normally be negative having the lesser charge. The difference in magnitude between the two charges was quite distinct. This indicates that one effect of moisture is to add to each surface a positive charge, superimposed upon the natural tendency to charge one positively and the other negatively.

There are three factors, affecting the sign of charge, to be considered. (1) The first is the one just mentioned. Its explanation will be discussed later. (2) The contact of one solid against the water on the other will charge the solid negatively and the water positively. Similarly the second solid acquires a negative charge from the water on the other surface. These effects may be small but the result will be to leave an excess of positive charge on that

[1] As will be shown later, the corresponding negative charges, which must have been generated, were acquired by the air.

surface which under normal conditions would charge positively and an equal negative charge on the other. (3) Whenever, by breaking through the moisture film, the two solids come into direct contact, they will charge according to their natural tendency, one positively, the other equally negatively.

The combined effect of (2) and (3) is to charge the two solids equally and oppositely. (1) adds a positive charge to both materials. The resultant will depend on the relative magnitudes of the two effects. (1) will be more predominant at higher humidities; the combined effect of (2) and (3) will increase as the two surfaces are further apart in the series.

Thus at 100% humidity the added positive effect was sufficient in all cases to overcome the other effects, and both substances were positively charged. Of course, the naturally positive substance had the greater charge.

With a relative humidity of 75% the effect due to moisture was not so great. In some cases instead of both substances being positively charged, one acquired a positive and the other a much smaller negative charge. Thus quartz and silver are near enough in the series so that the positive charge due to moisture was greater than the negative charge acquired by silver from contact with quartz; both were therefore positively charged. Similarly the CI is near enough to quartz so that both acquired a positive charge; but the difference between silver and CI is great enough to make the former charge slightly negatively.

At 50% humidity the effect due to moisture had decreased considerably. Under these conditions, the water was sufficiently important only in the cases of sealing-wax and silver, and of CI and quartz to cause both to charge positively; other pairs of substances charged unequally and oppositely.

The importance of moisture at 25% humidity was relatively small. No two substances acquired a positive charge simultaneously. The negative charges were more nearly equal to the positive charges than at higher humidities. This indicates that the natural opposite charges are greater than the positive charge added to both surfaces due to the water at this humidity.

It can readily be seen from these data that they support the previous statement: The effect of moisture is an added positive charge,[1] increasing with the humidity and decreasing as the distance in the series between substances increases.

If the effect becomes greater with the amount of water present on a surface, as would happen with increasing humidity, there must be some pairs of materials which differ so greatly in the amount of water they will adsorb at the same humidity that there will be a marked difference in the magnitude of the moisture effect. To verify this the following pairs were selected: serpentine and fur; calcite and cheesecloth; and beryl and blotting-paper. In each case the first is normally positive to the second; they are very near each other in the series; and the second is capable of much greater adsorption of moisture. These substances were allowed to come to equilibrium with water vapor and then rubbed on each other. In each case it was found that the

[1] The corresponding negative charge is acquired by the air in contact with the film.

normally negative substance of each pair, could, due to its much greater adsorption of moisture, become more positive than the other, normally positive, material.

Since, at this point, it seemed evident that the effect of moisture must be due to the same phenomena as Lenard's "Wasserfallelektrizität",[1] it was thought desirable to see whether solutions of electrolytes behaved similarly.

It was found that if two solids were rubbed together with a 2% NaCl solution on their surfaces the previous effect was reversed, that is, a negative charge was added to each. This would lead one to expect that at some lower concentration there must be a point where the solution would not add a charge of either sign. On trying various strengths of solution with a few pairs of solids,[2] it was found that below .01 N the added charge was in the same sense as for water, while above .1 N it was the reverse. This method was not sufficiently sensitive to determine the effects between these strengths but it fixed the approximate limits within which the inversion point must lie.

A .1 N solution of HCl was also tried with these materials;[3] its presence added a negative charge to both solids.

No appreciable charges were observed on two surfaces covered with .1 N NaOH, when they were rubbed together. At normal concentration, NaOH solutions acted oppositely from water, adding a negative charge to each solid.

The facts, then, as to the effects of the presence of films of moisture, or of solutions of acid, alkali, or salts are quite simple. Water tends to add a positive charge; the others, when sufficiently concentrated, add a negative charge. The real problem, therefore, is to explain the causes of these effects.

In the case of pure water, the excess of positive charge on the substances being studied shows that negative electricity has disappeared, presumably into the air. Similarly, the solutions must have lost a positive charge to the air. This indicates that we must be dealing with another variation of a well-known phenomenon, the "Wasserfallelektrizität" of Lenard.

During the rubbing together of two solids covered with liquid films, the result is the mechanical disintegration of the films, causing the liquid to be charged electrically, the air in contact with the film acquiring an equal opposite charge.

A study of the causes of this effect is the same as an investigation of the reasons for various similar phenomena. Before discussing any further experimental work, it would be well to see what these other effects are, and what the most important researches along this line have been.

## "Wasserfallelektrizität"

Although a few previous observers had noted the fact that the air near water-falls is negatively charged, it was Lenard[4] who first made a thorough

[1] This will be discussed on p. 880.

[2] The different combinations of: topaz, glass, calcite, quartz, orthoclase, sphalerite, and silver.

[3] Calcite and sphalerite were not used because the acid would attack them.

[4] Lenard: Wied. Ann., **46**, 584 (1892).

study of the subject. His original paper may be said to be the basis for all further work in this field. Lenard showed that when water drops were broken up in a falls, the air was charged negatively, and the water positively. He also found that the sign of charge was the same when different gases were used. Various liquids and solutions were similarly tested. In testing NaCl solutions of different strengths, the charge of the liquid was observed to be positive up to .011% NaCl, and negative above this concentration. Lenard believed the cause of the phenomenon was a contact potential difference between liquid and gas.

The inverse, namely the bubbling of gas through liquids was first studied by Kelvin, MacLean, and Galt.[1] Although some of their results were incorrect, they established the fact that a gas would become charged when bubbled through a liquid, such as water, or a solution of an electrolyte.

Kösters[2] determined the charges on hydrogen and oxygen when bubbled through various liquids. In either case, the gas acquired a negative charge from water, whereas electrolyte solutions above a certain concentration charged the gas positively.

By far the most thorough work on this phase of the subject was done by Mozer.[3] In particular, hydrogen and oxygen were bubbled through quite a number of liquids and solutions of different concentrations. Qualitatively the effect of the two gases was the same. Electrolytes below a certain strength charged the gas negatively and above this the gas became positively charged. This concentration was determined for various acids, salts, and bases. It was found to be lower for acids than for their salts, while that for the corresponding base was higher. Mozer suggested that the action of an electrolyte might be due to adsorption of its ions by the gas.

Another interesting point that he brought out was the fact that a bubble of gas in a liquid is electrically charged, and with the same sign that it bears on leaving the liquid. This was shown by the motion of the bubble under an electric field.

This particular point has been the subject of several researches by McTaggart[4] who showed that an air bubble in contact with water bears a negative charge. The charges on bubbles in various solutions were tested. With $Th(NO_3)_4$ in solution the charge on the bubble could be reversed.

Numerous other workers have studied this subject. The essential facts have all been in agreement with those brought out in the papers just mentioned. The results are the same whether liquids be broken up in a gas atmosphere, or a gas be bubbled through a liquid, or even when a gas bubble is in contact with a liquid. With water the gas charges negatively, and with electrolytes above a certain strength positively; the liquid always bearing an opposite charge.

---

[1] Kelvin, MacLean, and Galt: Proc. Roy. Soc., **57**, 335 (1895).

[2] Kösters: Wied. Ann., **69**, 12 (1899).

[3] Mozer: Dissertation, Göttingen (1913); Coehn and Mozer: Ann. Physik, (4) **43**, 1048 (1914).

[4] McTaggart: Phil. Mag., **27**, 297 (1914); **28**, 367 (1914); **44**, 386 (1922).

An interesting summary of all the previous work in this field is found in an article by Becker.[1]

Lenard[2] also has summarized what was done up to 1915. According to his latest theory, the cause of electrification is not a contact potential difference, but is caused by mechanical processes, and is due to the liquid only. It is assumed that in water there exists a double layer of ions at the liquid-gas interface, the $OH^-$ ions in the outer, and the $H^+$ ions in the inner layer. Electrolytes tend to have their cations on the outside, and their anions nearer the interior.

Mechanical breaking up of a drop would tear off the outer layer most readily, and the gas would acquire a charge due to the fine particles of charged liquid in it. The greater the concentration of an electrolyte, the more positive would be the outer layer of the liquid.

This explanation accounts for the charges developed by bubbling gases through liquids, or by pulverizing liquids in a gas. It does not account for the charge on bubbles, which has been definitely observed by McTaggart and others.

With this brief summary of previous work in mind, we can proceed to a consideration of the causes underlying all these similar phenomena. In the cases of bubbling, or of water-falls, it is a question of the results of disturbing conditions suddenly at a liquid-gas boundary. With bubbles in liquid, the conditions existing on the surface before anything has disturbed them are evident.

The potential difference between gas and liquid cannot be due to any strictly electrochemical process, since such chemically opposite gases as hydrogen and oxygen produce the same result, as does also the inert gas nitrogen. The fact that un-ionized organic compounds in solution do not alter the action of water appreciably, and that weak, (slightly dissociated), electrolytes do not reverse the effect as strong electrolytes do, shows that the action of substances in solutions is due to their ions. The logical conclusion is that the charge on the gas is caused by its selective adsorption of ions from the solution, the sign of charge depending on whether the positive or the negative ions are adsorbed more strongly. The existence in the gas of both positive and negative carriers of charge has been shown experimentally.[3] Most interesting is the experiment of Aselmann[4] in which he found that the gas bubbled through a NaCl solution contained both positive and negative carriers, those with positive charge containing Na, as shown by a flame test, the others being free of Na. This is exactly what would be expected on the basis of adsorption. The gas would adsorb both positive and negative ions, the concentration of the ions determining which was adsorbed more.

---

[1] Becker: Jahr. Rad., 9, 52 (1912).
[2] Lenard: Ann. Physik, (4) 47, 352 (1915).
[3] Bloch: Ann. Chim., 22, 370; 23, 28 (1911).
[4] Aselmann: Ann. Physik, (4), 19, 960 (1906).

The process by which the gas acquires its charge is quite simple. As long as the gas and liquid are in contact, adsorptive forces hold some of the ions of the solution to molecules of the gas. The bubble in the liquid, or the gas surrounding a liquid drop or surface, will have a charge at the boundary. If then, due to some sudden mechanical disturbance, either the bubble forces its way out of the liquid, or the drops of liquid are broken into finer drops, or the liquid films on the surface of a solid are torn apart and pulverized, the gas is violently separated from the liquid, and in the process carries with it some of the adsorbed ions.

The extent to which any particular ion is adsorbed is, of course, dependent on its concentration. Although sufficient data were available to show what certain ions would do, no record had been made of the action of certain others.

For this reason it was desirable to measure the effects of various solutions not previously investigated. The method of bubbling gas through a liquid was chosen as being more accurate and convenient than that of testing solutions by rubbing them on the surface of solids. Air was used as the gas, since this is the atmosphere that is normally present in experiments. A few solutions, whose action in connection with hydrogen and oxygen had been examined by Mozer, were tried to show the comparison between air and other gases.

## Experimental

In determining the charges developed by bubbling air through various liquids, use was made of apparatus very similar to that described by Coehn and Mozer. To purify the air it was passed through KOH solution to remove $CO_2$ and then through $H_2SO_4$ to dry it. The reason for removing $CO_2$ was to prevent changes in dilute alkaline solutions during prolonged bubbling. The purified air was then passed through a grounded copper tube containing fine brass gauze, to remove any charge it might have acquired. The solution itself was contained in a flask, this part of the apparatus being like that used by Mozer. Just above the opening of the side-arm leading from the flask was suspended a perforated platinum cone covered at theb ase with 80-mesh platinum gauze. The cone was connected to one set of quadrants of the electrometer, by means of wires insulated and shielded as described before. The cone and the flask containing the liquid were enclosed in a grounded metal container.

As gas bubbled through the liquid and went out through the side-arm it gave up the charge it acquired to the gauze, the electrometer deflection being proportional to this charge. In order to compare all the experiments on the same basis, measurement was made in each case of the change in deflection during the 15 minutes from 5 min.-20 min. after commencing the bubbling of the gas. During the first few minutes the action of the instrument was usually erratic.

Since the value of scale divisions in terms of quantity of charge may vary from day to day, a solution of .1 N $NaNO_3$ was used daily as a standard of

comparison. For this reason all the results recorded are calculated with reference to the effect of .1 N $NaNO_3$ as unity.

The rate at which it is desirable to bubble the air depends on two considerations. First, if it is done too slowly, the rate of development of charge is not great enough to make measurements accurate. However, if it is too rapid, particles of liquid may be carried along and strike the gauze, causing erroneous results. The rate of flow was varied until a satisfactory speed was found. This was maintained throughout all the experiments.

Great care had to be exercised to guard against the presence of any impurities in the solutions. The smallest traces of some substances will cause results to vary greatly from their true values. For example, a very small

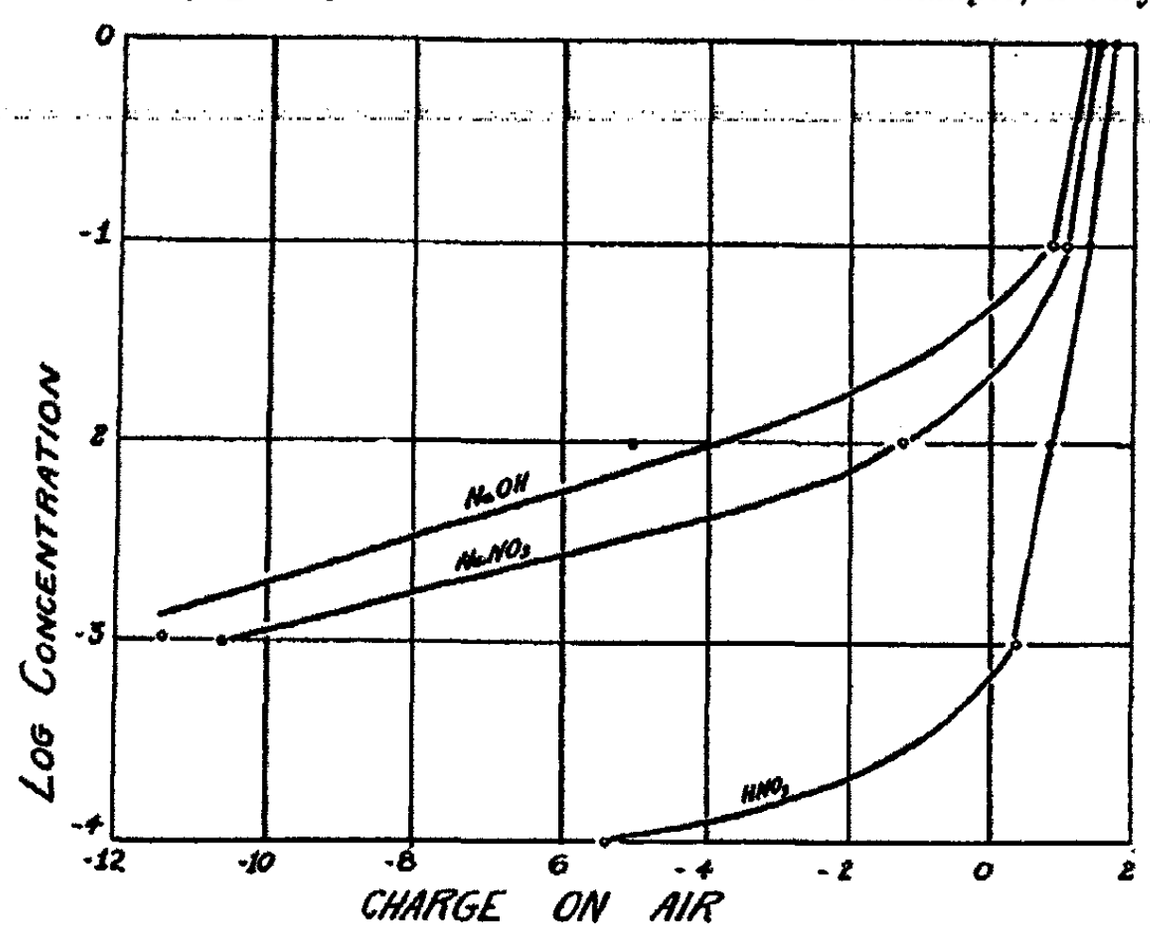



FIG. 1

*Variation in Charge on Air after bubbling through Solutions NaOH, $NaNO_3$, and $HNO_3$.*

amount of acid in a salt solution will lower the inversion concentration considerably. Therefore the flask was thoroughly rinsed several times when changing from one solution to another. Also the flask and other glassware, such as pipettes and graduates, were cleaned with bichromate-sulfuric acid mixture every day before using. In this way, it was possible to obtain consistent and reproducible results.

A tabulation of the results obtained follows. The concentrations are those of ionized compound in solution, these being calculated from conductivity data. Concentrations were expressed in this manner because the object of getting the data was to show the variation in adsorption of the ions with change in their concentrations.

Determinations were usually made of the charges on the gas after bubbling through 1, .1, .01, and .001 N normal solutions. In some cases other concentrations were also found necessary. From the charges so obtained, the prob-

TABLE II

Charge on Air after bubbling through Solutions

Effect of .1 $NaNO_3$ taken as unity.

$NaNO_3$

| N[1] | Charge |
|---|---|
| .001 | −10.6 |
| .01 | − 1.17 |
| .1 | + 1.00 |
| 1 | + 1.5 |

Inv. Conc. = .018 N

NaOH

| N | Charge |
|---|---|
| .001 | −11.3 |
| .01 | − 5.0 |
| .1 | + 0.87 |
| 1 | + 1.45 |

Inv. Conc. = .031 N

NaCl

| | |
|---|---|
| .001 | −10 |
| .01 | − 1.3 |
| .1 | + 0.91 |
| 1 | + 1.34 |

Inv. Conc. = .023 N

KOH

| | |
|---|---|
| .001 | −9.1 |
| .01 | −4.4 |
| .1 | +1. |
| 1 | +1.6 |

Inv. Conc. = .025 N

$HNO_3$

| | |
|---|---|
| .0001 | −5.3 |
| .001 | +0.34 |
| .01 | +0.80 |
| .1 | +1.32 |
| 1 | +1.61 |

Inv. Conc. = .0003 N

HCl

| | |
|---|---|
| .0001 | −6.0 |
| .001 | +0.21 |
| .01 | +0.73 |
| .1 | +1.12 |
| 1 | +1.41 |

Inv. Conc. = .0003 N

[2] $Th(NO_3)_4$

| N | Charge |
|---|---|
| .001 | −0.61 |
| .01 | +1.71 |
| .1 | +7.9 |

Inv. Conc. = .0015 N

$K_3Fe(CN)_6$

| N | Charge |
|---|---|
| .001 | −15 |
| .01 | − 6.8 |
| .1 | + 0.41 |
| 1 | + 0.82 |

Inv. Conc. = .06 N

$BaCl_2$

| | |
|---|---|
| .001 | −8.1 |
| .01 | 0 |
| .1 | +1.10 |
| 1 | +1.54 |

Inv. Conc. = .01 N

* $H_2O$ (distilled) −150

[1] Concentrations refer to concentrations of ions of the substance. Thus, .119 N NaCl is about 84% dissociated, and therefore is .1 N with reference to Na and Cl ions.

[2] In the cases of $Th(NO_3)_4$ and $K_3Fe(CN)_6$, the concentrations given refer to the normality of the solution in terms of total dissolved salt, and not merely the ionized portion.

*Owing to the abnormally high value of the charge due to water, its relative value with reference to the others is only approximate.

able inversion concentration was estimated. A solution of this strength was then tested, and using the results of this with the other determinations, the inversions concentration was determined graphically. The results are given in Table II.

Three curves, showing the variation in charge on the gas with concentration of ionized $HNO_3$, $NaNO_3$, and NaOH are shown in Fig. 1. These compounds were chosen as examples of an acid, a salt, and a base.

## Discussion

The curves shown in Fig. 1 are typical of the actions of all well-ionized electrolytes. In dilute solutions they impart to the gas a negative charge, which decreases rapidly with increasing concentration. At a definite concentration, the gas acquires no charge; above this the gas becomes positively charged, the magnitude of charge increasing only slowly with the concentration beyond this point. Mozer's curves are similar to these, although, of course, the relative values of charges at different concentrations, and the zero-point are somewhat different. This is due partly to the use of a different gas, and also to the difference in experimental conditions, such as the velocity of the gas, and the size of orifice through which it entered the solution.

The first point that strikes one on looking over the data is the relatively high negative charge due to water itself. This means that at concentrations as low as $10^{-7}$ the $OH^-$ ion is adsorbed very strongly: $H^+$ practically not at all. (Mozer could find no positive carriers in the gas after it had bubbled through pure water). In the case of solutions of electrolytes, it is therefore to be expected that the ions of water will have an effect which will be to make the gas negative.

Let us consider some examples of solutions of electrolytes. The curves shown for $HNO_3$, $NaNO_3$, and NaOH are typical for acids, salts, and bases.

The action of a solution on a gas is a resultant of the combined actions of the ions of water and those of the solute. The ions of the water, as just stated, due to the much greater adsorption of the $OH^-$ ion, tend to charge the gas negatively. The effect of the presence of the ions of the electrolyte is to change the charge in the positive direction. As the concentration of the solute increases the relative importance of the water decreases. Thus in .001 N solution the water ions are outnumbered 10,000 to 1; in 1 N solution, 10,000,000 to 1. In the latter case the water ions must play a much less important part than in the former. The charge on the gas should therefore be a resultant of a negative component, decreasing with increased concentration, and a positive component, increasing with the concentration. In examining the charge on hydrogen after bubbling through $KNO_3$ solutions, Mozer found the following distribution of positive and negative carriers:

| Conc. | Pos. | Neg. |
|---|---|---|
| .001 | 5 | 50 |
| .01 | 13 | 22 |
| .1 | 15 | 11 |

The negative charge is due to the sum of the adsorption of $OH^-$, decreasing as the concentration of solute rises, and of the negative ion of the electrolyte, increasing with the concentration. The displacement of $OH^-$ by another anion results in the decrease of the adsorption of negative ions. The positive charge is the resultant of the increasing adsorption of the cation, and the practically negligible adsorption of $H^+$, and therefore increases with the concentration. The total result is to make the charge more positive as the solution contains more of the electrolyte.

With alkalis or acids, the situation is somewhat different from the case of a salt. In alkaline solutions, the only negative ion present is the $OH^-$ ion. The negative charge on the gas must therefore increase with the concentration. The adsorption of $H^+$ is negligible. As the concentration increases, the adsorption of cation may increase more rapidly than that of the $OH^-$ ion, and at some point exceed it. This is found to be the case, but of course this concentration must be higher than that for all salts of the base in which the anion at low concentrations is less readily adsorbed than $OH^-$.

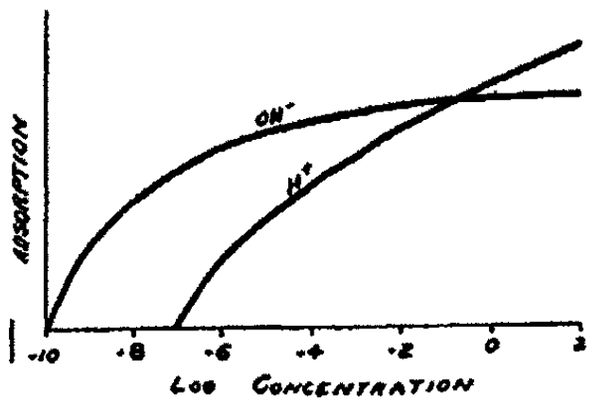



FIG. 2

Variation of Adsorption by Air with Concentration of Hydrogen and Hydroxyl Ions.

In acids the conditions are reversed. The concentration of $OH^-$ in solutions from .0001 N up is small enough to make its adsorption of no effect. The negative charge will at all strengths of solutions be less than in the case of salts of the acid, but it will increase with the concentration. The inversion point for acids will therefore occur at lower concentrations than are necessary for salts of the acid. It should be noted, however, that this would not necessarily be due to the adsorption of $H^+$ being greater than that of other positive ions, but might be due essentially to the decreased negative effect of $OH^-$ ions in acid solutions.

It may be well to point out why the difference between the inversion point for acids and that for salts is so much greater than the difference between inversion points of salts and bases. For examples these concentrations are for $HNO_3$ .0003 N, for $NaNO_3$ .018 N, and for NaOH .031 N. When we consider the probable relations between adsorption and concentration for both the $OH^-$ and the $H^+$ ion, the reason is apparent.

The data indicate that the adsorption isotherms for these two ions are qualitatively as shown in Fig. 2.

This is based on the assumption that at a concentration of $10^{-7}$, $OH^-$ has reached nearly its maximum of adsorption, this increasing very slowly beyond this concentration. $H^+$ at a concentration of $10^{-7}$ is practically not adsorbed at all. The evidence is that at normal concentration the hydrogen ion is adsorbed more than the hydroxyl ion.

It will be obvious that while in acid solutions the effect of the otherwise strongly adsorbed $OH^-$ is cut down very much, and the effect of $H^+$ increased considerably above its value at $10^{-7}$ concentration, in alkaline solutions the increase in $OH^-$ adsorption is not so great, and the effect due to removing the already negligible $H^+$ is nothing. Hence the acid inversion point should be much further below that of the salt, than the latter is below the alkali zero-point.

The question may arise as to why the $OH^-$ ion of the water is considered as having any effect in a salt solution where other anions are present in so much greater number. The large negative charge due to pure water shows that the adsorption of the hydroxyl ion is enormous in concentrations as low as $10^{-7}$. So although in a salt solution there are many more negative ions present, trying to be adsorbed by the gas, the $OH^-$ ions are much better at it, and will therefore have an appreciable effect. Of course, the greater the concentration of the salt, the more will its anions displace the $OH^-$ ion.

Some other interesting information can be obtained from these data. For example, $BaCl_2$ changes its action at .01 N, whereas NaCl must be .023 N before it changes. This means that the divalent $Ba^{++}$ ion is adsorbed more strongly than the monovalent $Na^+$. Also the tetravalent $Th^{++++}$ is even much more effective, showing that it is very strongly adsorbed. This indicates increasing adsorption with increase in valence.

On the other hand, the trivalent anion $Fe(CN)_6^{---}$ is even more strongly adsorbed than $OH^-$ and therefore the inversion for $K_3Fe(CN)_6$ is higher than for KOH.

It is reasonable to assume that in normal concentration the effect due to the ions of water does not amount to much, and that therefore the relative charges give a measure of the relative adsorptions of the various ions. On this basis we find that the order of adsorption from greatest to least is:

$Th^{++++}$, $H^+$, $Ba^{++}$, $K^+$, $Na^+$, $Fe(CN)_6^{---}$, $OH^-$, $Cl^-$, $NO_3^-$.

## Applications to Frictional Electricity

One of the objects of this investigation has been to see how the observed effects of moisture account for anomalies previously observed. It is evident that since certain films on the surface of a solid tend to add a negative charge while others tend to add a positive one, the possible variations of effects are many.

For example, the normally positive surface might have on it a film which would acquire a negative charge, while the other substance was covered with a film tending to become positive. The results obtained in this case would vary with the extent to which the two solids were rubbed together. No doubt much of the confusion in the past has been due to effects of this nature.

To consider an actual case, Shaw found that mica when beaten lightly on glass became positively charged, when it should have become negative. When rubbed firmly the mica charged negatively. This is what would be expected if the mica, (which has a strong tendency to adsorb moisture), were

wet. If a clean, dried mica surface be used, it becomes negatively charged even if only rubbed lightly.

In some experiments on sand, Phillips[1] found that if it were allowed to slide over a filter paper, the paper charged positively when it should charge negatively. He explained this on the basis that sharp edges of sand will charge the paper positively, while dull surfaces of sand would cause a negative charge. There is no apparent reason why the paper in this experiment came into contact mainly with the sharp edges of the sand. It is interesting to note that Phillips considered moistness of the paper a prerequisite for the experiment.[2] It is to be expected that if the paper were sufficiently moist, it would acquire a positive charge when rubbed by the sand. His experiment has however not been repeated here.

During a previous investigation,[3] carried out in this laboratory, some unusual effects were noted when gases were bubbled over metal electrodes in acid solutions.

It was found that, using oxygen on one of two copper electrodes, the aerated one was anode, contrary to expectations. Iron or nickel electrodes acted as they should; they were cathode when oxygen was bubbled over them. One should also have expected that hydrogen would reverse the results, but actually it acted in exactly the same way as oxygen; copper was anode, and iron or nickel cathode when the gas was bubbled over them. Similar results were obtained with nitrogen, air, illuminating gas, and carbon dioxide.

No attempt will be made here to explain why copper acts differently from iron and nickel. But the point of interest is that the charge producing these effects must be due to the same phenomenon that we are discussing here; namely the charge acquired by a gas due to selective adsorption of the ions of a solution.

This indicates at once that the potential of a gas electrode may be affected somewhat by this action. In a recent paper by Arkadjev,[4] it is shown that the potential of a hydrogen electrode with reference to a .1 N HBr solution is increased, that is, made more positive, by the addition to the solution of a neutral salt.

With $KNO_3$ and KCl the lowest concentrations made the electrode more negative; then with increasing concentration it became more positive. With NaCl, LiCl, KBr, and LiBr, the action was to make the electrode more positive with greater concentration.

It seems reasonable that these results are due, at least in part, to the adsorption phenomena discussed in this paper.

---

[1] Phillips: Proc. Roy. Inst., 19, 742 (1910).

[2] "I need hardly point out that the filter paper used should not be specially dried. Pieces which have been left about in a room for a few hours adsorb sufficient moisture to insure the right degree of conductivity."

[3] Bancroft: J. Phys. Chem., 28, 842 (1924).

[4] Arkadjev: Z. physik. Chem., 104, 192 (1923).

In this study of the effect of moisture, certain anomalies observed by previous workers have been explained; and the possible explanation of others not discussed is thereby suggested. The necessity of working in the absence of moisture, if reproducible results are desired, is apparent.

## Summary

The results of this investigation have been the following:

1. A frictional electric series has been established, including several substances not previously placed, and showing the effect of using different crystal faces.

2. An explanation of frictional electricity has been proposed, using the electronic structure of matter as a basis.

3. A suggestion as to the physical significance of "Coehn's rule" has been offered.

4. The effect of moisture films on frictional electric charges has been shown to be related to Lenard's "Wasserfallelektrizität".

5. The charges produced when air is bubbled through various solutions have been measured.

6. An explanation of these effects, (4 and 5), has been presented on the basis of the selective adsorption of ions by a gas.

The writer wishes to express his sincere appreciation to Professor W. D. Bancroft, under whose direction this investigation was carried out, for his valuable criticisms and helpful suggestions.

*Cornell University.*

# IONISATION BY RADON IN SPHERICAL VESSELS

BY W. MUND

In quantitative work on the chemical effects of $\alpha$ rays, it is found very convenient to mix a given amount of radon with the homogeneous system to be studied. Very often one wishes to know the number of pairs of ions which are formed in the reaction vessel.

In a liquid the range of $\alpha$ rays is so small that adsorption by the walls of the vessel may be disregarded. In a gaseous mixture the loss of ionisation that occurs through many particles encountering the glass has to be taken into account.

This problem was solved by S. C. Lind[1] for small spherical bulbs having diameters about half the range of the $\alpha$ particles from radon.

Ionisation per unit length of path varies for an $\alpha$ ray with the distance $r - x$, from the end point of the range. According to Geiger's law it is expressed by

$$i = k(r - x)^{\frac{1}{2}}$$

From this relation it may be shown that for values of $x$ not exceeding 2 or 3 cms the $\alpha$ particle leaves on its track a number of ions very nearly proportional to $x$. Assuming this simplification S. C. Lind has been able to calculate the ionisation in small spheres.

The following results may be looked upon as a further step in the direction opened by Lind.

Two assumptions have been found necessary:

1. The validity of Geiger's law.

2. That all the Ra A and Ra C as soon as formed in the bulb is deposited on the walls.

If these points are granted the merely mathematical problem is solved in two steps without any further simplification.

I. Let $N_0$ atoms of radon be uniformly spread in a sphere of radius R; let $r$ be the range of every $\alpha$ particle emitted by the radon; and $k\,r^{\frac{1}{2}}$ the number of pairs of ions which the particle would produce if not stopped by the wall. The total number of pairs of ions formed during the time $t$ is given by:

$$I_1 = N_0(1 - e^{-\lambda t})kr^{\frac{1}{2}}\left[1 - \frac{9}{20}\frac{r}{R} + \frac{81}{3520}\left\{\left(\frac{r}{R}\right)^3 + \left(1 - \frac{2R}{r}\right)^{\frac{5}{2}}\left(\frac{32}{3}\frac{r}{R} - \frac{10}{3}\frac{r^2}{R^2} - \frac{r^3}{R^3}\right)\right\}\right]$$

In this formula the difference $r - 2R$ is supposed to be positive; if $2R > r$, a much simpler formula is obtained:

$$I_1 = N_0(1 - e^{-\lambda t})kr^{\frac{1}{2}}\left\{1 - \frac{9}{20}\frac{r}{R} + \frac{81}{3520}\left(\frac{r}{R}\right)^3\right\} \qquad (2)$$

[1] S. C. Lind: "The Chemical Effects of Particles and Electrons", 82 (1921).

II. Let equilibria amounts of Ra A be spread on the walls of the vessel corresponding to the initial number $N_0$ of atoms of radon. Let r′ be the range of $\alpha$ particles from Ra A. The total ionisation is given by:

$$I_2 = N_0(1 - e^{-\lambda t})kr'^4\left\{\frac{1}{2} - \frac{3}{20}\frac{r'}{R} + \frac{3}{20}\left(1 - \frac{2R}{r}\right)^4\frac{(r' - 2R)}{R}\right\} \qquad (3)$$

A similar formula applies to ionisation, $I_3$ from Ra C, r″ being the range of particles, from this source.

Again $r' - 2R$ and $r'' - 2R$ are supposed to be positive. If they are not the formula becomes:

$$I_2 = N_0(1 - e^{-\lambda t})kr'^4\left(\frac{1}{2} - \frac{3}{20}\frac{r'}{R}\right) \qquad (4)$$

The mathematical argument leading to formulas (1), (2), (3) and (4) is fully developed in an earlier (French) paper[1]. It may be briefly outlined thus:

Consider a surface element of area *ds* on the wall of the spherical vessel. Using Geiger's law the loss of ionisation is calculated which occurs through $\alpha$ rays striking *ds*. The double integration takes into account the $\alpha$ rays of every direction and from every distance compatible with the radius R, the ranges r, r′ and r″ and the distribution of the radiating source.

The formulas referring to radon Ra A and Ra C must be combined in different ways according to the size of the vessel:

1. In small spheres ($2R < r$) the total ionisation is expressed by

$$I = I_1 + I_2 + I_3 = N_0(1 - e^{-\lambda t})kr^4 F \qquad (5)$$

Putting $r'/r = a$, $r''/r = b$ and $r/R = \rho$ the function F is given by:

$$F = 1 + \tfrac{1}{2}a^4 + \tfrac{1}{2}b^4 - \frac{3}{20}\rho\left\{3 + a^{5/3} + b^{5/3} - \left(a - \frac{2}{\rho}\right)^{5/3} - \left(b - \frac{2}{\rho}\right)^{5/3}\right\} \qquad (6)$$

$$+ \frac{f\,1}{3520}\left\{\rho^3 + \left(1 - \frac{2}{\rho}\right)^{5/3}\left(\frac{32}{3}\rho - \frac{10}{3}\rho^2 - \rho^3\right)\right\}$$

Assuming for *a* and *b* the numerical values

$$a = \frac{4.50}{3.94} = 1.142;\ b = \frac{6.57}{3.94} = 1.667$$

Formula (6) may be written:

$$F = 2.249 - 0.989\rho + 0.15\rho\left\{\left(1.142 - \frac{2}{\rho}\right)^{5/3} + \left(1.667 - \frac{2}{\rho}\right)^{5/3}\right\}$$

$$+ 0.02301\left\{\rho^3 + \left(1 - \frac{2}{\rho}\right)^{5/3}\left(\frac{32}{3}\rho - \frac{10}{3}\rho^2 - \rho^3\right)\right\} \qquad (a)$$

[1] Ann. Soc. Scient. Bruxelles, 44, 336. The expression (l) given in the present text is identical with formula (16) on p. 344 of my former paper. Being a somewhat simpler form of the same relation it should be preferred in numerical calculations. Another identical expression has been kindly brought to my notice by Dr. D. C. Bardwell.

2. If $2 > \rho > 2/1.142 = 1.75$

$$F = 2.249 - 0.989\rho + 0.15\rho\left\{\left(1.142 - \frac{2}{\rho}\right)^{5/3} + \left(1.667 - \frac{2}{\rho}\right)^{5/3}\right\} + 0.02301\rho^3 \quad (b)$$

3. If $1.75 > \rho > 2/1.667 = 1.2$

$$F = 2.249 - 0.989\rho + 0.15\rho\left(1.667 - \frac{2}{\rho}\right)^{5/3} + 0.023\rho^3 \quad (c)$$

4. If $1.2 > \rho$

$$F = 2.249 - 0.989\rho + 0.023\rho^3$$

The calculations may be avoided by plotting a curve from the following tables:

Formula (a)
From $\rho = \infty$ to $\rho = 2.0$

| $\rho$ | F | $\rho$F |
|---|---|---|
| 00 | 0.000 | —— |
| 10.0 | 0.111 | 1.110 |
| 5.0 | 0.226 | 1.130 |
| 4.0 | 0.287 | 1.148 |
| 3.0 | 0.391 | 1.173 |
| 2.5 | 0.480 | 1.200 |
| 2.4 | 0.504 | 1.209 |
| 2.3 | 0.530 | 1.218 |
| 2.2 | 0.556 | 1.224 |
| 2.1 | 0.587 | 1.232 |

Formula (b)
From $\rho = 2$ to $\rho = 1.75$

| $\rho$ | F | $\rho$F |
|---|---|---|
| 2.0 | 0.621 | 1.241 |
| 1.9 | 0.659 | 1.252 |
| 1.8 | 0.706 | 1.270 |

Formula (c)
From $\rho = 1.75$ to $\rho = 1.2$

| $\rho$ | F | $\rho$F |
|---|---|---|
| 1.75 | 0.731 | 1.279 |
| 1.7 | 0.759 | 1.290 |
| 1.6 | 0.817 | 1.307 |
| 1.5 | 0.880 | 1.320 |
| 1.4 | 0.946 | 1.324 |
| 1.3 | 1.020 | 1.326 |
| .... | | |

Formula (d)
From $\rho = 1.2$ to $\rho = 0$

| $\rho$ | F | $\rho$F |
|---|---|---|
| 1.2 | 1.101 | 1.321 |
| 1.1 | 1.191 | 1.310 |
| 1.0 | 1.283 | 1.283 |
| 0.9 | 1.376 | 1.238 |
| 0.8 | 1.470 | 1.176 |
| 0.7 | 1.565 | 1.095 |
| 0.6 | 1.661 | 0.997 |
| 0.5 | 1.757 | 0.878 |
| 0.4 | 1.855 | 0.742 |
| 0.3 | 1.953 | 0.586 |
| 0.2 | 2.051 | 0.410 |
| 0.1 | 2.150 | 0.215 |
| 0.0 | 2.249 | 0.000 |

In using these tables the ratio $\rho = r/R$ must be known, r is easily found when the specific ionisation s of the gaseous mixture is given. It is then expressed by the relation.

$$r = \frac{3.94}{s} \cdot \frac{76}{P} \cdot \frac{273 + t}{273} \quad (7)$$

The product $\rho$F tabulated in the third column becomes nearly constant for values of $\rho$ increasing beyond 3.

Between $\rho = 3$ and $\rho = 1.75$ the error that would be made on assuming $\rho F$ to be constant and equal to its limiting value of about 1.10, never exceeds 20% and vanishes again for $\rho = 1.75$. This approximative constancy of $\rho F$ for large values of $\rho$ means that in small bulbs the ionisation is almost proportional to the pressure P

$$I = KP \qquad (8)$$

For large diameters or pressures, on the contrary, $\rho^3$ becomes negligible and the ionisation formula (d) may be further simplified

$$I = N_o(1 - e^{-\lambda t})kr^{3/5}(2.249 - 0.989\ r/R)$$

or

$$I = I_\alpha(1 - A/RP) \qquad (9)$$

Where

$$I_\alpha = N_o(1 - e^{-\lambda t})k\rho^{3/5} \times 2.249$$

and

$$A = \frac{0.989}{2.249} \times 3.94 \times 76 \times \frac{(273 \times t)}{273} \times \frac{1}{8}$$

For air at 76 cm and 15°C

$$A = 138.84 \text{ and } I_\alpha = N_o(1 - e^{-\lambda t})1.69 \times 10^6 \times 2.249$$

Let C be the quantity of radon in curies. The ionisation for the duration of one second will be:

$$dI/dt = C \times 3.72 \times 10^{10} \times 1.69 \times 10^5 \times 2.249\ (1 - 138.8/RP)$$

$$dI/dt = C \times 14.7 \times 10^{15}(1 - 138.8/RP) \qquad (10)$$

This allows a comparison with the empirical formula of Duane and Laborde[1] for cylindrical vessels at 15°C:

$$I_{max} = X \times 13.5(1 - 0.572\ S/V)$$

$I_{max}$ is the saturation current in electrostatic units. If $4.77 \times 10^{-10}$ E.S.U. is the charge of every ion

$$I_{max} = dI/dt \times 4.77 \times 10^{-10}$$

X is the quantity of radon expressed in gram-seconds of Ra

$$X = \frac{1.77 \times 10^{16}}{3.72 \times 10^{16}} C = 4.75 \times 10^5 C$$

S is the surface and V is the volume of the vessel. If the formula of Duane and Laborde were to be tested in the case of a spherical vessel, we would write.

$$\frac{S}{V} = \frac{4\pi R^2}{4/3\ \pi R^3} = \frac{3}{R}$$

and

$$dI/dt \times 4.77 \times 10^{-10} = C \times 4.75 \times 10^5 \times 13.5(1 - 1.716/R$$

For a pressure P = 76

$$dI/dt = C \times 13.6 \times 10^{15}\,(1 - 130.4/RP)$$

[1] Le Radium, 7, 162 (1910).

So there is found a fair agreement between the theoretical and the empirical ionisation formula though the latter originated from measurements on cylindrical vessels. This supports the statement made by Lind that the ionisation in a cylindrical tube may be put approximately equal to the ionisation in a spherical bulb of the same volume.

Though nothing very definite is known on the mechanism of radiochemical reactions, it is quite possible that in several cases the intensity of chemical effects varies along the path of the $\alpha$ particle according to the same law as intensity of ionisation. If this could be proved to be true, the function F which expresses from the stand-point of ionisation the utilisation coefficient of the radon, would hold for chemical action as well.

As a matter of fact, the simplified formula 8 has worked quite satisfactorily in expressing Lind's results[1] on the radiochemical water synthesis as well as one single result of those of Scheuer[2]. Formula (9) is identical with the empirical law that Wourtzel[3] has deduced from his very careful measurements on the decomposition of $H_2S$ by means of radon[4]. Recently the formulas (d), (c) and (b) have yielded a constant ratio M/I in studying the radiochemical condensation of acetylene[5]. Nevertheless it must be admitted that the available data are scarcely accurate enough to settle the question.

## Summary

Assuming Geiger's law, formulas and numerical tables are given for the calculation of the number of ions which are produced in a spherical vessel by the $\alpha$ rays of a given amount of radon in equilibrium with Ra A and Ra C wholly deposited on the walls.

*Louvain*
*March, 1926.*

---

[1] S. C. Lind: J. Am. Chem. Soc., **41**, 531 (1919).

[2] O. Scheuer: Compt. rend. **159**, 423 (1914).

[3] E. Wourtzel: Le Radium, **2**, 289 (1919).

[4] Wourtzel's formula: $M = M_\infty(1 - A/RP)$ was used by him to calculate by extrapolation the amount of chemical reaction per curie of radon in a bulb of infinite radius. He assumed that, at infinite radius, RaA and RaC would not reach the walls and that therefore the alpha radiation would be utilized completely. Thus $I_\infty = N_0(1 - e^{-\lambda t})(1.69 + 1.84 + 2.37)10^5$. By equation above $I_\infty = N_0(1 - e^{-\lambda t})1.69 \times 10^5 \times 2.249$. The value taken by Wourtzel for $I_\infty$ is therefore 1.55 times that arrived at by equation 9.

[5] W. Mund and W. Koch: Bull Soc. chim. belg. **34**, 241 (1925): J. Phys. Chem., **30**, 289 (1926).

3-86

# THE FORMATION OF CARBON DIOXIDE FROM ALCOHOLS*

BY WILBUR A. LAZIER AND HOMER ADKINS

The production of small amounts of carbon dioxide from ethanol, over various oxide catalysts, along with the main reactions of dehydrogenation or dehydration has been reported by several investigators and various attempts have been made to explain its formation. Brown and Reid[1] have suggested two possible explanations. According to the first, the aldehyde formed by dehydrogenation may condense to the ester which on decarboxylation would yield carbon dioxide. The other explanation depends upon the rupture of the aldehyde and the production of elementary carbon and carbon dioxide from the resulting carbon monoxide. The latter idea has been carried over from the work of Sabatier on the effect of nickel on aldehydes and has been applied to oxide catalysts. There is a possibility that carbon dioxide might also be produced thru the reaction of carbon monoxide with water, i.e., thru the "water gas reaction". Pease and Yung[2] reported that no carbon dioxide was produced by alumina provided air was excluded from the catalyst. Adkins believes that over the temperature range studied by Pease and Yung, no carbon dioxide is produced from a sufficiently pure alumina catalyst, regardless of whether air is adsorbed on the catalyst or not.

In view of the experience gained in this laboratory it is believed that none of these explanations are adequate to explain the facts in the case of alcohols other than methanol. No products of the decarboxylation of esters other than carbon dioxide have been found among the products of the reaction of ethanol over zinc oxide. No methane has been found, therefore excluding the possibility of a splitting up of acetaldehyde into carbon monoxide and methane. Also the amount of carbon deposited on the catalyst is entirely inadequate to account for the formation of carbon dioxide from the monoxide. It will be necessary, before presenting an explanation of the reaction, to review some of the facts reported elsewhere and also to present some new data bearing on this question.

Dr. Bischoff, in this laboratory, has noted the formation of 1.5 to 3.5% of carbon dioxide in the gases produced by ethanol over titania at 430°. Under the same conditions butanol produced from 1 to 2%. A brown water-insoluble unsaturated resinous substance was always found. The same observation has been made with zinc oxide as a catalyst and 5% or more of carbon dioxide may be produced from ethanol by the zinc oxide from zinc isopropoxide. It has been shown that this property of the catalyst is also dependent upon the method of preparation, for zinc oxide from the hydroxide yields less than 1% of carbon dioxide.

*Contribution from the Laboratory of Organic Chemistry of the University of Wisconsin.

[1] J. Phys. Chem., **28**, 1081 (1921).

[2] J. Am. Chem. Soc., **46**, 390 (1924).

It has been noted that there is an important relation between the amount of resinous material in the distillate and the volume of carbon dioxide produced. Acetaldehyde which gave 40% of carbon dioxide over precipitated iron oxide at 400°, produced a very dark distillate containing several cc. of the insoluble resin, while reduced nickel, which produced no carbon dioxide, gave a distillate that was almost water-white. All of the samples of zinc oxide produced varying amounts of carbon dioxide from acetaldehyde and in every case the resin formation was of the same relative magnitude as the formation of this gas. Another constant characteristic of the reactions of alcohols at the surface of oxide catalysts is the production of a low acidity in the distillate.

The effect of various factors upon the carbon dioxide and acid productions over zinc oxide catalysts has been observed. The factors considered are: 1. the depth of the catalyst bed, 2. the presence of water in the alcohol, 3. the temperature of reaction, 4. the previous heat treatment of the catalyst, and 5. the structure of the alcohol. The experimental methods were those previously described[1]. The data are summarized in Table I. The "acidity" referred to in the last column of the table is that of the distillate (for one hour) and is expressed in terms of the number of cc. of 0.4 N alkali necessary for its neutralization, carbon dioxide having been removed.

Certain conclusions may be drawn from these data. 1. The production of carbon dioxide was not dependent on the depth of the catalyst bed although the production of acid was slightly affected by this factor. 2. Water in the alcohol cut down the total activity and decreased the proportion of ethylene while increasing the proportion of carbon dioxide and hydrogen. There also was formed a small amount of saturated hydrocarbons in the runs in which the alcohol was diluted with water. The degree of acidity developed was increased by the water. 3. An increase in the temperature of reaction increased the proportion of carbon dioxide formed. 4. Heat treatments of the catalyst lowered the total activity but affected carbon dioxide production to a still greater extent. 5. Carbon dioxide production was decreased with increase in molecular weight of the alcohol and was almost nil in the case of secondary alcohols.

It is believed that the formation of carbon dioxide can be best explained by assuming the dehydrogenation of acetaldehyde. We are familiar with the conversion of acetone into ketene[1] at the surface of clay plate at 650°. This reaction consists of removing a molecule of methane from the acetone molecule leaving ketene. The position of the equilibrium is very favorable for this reaction and therefore the two products are obtained after cooling. Assuming that aldehydes are capable of dehydrogenation, ketenes should also be formed from these compounds; but hydrogen reacts with ketene at room temperature to regenerate the aldehyde so no ketene is obtained. This reaction is extremely rapid so that the ketene is immediately combined with hydrogen as soon as the reaction mixture is cooled. But the ketene may also react with

[1] Lazier and Adkins: J. Am. Chem. Soc., 47, 1719 (1925).
[1] Schmidlin and Bergman: Ber., 43, 2821 (1910).

water or aldehyde. The formation of acetic acid would result from the reaction with water. It is known that the following reaction takes place between aldehydes and ketones and ketenes:

$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!C=C=O + O=C\!<\!\!\begin{matrix} R'' \\ R''' \end{matrix} = CO_2 + \begin{matrix} R \\ R' \end{matrix}\!\!>\!C=C\!<\!\!\begin{matrix} R'' \\ R''' \end{matrix}$$

## Table I

Ethanol at 425° over various weights of zinc oxide ("Dry Process")*

| g. of ZnO | l. gas per hr. | %$CO_2$ | %$C_nH_{2n}$ | %$H_2$ | "Acidity" |
|---|---|---|---|---|---|
| 2 | 2.0 | 1.0 | 13.0 | 86.0 | 0.4 |
| 5 | 3.2 | 1.0 | 15.0 | 84.0 | 1.0 |
| 10 | 5.3 | 1.5 | 14.5 | 84.0 | 2.0 |

Ethanol + water at 425° over 1 g. zinc oxide (Ex-isopropoxide)

| %water in alcohol | | | | | |
|---|---|---|---|---|---|
| 0% | 3.9 | 3.5 | 18.0 | 78.5 | 1.1 |
| 27.5% | 1.6 | 6.6 | 7.0 | 82.5† | 5.3 |
| 38.8% | 1.3 | 7.0 | 6.4 | 84.8† | 5.9 |

Ethanol over 2 g. zinc oxide ("Dry Process")

| Temp. | | | | | |
|---|---|---|---|---|---|
| 350° | 1.3 | 1.0 | 10.0 | 89.0 | — |
| 400° | 3.2 | 3.5 | 12.0 | 84.5 | — |
| 450° | 5.4 | 6.5 | 10.0 | 83.5 | — |

Ethanol over 1 g. zinc oxide (Ex-isopropoxide) previously heated

| Heat Treatment | | | | | |
|---|---|---|---|---|---|
| 4 hrs. at 650° | 0.2 | — | — | — | 0.0 |
| 2 hrs. at 500° | 2.3 | 0.9 | 22.0 | 77.1 | 0.6 |
| None | 3.9 | 3.5 | 18.0 | 78.5 | 1.1 |

Various alcohols over 1 g. zinc oxide (Ex-isopropoxide) at 450°

| | | | | | |
|---|---|---|---|---|---|
| Ethanol | — | 5.0 | 19.0 | 76.0 | — |
| Propanol | — | 4.2 | 2.0 | 93.8 | — |
| Butanol | — | 1.7 | 3.5 | 94.8 | — |
| iso-Butanol | — | 1.4 | 1.0 | 97.6 | — |
| iso-Propanol | — | 0.4 | 6.9 | 92.7 | — |

* This sample of zinc oxide was a high grade commercial product.
† One or two % saturated hydrocarbons were present.

The expected reaction between an adsorbed ketene molecule and an adjacent molecule of an aldehyde would yield carbon dioxide and an unsaturated hydrocarbon. High temperature favors the polymerization of these highly unsaturated radicals, especially in the presence of ketene which is itself readily polymerized, so instead of the low boiling hydrocarbons the resinous material observed in the experiments is obtained. It is interesting to note that Hurd and Kocour[1] during the preparation of ketene obtained resins in their distillates having the same general properties as those noted above.

The presence of acetic acid in the distillates is explained by the reaction of the adsorbed ketene molecules with water molecules from water originally in the alcohol or from that formed by the dehydration reaction. It has been shown that water in the alcohol favors this reaction but at the same time cuts down the other reactions.

The difficulty of formation of the higher ketenes is evidenced by the negative results which have been reported (Hurd and Kocour, above reference) and there has been less carbon dioxide observed with the higher alcohols. Since ketones are much less reactive than aldehydes, the temperature range studied for the alcohols is too low to allow the splitting off of methane from acetone and so no carbon dioxide is produced from isopropyl alcohol. Little more than a trace of carbon dioxide has been observed in experiments with this alcohol.

The reaction in which carbon dioxide is formed is not secondary in that the acetaldehyde formed at one point is adsorbed at another to undergo this reaction, for if such was the case, a larger amount of catalyst should give a higher proportion of carbon dioxide which has been shown to be contrary to fact. The reaction is only secondary in the sense that a molecule of aldehyde formed by dehydrogenation of the alcohol, instead of leaving the catalyst undergoes another dehydrogenation to form an adsorbed molecule of ketene which may then react with its neighboring molecules.

*Madison,*
*Wisconsin.*

---

[1] J. Am. Chem. Soc., 45, 2170 (1923).

# THE THERMAL DECOMPOSITION OF METHANE. II

BY R. C. CANTELO

The equation $CH_4 \rightleftharpoons C + 2H_2$ accurately expresses the methane equilibrium[1]. It is evident from this that the rate of decomposition of methane is proportional to the concentration of methane at any instant; while the reverse reaction proceeds at a rate proportional to the square of the concentration of hydrogen.

In the following treatment

$x$ = decrease in partial pressure of methane at time t.

$x_\infty$ = decrease in partial pressure of methane when $t = \infty$ i.e. when equilibrium has been reached.

The following table is then self-explanatory.

TABLE I

| Time | Partial Pressures $CH_4 \rightleftharpoons C + 2H_2$ | |
|---|---|---|
| o | a | b |
| t | $a - x$ | $b + 2x$ |
| $t_\infty$ | $a - x_\infty$ | $b + 2x_\infty$ |

Then $d(b + 2x)/dt = k_1(a - x) - k_2(b + 2x)^2$

$2\,dx/dt = k_1(a - x) - k_2(b + 2x)^2$

At equilibrium $o = k_1(a - x_\infty) - k_2(b + 2x_\infty)^2$

Subtracting $2\,dx/dt = k_1(x_\infty - x) + 4k_2[b(x_\infty - x) + (x^2_\infty - x^2)]$

$= (x_\infty - x)[k_1 + 4k_2(b + x_\infty + x)]$

$= 4k_2(x_\infty - x)[k_1/4k_2 + b + x_\infty + x]$

But $k_1/k_2 = \overline{K} = p^2_{H_2}/p_{CH_4}$

$\therefore \quad dx/dt = 2k_2(x_\infty - x)[\overline{K}/4 + b + x_\infty + x]$

Put $[\overline{K}/4 + b + x_\infty] = B.$

Then $dx/dt = 2k_2(x_\infty - x)(x + B).$

$dx/(x_\infty - x)(x + B) = 2k_2dt$

which integrated and the constant of integration added gives

$$\ln (x + B)/(x_\infty + x) - \ln B/x_\infty = 2k_2(x_\infty + B)t \qquad \text{or}$$

$$\log (x + B)/(x_\infty - x) - \log B/x_\infty = 2k_2(x_\infty + B)t \times 0.4343$$

$$\log (x + B)/(x_\infty - x) - \log B/x_\infty = 0.8686\, k_2(x_\infty + B)t \qquad \text{(Eq. 1)}$$

from which $k_2$ can be determined for any value of t, when x and $x_\infty$ are known.

The meaning of x and of $x_\infty$ requires careful consideration. These are changes in the partial pressure of methane, respectively at time t and when equilibrium has been reached.

From the equation $CH_4 \rightleftharpoons C + 2H_2$, it is evident that when the partial pressure of methane has decreased by x the total pressure has become $1 + x$. Thus x and $x_\infty$ are not values measured under atmospheric pressure but under a pressure of $1 + x$ atmospheres. It is usual, however, in experimental work

[1] Bone and Coward: J. Chem. Soc., 93, 1197 (1908); Mayer and Altmayer: Ber. 40, 2134 (1907); Coward and Wilson: J. Chem. Soc., 115, 1380 (1919).

to allow the volume to change while the pressure is kept constant at one atmosphere. The partial pressures obtained under these conditions are obviously such that the total pressure is one atmosphere. Yet the values of x and $x_\alpha$ can be calculated from analytical data for atmospheric pressure. The "physical" correction for the partial pressure of hydrogen determined under a total pressure of one atmosphere is given by the equation $2x_\alpha/(1+x_\alpha) = p_{H_2}$, but in addition it is necessary strictly to apply a "chemical" correction as well. This will be apparent from the following concrete example.

For 1000°C., the equilibrium concentration of hydrogen, calculated by the method given below, is 0.98 atmospheres.

$$2x_\alpha/(1 + x_\alpha) = 0.98, \text{ whence } x_\alpha = 0.96,$$

i.e. the partial pressures of hydrogen and methane respectively are 1.92 and 0.04 atmospheres under a total pressure of 1.96 atmospheres.

But $p^2_{H_2}/p_{CH_4} = K_p$; and it is evident that the value of the expression on the left hand side of the equation tends to increase, assuming no reaction to take place. Therefore, to restore the equilibrium ratio $K_p$, combination of hydrogen with carbon must occur to form methane. In the present example, let y = this decrease in partial pressure of hydrogen. Then

$$\frac{(1.92 - y)^2}{(.04 + y)} = K_p = 55.5 \text{ (for 1000°C.)}$$

y by trial is found to be between 0.02 and 0.03. Since, however, the value 0.98 calculated for the equilibrium concentration of hydrogen is itself in error 3% at least, the refinement obtained by applying this second correction (in itself strictly accurate) would be solely imaginary. The writer has therefore used the expression

$$2x_\alpha/(1 - x_\alpha) = p_{H_2}$$

as a first approximation to determine $x_\alpha$. In the case of the determination of x, the "physical" correction is the only one that can be applied.

It is possible now to test Equation 1 by data for 985°C., given by Bone and Coward[1]. Table II gives the results of a series of experiments in which methane was shut up in heated tubes (unpacked) at atmospheric pressure for different periods of time.

TABLE II

| Temperature | 985 | 985 | 1000 | 985 | 985 |
|---|---|---|---|---|---|
| Time in minutes | 1 | 5 | 15 | 30 | 60 |
| $C_2H_2$ | 0.5 | 0.5 | nil | nil | nil |
| $C_2H_4$ | 0.3 | 0.5 | 1.3 | 0.3 | nil |
| $CH_4$ | 90.4 | 75.4 | 65.25 | 61.85 | 48.2 |
| $H_2$ | 8.8 | 23.6 | 33.3 | 38.8 | 51.2 |

For purposes of calculation we can call the temperature 1000°C., and it is necessary now to determine $K_p$ and $x_\alpha$ for this temperature.

Saunders[2] develops the following equation for the equilibrium constant for the reaction between methane, hydrogen and *amorphous* carbon:

[1] J. Chem. Soc., 93, 1197 (1908).
[2] J. Phys. Chem., 28, 1151 (1924).

$$\log K_p = 4{,}583/T - 1.75 \log T + 0.000630\,T - 0.7$$

and shows that this gives results in agreement with Mayer and Altmayer's[1] determined constants. For T = 1273°K. this gives $K_p = 55.5$, from which the equilibrium values of hydrogen and methane can be obtained by the method given by the writer in a previous paper[2], $p_H = 0.98$, whence $x_\alpha = 0.96$. Again in this series of experiments b = 0, so that $B = 55.5/4 + .96 = 14.86$.

It is necessary now to calculate the values of x corresponding to the analytical data of Table II. These values follow:

| Time (mins.) | 1 | 5 | 15 | 30 | 60 |
|---|---|---|---|---|---|
| x | 0.046 | 0.134 | 0.200 | 0.241 | 0.345 |

The fact that x at the end of 60 minutes is 0.345 while $x_\alpha = 0.96$ is in itself sufficient evidence of the slowness of the decomposition of methane.

Equation 1 may be rearranged:

$$k_2 = \frac{1}{0.8686\,(x_\alpha + B)t} \cdot \log \frac{x + B}{x_\alpha - x} - \log \frac{B}{x_\alpha}$$

Table III gives the calculated values of $k_2$.

TABLE III

| Time (mins.) | 1 | 5 | 15 | 30 | 60 |
|---|---|---|---|---|---|
| $k_2 \times 10^3$ | 1.7 | 0.96 | 0.52 | 0.32 | 0.32 |

Bone and Coward[3] emphasize the fact that an abnormal period occurs at the start of the reaction, this in their opinion being due to the reaction taking place at the walls of the reaction tube. After these have become coated with deposited carbon, the reaction proceeds to a greater degree normally. Table IV gives the values for $k_2 \times 10^3$ calculated with the fifth minute considered as the zero point.

TABLE IV

| Time (mins.) | 1 | 5 | 15 | 30 | 60 |
|---|---|---|---|---|---|
| $k_2 \times 10^3$ | — | — | 0.24 | 0.16 | 0.15 |

The agreement is much better.

To complete the mathematical analysis, the graphical solution is added:

Let $Y = \log x + B/x_\alpha - x$

$b = \log B/x_\alpha$

$m = 0.8686\,k_2(x_\alpha + B)$

Then $Y = m\,t + b$

and if the values of Y as ordinates be plotted against the values of t as abscissae, the points will lie on a straight line. The most probable straight line may be drawn by determining two Average Points and connecting them. The slope of this line gives m; from which $k_2$ (the value of $k_2$ for the whole process) may be calculated.

*Department of Chemistry,*
*University of Cincinnati,*
*Cincinnati,*
*Ohio.*

[1] Ber., 40, 2134 (1907).
[2] Cantelo: J. Phys. Chem., 28, 1035 (1924).
[3] J. Chem. Soc., 93, 1197 (1908).

# THE ORIGIN OF THE CHARGE ON COLLOIDAL PARTICLES

BY HENRY BOWEN OAKLEY

Many investigators[1] have suggested that the charge of a colloidal particle may be due to the ionisation of the molecules on its surface. The fact that colloids of a basic nature usually carry a positive charge and those of an acidic nature a negative one is strongly suggestive of this view as has been pointed out by Noyes[2], Burton[3] and others.

According to the above idea the positive charge on a ferric hydroxide sol which contains a small quantity of hydrochloric acid, is due to the power of the molecules on the surface of the particle to dissociate into positively charged iron ions and negative chlorine and possibly hydroxyl ions. The iron ions are held to the particles because they form part of the complex molecular aggregate of ferric hydroxide. The chlorine ions, on the other hand are in true solution but, unless there are other negative ions distributed in the solution to replace them, they are unable to diffuse far from the surface of the particle because of the development of a strong electrostatic attraction by the positive ions on the surface.

In the same way the negative charge of a silicic acid sol containing a small quantity of sodium hydroxide may be regarded as being due to the ionisation of the surface layer of silicic acid and complex sodium silicate into hydrogen and sodium ions. The complex silicate ion remains on the surface of the particle because it forms a structural part of the large molecular aggregate. The sodium and hydrogen ions, although in true solution, are unable to diffuse away from the particle because of the electrostatic attraction of the negative ions on the surface.

Michaelis[4] has put forward a similar view to explain the charge and stability of mastic solutions and the swelling of agar gels. But it is Loeb[5] who has done most to develop this theory, and has applied it with remarkable success to the explanation in detail of the electrical and physical behavior of proteins.

Loeb showed that if this surface ionisation was a fact the distribution of ions between the surface layer and the bulk of the solution should be governed by the Donnan[6] equilibrium, and a potential difference between the particle and the solution should be the result of this equilibrium.

---

[1] J. A. Wilson: J. Am. Chem. Soc., **38**, 1892 (1916); J. A. and W. H. Wilson: **40**, 886 (1918).

[2] A. A. Noyes: J. Am. Chem. Soc., **27**, 85 (1905).

[3] Burton: "The Physical Properties of Colloidal Solutions", (1921).

[4] L. Michaelis: "Colloid-Symposium Monograph", **2**, (1925).

[5] Jacques Loeb: "Proteins and the Theory of Colloidal Behaviour".

[6] F. G. Donnan: Z. Elektrochem., **17**, 572 (1911); Donnan and Allmand: J. Chem. Soc., 105, 1963 (1914).

## The Donnan Equilibrium

This equilibrium deals with the distribution of electrolytes on either side of a membrane. On one side of the membrane is an electrolyte one of whose ions is unable to diffuse through. All the other ions are diffusible.

The conditions satisfying the equilibrium for univalent ions may be briefly summarised as follows:—

Let $z$ = concentration of non-diffusible negative ions.
then $z$ = concentration of positive ions which are "partners" to the non-diffusible ions.
$y$ = concentration of "free" positive ions on the same side of the membrane as the non-diffusible ions.
then $y$ = concentration of the "free" negative ions on this side.
$x$ = concentration of positive ions outside the membrane
then $x$ = concentration of negative ions on this side.

Then on thermodynamic reasoning it can be shown that the product of the concentration of any two kinds of oppositely charged diffusible ions on one side of the membrane must always equal the product of the concentrations of the same two kinds of ions on the opposite side of the membrane.

$$\text{Hence } x^2 = y\,(y+z)$$

The membrane will be the seat of a potential difference between its two sides. By equating the electrical work done by moving one equivalent of ions across the membrane to the osmotic work done it may easily be shown that the potential difference is given by:—

$$\text{P.D.} = (RT/F) \log (y/x) = 0.058 \log y/x$$

$y/x$ represents the ratio of the concentrations of the negative ions on the two sides of the membrane. If there are several kinds of negative ions, a, b, c..... and a′, b′, c′.

$$\text{then } a/a' = b/b' = c/c' = (a+b+c) / (a'+b'+c')$$

Similarly if there are several kinds of positive ions
p, q, r and p′, q′, r′.

$$\text{then } p'/q = q'/q = r'/r = (p'+q'+r')/(p+q+r) = a/a'$$

Where the letters with a dash in both cases represent the concentration of the ions on the side of the membrane opposite to that of the non-diffusible ion.

In the first case the P.D. = $.058 \log a/a'$
and in the second case the P.D. = $.058 \log p'/p$

For a non-permeable acid the expressions $a/a'$ or $p'/p \leq 1$ and the logarithm and P.D. will be negative.

For a non-permeable base the expressions $a/a'$ or $p'/p \geq 1$ and the logarithm and P.D. will be positive, reckoned in both cases with respect to the side containing the freely diffusable substance only.

## Application of the Donnan Equilibrium to Surface Ionisation

It will be realized from the foregoing that the important condition for the establishment of a Donnan equilibrium is that one kind of an ion shall be prevented from diffusing where all the others can so diffuse. This condition

is fulfilled in the case of surface ionisation. Here the diffusion of one kind of ion is prevented, not by a membrane, but by its forming a structural part of a large molecular aggregate. The idea of a membrane is therefore to be replaced by the idea of a certain boundary near the surface of the particle beyond which the anions or cations, which are "partners" to the colloidal cations or anions as the case may be, are unable to diffuse because of electrostatic attraction.

It is not necessary to regard this boundary as being the position of a well-defined shell of ions, it is more natural to regard it as a "diffuse" boundary in which the ions are widely distributed about a mean position of equilibrium. The distance of this boundary from the surface must be regarded as being the average position at which the electrostatic attraction of the ions by the layer of non-diffusible ions just counterbalances the resultant osmotic pressure which tends to make the ions concentrated near the surface diffuse evenly throughout the solution.

Of course all the ions must be pictured in dynamic and not in static equilibrium.

Now let us apply this to a hypothetical case of a colloid acting as a weak acid, silicic acid for example:—

Four cases may profitably be considered.

(1) When the silicic acid contains no added electrolyte.

(2) When the only added electrolyte is a little hydrochloric acid.

(3) When the only added electrolyte is sodium hydroxide.

(4) When a neutral salt such as sodium chloride is also present in a neutral or alkaline solution.

Throughout what follows it will be assumed:—

(a) That the acid obeys the mass action law in dissociating[1].

(b) That the sodium salt is completely ionised.

(c) That neutral salts do not suppress the ionisation of the acid or its salt, and are themselves completely ionised.

Of course these assumptions can only be very roughly correct, but even wide deviations will not affect the general results in what follows.

### (1) When there is no added electrolyte

Then if there is no silicic acid in true solution the aqueous phase will be neutral.

---

[1] The forthcoming mathematical treatment may, perhaps, lay undue stress on the importance of the validity of the dissociation equation to the theory. All that is really required for the argument is:—

(a) That the surface salts of a weak colloidal acid or base with a strong base or acid are much more highly ionised than the free acid or base.

(b) That these salts, owing to hydrolysis, are only formed in quantity when the solution in contact with them has a hydroxyl or hydrogen ion concentration above a certain minimum value depending on the strength of the acid or base. These conditions may still hold even if the dissociation equation is not valid.

Using the previous symbols:—

$z$ = concentration of silicate ions bound to the surface of the particle.

then $z$ = concentration of hydrogen ions which are partners to the silicate ions.

$y$ = concentration of hydroxyl ions and also of the "free" hydrogen ions within the boundary.

$x$ = concentration of the hydrogen and hydroxyl ions in the bulk of the liquid, and will be equal to $10^{-7}$ since this is neutral.

Also let C = maximum possible concentration of the silicate ions on the surface.

$K_a$ = dissociation constant of silicic acid.

$K_w$ = dissociation constant of water.

[By the concentration of the active molecules (or ions) on the surface of a particle is meant the effective concentration as equivalents per unit volume in the surface layer of the particle of the molecules (or ions) actively participating in the equilibrium. The thickness of this layer would have to correspond to the depth below the surface to which the equilibrium extended in any particular case. This concentration, as indeed all the concentrations, should really be expressed as an "activity" or thermodynamic concentration, but this will not affect the validity of the argument].

It can be shown that the concentration of the ions of a weak non-basic acid is

$$\frac{CK_a}{\sqrt{CK_a + K_w}}$$

When, as is usually the case $CK_a$ is large compared with $K_w$ this reduces to the well known expression, $\sqrt{CK_a}$, for the ionic concentration of a weak acid.

It has been shown recently by work in this laboratory[1] that the first acid constant of $H_2SiO_3$ is about $10^{-10}$.

The value of C, the concentration of active silicic acid molecules on the surface of a particle is, of course, quite unknown. For the sake of argument suppose it is unity.

then $z = \sqrt{CK_a} = 10^{-5}$

$y$ = OH-concentration = $K_w/Z = 10^{-9}$

$x = 10^{-7}$

and the surface P.D.[2] = $.058 \log y/x = .058 \log x/y+z = -.116$ volts

If C = 0.01 instead of unity:

then $z = 10^{-6}$ $y = 10^{-8}$ $x = 10^{-7}$ and P.D. = $-.058$ volts

---

[1] Joseph and Oakley: J. Chem. Soc., 127, 2813 (1925).

[2] P. Ds. calculated in this paper are thermodynamic potential differences; these may not be identical with the "electrokinetic" potential differences, which are responsible for the migration of particles under an electric field. Which quantity may best be regarded as being the most important in preventing coagulation is quite unknown. Since the values set forth in this paper are not quantitative but only qualitatively illustrate relative differences found in practice even a rough parallelism between the two sorts of potential differences will be sufficient for the argument.

It will be noticed that the hydrogen ion concentration, $z+y$, near the surface of the particle is a hundred times and ten times respectively as great as that in the bulk of the solution.

This suggests a natural reason why such weakly acid substances such as clay or silica[1] can absorb the base and liberate the strong acid from such salts as sodium chloride.

There is much evidence that clay[2] is a weak acid, and the surface molecules of amphorous silica may be expected to become hydrated to form a complex silicic acid.

When sodium chloride is added to the water the sodium ions can replace the hydrogen ions from the surface of the clay or silica and these will now be free to disperse throughout the aqueous phase. The hydrogen ion concentration will be lowered near the surface and increased throughout the solution.

*Since the hydrogen ion concentration near the surface is lowered it necessarily* follows from the dissociation equation that the bound acid anions on the surface must increase.

This is brought about by the formation of the highly ionised sodium salt, equivalent in amount to the hydrogen ions liberated.

The above view also explains why silica or clay which has been treated with salt solution yields an alkaline solution on washing.

When the salt solution is replaced by pure water the sodium ions near the surface are replaced by hydrogen ions from the water, while the sodium ions diffuse into the aqueous phase and form sodium hydroxide. The action is that of hydrolysis taking place directly with the solid phase instead of through an intermediate solution phase.

### (2) When the only added electrolyte is hydrochloric acid

then z = concentration of the silicate ions on the surface.

also z = concentration of hydrogen ions which are "partners" to these silicate ions.

y = sum of concentrations of the chlorine and hydroxyl ions within the boundary.

x = concentration of hydrogen ions and also the sum of the concentrations of chlorine and hydroxyl ions outside the boundary.

Then from the dissociation equation:—

$$z = CK_a/K_a + (H^{\cdot}) \text{ but } (H^{\cdot}) = y + z$$

therefore $z = CK_a/K_a + y + z$, also $x^2 = y\,(y+z)$

Starting with assumed values of the hydrogen ion concentration within the boundary, $x$, $y$, and $z$ can be calculated, assuming $K_a = 10^{-10}$, $C = 1$

This has been done in Table I:—

[1] A. F. Joseph and J. S. Hancock: J. Chem. Soc., **123**, 2022 (1923); **125**, 1894 (1924).
[2] R. Bradfield: J. Am. Chem. Soc., **45**, 2669 (1923).

TABLE I

**Effect of Acid on the P.D. of a Negative Colloid.**
**x = hydrogen ion concentration.**

| y+z | z | y | $x=\sqrt{y^2+yz}$ | P.D. = .058 log y/x volts |
|---|---|---|---|---|
| $10^{-1}$ | $10^{-9}$ | $10^{-1}$ | $10^{-1}$ | 0 |
| $10^{-2}$ | $10^{-8}$ | $10^{-2}$ | $10^{-2}$ | 0 |
| $10^{-3}$ | $10^{-7}$ | $10^{-3}$ | $10^{-3}$ | 0 |
| $10^{-4}$ | $10^{-6}$ | $.99 \times 10^{-4}$ | $.995 \times 10^{-4}$ | .0001 |

Table I shows that acids are very effective in suppressing the P.D. of a negative colloid. There is no need to postulate a specific absorption of hydrogen ions. The powerful effect of acids is merely the natural result of the suppression of ionisation of a weak acid by a strong one.

Bradfield[1] and Billiter[2] showed that silicic acid sol does not coagulate until a much higher concentration of acid or salt is reached than that required to abolish the surface P.D. Loeb[3] and Michaelis[4] quote other examples. Such substances have been designated by the terms lyophilic, hydrophilic or emulsoid colloids. It appears that these owe their stability to "solution forces" similar to those which hold a truly soluble substance in solution. On the other hand substances which are readily coagulated by small quantities of electrolytes have been designated by the adjectives lyophobic, hydrophobic or suspensoid, and these owe their stability to the existence of a P.D. at their surface. They coagulate when this P.D. is suppressed sufficiently, the more rapidly the greater the suppression.

Clay suspensions belong to this class. The table shows that a given suspensoid should be coagulated by different acids at those concentrations at which their hydrogen ion concentrations are the same. This has been proved for clay by Bradfield[5]. Exactly analogous reasoning can be applied to the effect of alkalies on positive colloids.

### (3) When the only added electrolyte is sodium hydroxide

For the development of the theory we want to consider a negative colloid which does not go into true solution with sodium hydroxide.

This is not the case with silicic acid, which probably forms a system in which an equilibrium exists between colloidal aggregates of complex silicates and silicate molecules in true solution; the latter becoming the more predominant the greater the alkalinity of the solution.

Clay would appear to approximate more closely to the above conditions although even this is partially soluble in alkalies.

---

[1] "The Chemical Nature of a Colloid Clay". R. Bradfield: Bull. 60, University of Missouri, (1923).

[2] J. Billiter: Z. physik. Chem., 51, 150 (1905).

[3] Jacques Loeb: "Proteins and the Theory of Colloidal Behaviour", (1921).

[4] L. Michaelis: "Colloid Symposium Monograph", 2, (1925).

[5] R. Bradfield: J. Am. Chem. Soc., 45, 1243 (1923).

For the sake of direct comparison with the two previous cases we will consider the behaviour of an ideal substance having the same values of $K_a$ and C, and not passing into solution with alkalies.

Then z = concentration of the acid anions bound on the surface of the particle.

Also z = The sum of the concentrations of the sodium and hydrogen ions which are "partners" to these anions.

y = Sum of concentrations of the "free" sodium and hydrogen ions within the boundary.

Also y = Concentration of hydroxyl ions in the boundary.

x = The sum of the concentrations of the sodium and hydrogen ions outside the boundary.

Also x = Concentration of hydroxyl ions outside the boundary.

Then from the dissociation equation $z = CK_a/K_a + (H^{\cdot})$ but $(H^{\cdot}) = K_w/y$ so that $z = CK_a y/K_a y + K_w$, also $x^2 = y(y+z)$.

Assuming different values of y, Table II can be constructed showing the corresponding values of z, x, and the surface P.D.

TABLE II

Effect of NaOH on the P.D. of Pure Negative Colloid.
x = OH-concentration.

| y | z | x | P.D. = .058 log y/x |
|---|---|---|---|
| $10^{-7}$ | $10^{-3}$ | $10^{-6}$ | −.116 |
| $10^{-6}$ | $9.9 \times 10^{-3}$ | $9.95 \times 10^{-5}$ | −.116 |
| $10^{-5}$ | $9.1 \times 10^{-2}$ | $9.54 \times 10^{-4}$ | −.115 |
| $10^{-4}$ | 0.5 | $7.07 \times 10^{-3}$ | −.107 |
| $10^{-3}$ | 0.91 | $3.02 \times 10^{-2}$ | −.086 |
| $10^{-2}$ | 0.99 | 0.10 | −.058 |
| $10^{-1}$ | 1.00 | 0.33 | −.030 |
| 1 | 1.00 | 1.41 | −.009 |

Table II shows that for small concentrations of alkali the P.D. remains constant and has the same value as for the colloid in pure water. Increasing concentrations of alkali gradually suppress the P.D. to nearly zero.

Table III shows the effect of having a smaller concentration of acid at the surface. C = .01 instead of 1.

TABLE III

| y | z | x | P.D. volts |
|---|---|---|---|
| $10^{-6}$ | $9.9 \times 10^{-5}$ | $10^{-6}$ | .058 |
| $10^{-4}$ | $5 \times 10^{-3}$ | $7.14 \times 10^{-4}$ | .049 |
| $10^{-2}$ | $9.9 \times 10^{-3}$ | $1.41 \times 10^{-2}$ | .009 |
| $10^{-1}$ | $1 \times 10^{-2}$ | $1.05 \times 10^{-1}$ | .001 |

The same effect is observed except that the P. D. is less.

It should be remarked that the above results show, on the theory, that small quantities of alkali should not increase the P.D. of a negative sol and exactly similar reasoning may be applied to show that acids should not increase the P.D. of a positive sol.

This result is not in accordance with general experience. Thus Bradfield[1] found that the addition of sodium hydroxide to a clay sol increased the distance moved during twenty minutes in a cataphoresis experiment from 7.2 m.m. to 11.5 m.m., while further addition decreased the distance. Similarly ferric hydroxide has a greater migration velocity under an electric gradient in the presence of a small quantity of hydrochloric acid.

It will be shown, however, in the next section, that if there is a small quantity of neutral electrolyte present the theory predicts that the addition of alkali should at first greatly increase the P.D. and then depress it. Thus the observed results may be due to the presence of a small quantity of electrolyte.

It may be as well to emphasise the fact that the above result for the identity of the P.D. of the colloid in pure water with the value in the presence of alkali is only arrived at on the assumption that the surface acid (or base) of the colloid dissociates strictly according to the mass action law.

The fact that ferric hydroxide sol becomes unstable when very highly purified from hydrochloric acid may be taken to indicate, according to the views expressed in this paper that the ferric hydroxide itself does not undergo surface ionization to an appreciable extent, but that it is only a ferric hydroxide-chloride complex that ionises.

### (4) When both sodium hydroxide and sodium chloride are present

It has been shown that the surface P.D. is proportional to the logarithm of the ratio of the concentration of an ion near the surface to the concentration of the same kind of ion in the bulk of the solution.

In a neutral or very slightly alkaline solution the concentration of the sodium ions near the surface of the particle is small. But their concentration in the neutral or slightly alkaline aqueous phase is so much smaller that the ratio of these two concentrations remains large. A very small addition of a neutral electrolyte will therefore be sufficient to equalize this ratio and abolish the P.D.

If alkali is now added the surface ionisation of the weak colloidal acid is immensly increased and a P.D. will again be established which will require a much greater addition of neutral electrolyte for its suppression.

This will be made clearer by working an example. In this case it is necessary to distinguish between the concentrations of the ions of sodium hydroxide and sodium chloride.

---

[1] "The Chemical Nature of a Colloidal Clay". R. Bradfield: Bull. 60, University of Missouri, (1923).

As before let $z$ = Concentration of the anions bound to the surface of the particle.

Also $z$ = Sum of concentrations of sodium and hydrogen ions which are "partners" to these anions.

$y_1$ = Concentration of hydroxyl ions within the boundary.

Also $y_1$ = Concentration of "free" sodium ions which are "partners" to these hydroxyl ions.

$y_2$ = Concentration of chlorine ions within the boundary.

Also $y_2$ = Concentration of "free" sodium ions which are "partners" to these chlorine ions.

$x_1$ = Concentration hydroxyl ions outside the boundary.

Also $x_1$ = Concentration of sodium ions which are "partners" to these hydroxyl ions.

$x_2$ = Concentration of chlorine ions outside the boundary.

Also $x_2$ = Concentration of sodium ions which are "partners" to these chlorine ions.

Then at equilibrium:—

$$(OH)_1\,(Na)_1 = (OH)_2\,(Na)_2$$
$$(Cl)_1\,(Na)_1 = (Cl)_2\,(Na)_2$$

Where the bracketed terms represent the concentration of the appropriate ion, and the suffixes 1 and 2 refer to opposite sides of the boundary.

Referring to the definitions we can write this as:—

$$x_1\,(x_1 + x_2) = y_1\,(y_1 + y_2 + z) \quad \ldots\ldots 1.$$
$$x_2\,(x_1 + x_2) = y_2\,(y_1 + y_2 + z) \quad \ldots\ldots 2.$$

As before $z = CK_a y_1 / K_a y_1 + K_w$ ..... 3.

Dividing 2. by 1. we get $x_2/x_1 = y_2/y_1$ or $y_2 = y_1 x_2/x_1$ ..... 4.

Two special cases are of interest.

(a) To calculate the distribution of electrolytes and the P.D. when the concentration of the sodium chloride in the aqueous phase is kept constant but the alkali concentration is varied.

$x_2$ is kept constant; $x_1$ is varied at will. If $y_2$ is eliminated from equation 1. by substitution from 3. & 4. the result is a cubic equation in $y_1$ which is not easy to solve.

By solving for $y_2$ in 1. we get:—

$$y_2 = \frac{x_1(x_1 + x_2)}{y_1} - z - y_1 \quad \ldots\ldots 5.$$

Equations 4. & 5. may conveniently be solved graphically.

For every value of $x_1$, ($x_2$ having an assumed constant value) two series of values of $y_2$ are calculated from 4. & 5. for different assumed values of $y_1$. These can be plotted against $y_1$ and the place where the curves cut gives the required values of $y_1$ and $y_2$.

Table IV shows in addition the pH values of the solution, calculated for tenth normal sodium chloride ($x_2 = 0.1$), and the previous values for $K_a$ and C.

TABLE IV

Effect of NaOH on the P.D. of a Negative Colloid in the Presence of 0.1 N. NaCl. $x_1$ = OH-concentration

| $x_1$ | pH | z | $y_1$ | $y_2$ | $y_1/x_1$ | P.D. |
|---|---|---|---|---|---|---|
| $10^{-7}$ | 7 | 0.001 | $10^{-7}$ | 0.100 | 1.00 | 0 |
| $10^{-6}$ | 8 | .0094 | $9.5 \times 10^{-7}$ | .095 | .95 | −.001 |
| $10^{-5}$ | 9 | .068 | $7.3 \times 10^{-6}$ | .073 | .73 | −.008 |
| $10^{-4}$ | 10 | .256 | $3.45 \times 10^{-5}$ | .033 | .34 | −.027 |
| $10^{-3}$ | 11 | .615 | $1.60 \times 10^{-4}$ | .016 | .16 | −.046 |
| $10^{-2}$ | 12 | .909 | $1.20 \times 10^{-3}$ | .012 | .12 | −.053 |
| $10^{-1}$ | 13 | .995 | $1.93 \times 10^{-2}$ | .019 | .19 | −.041 |
| 1 | 14 | 1.00. | $6.45 \times 10^{-1}$ | .060 | .60 | −.011 |

It will be seen that the sodium chloride is at first sufficient to suppress entirely the P.D. but that as the pH increases the P.D. rises to a maximum and then falls again.

With a stronger acid the position of this maximum would be at a lower pH value; it occurs when the alkali concentration near the surface is sufficient to convert nearly completely the weak acid into its ionised sodium salt.

The theory thus offers a natural explanation why alkalies are usually good deflocculants of negative colloids.

Precisely analogous results hold for the effect of acids on a positive colloid acting as a weak base.

The ratio of the hydrogen ion concentration in the bulk of the solution to that near the surface of the particle must also be equal to $y_1/x_1$; thus the hydrogen ion concentration near the surface of the particle is only equal to that in the bulk of the solution when this ratio is unity. That is to say when sufficient salt is present to suppress the P.D. to zero. Therefore in determining the strength of a colloidal acid such as clay by means of a pH-titration curve sufficient salt should be present to flocculate the clay.

### Coagulation of Silicic Acid by Calcium Salts

Comber[1] has shown that silicic acid is very much more readily flocculated by calcium salts in an alkaline medium than in a neutral or slightly acid one.

Now calcium silicate is very insoluble, while the sodium silicates are very soluble.

The surface sodium silicate we have been considering may be regarded as being constructed of highly polar molecules. That is to say, while the acid groups and their attached sodium atoms (ions) have a very strong affinity for water, the silica groups forming the rest of the molecule have a much stronger affinity for each other than for the water. The result is a compromise, a colloidal solution.

[1] N. M. Comber: J. Agr. Sci., 19, 425 (1920).

On the other hand the calcium silicates have practically no affinity for water in this sense, as is shown by their insolubility. Thus the complex calcium silicate aggregates will show little or no tendency to surface ionisation.

Since silicic acid is very weak its salt will not be formed to any extent until the solution is alkaline. Directly the alkalinity is such that surface calcium silicates can be formed, these will be unionized and the silicic acid and silicates will be precipitated. The fact that neutral salts only coagulate silicic acid at high concentrations is to be ascribed to its lyophilic nature, as mentioned when discussing the effect of acids.

(b) The second case of interest is to assume a certain constant low value of the P.D. and to calculate the amount of sodium chloride required to depress it to this value for different concentrations of alkali.

Let the P.D. be kept constant at $-.058/10$ volts.

Then $\log y_1/x_1 = -1.0 = \bar{1}.9$ whence $y_1 = 0.7943\ x_1$ and since $y_1/x_1 = y_2/x_2$ therefore $y_2 = 0.7943\ x_2$ ..... 6.

Then substituting equation 6. in equation 1. and solving for $x_2$ we obtain:—

$$x_2 = (y^2_1 + y_1 z - x^2_1)/(x_1 - .7943 y_1)$$ where $z$ is given by 3.

Then by assuming values for $x_1$ all the other quantities may be calculated as in Table V.

TABLE V

$K_a = 10^{-10}$ P.D. = .0058 volts $C = 1$

The minimum sodium ion concentration required for the coagulation of a negative colloid at different pH values.

Na-ion concentration $= x_1 + x_2$

| $x_1$ | pH | $y_1$ | $z$ | $x_2$ | $y_2$ | $x_1+x_2$ |
|---|---|---|---|---|---|---|
| $10^{-7}$ | 7 | $7.94 \times 10^{-8}$ | .0008 | .002 | .0017 | .0021 |
| $10^{-6}$ | 8 | " $10^{-7}$ | .0078 | .017 | .0135 | .017 |
| $10^{-5}$ | 9 | " $10^{-6}$ | .073 | .158 | .125 | .158 |
| $10^{-4}$ | 10 | " $10^{-5}$ | .443 | .953 | .76 | .953 |
| $10^{-3}$ | 11 | " $10^{-4}$ | .889 | 1.91 | 1.52 | 1.91 |
| $10^{-2}$ | 12 | " $10^{-3}$ | .988 | 2.1 | 1.67 | 2.11 |
| $10^{-1}$ | 13 | " $10^{-2}$ | .999 | 2.05 | 1.27 | 2.15 |
| 1 | 14 | " $10^{-1}$ | 1.000 | 1.15 | 0.90 | 2.15 |

The last column of Table V shows the total sodium ion concentration in the bulk of the solution, while the second column shows the pH of this solution. If this particular colloid just became unstable when the P.D. of its particles was reduced to .006 volts, then the last column would represent the minimum concentration of sodium ions required to produce coagulation.

If this quantity is plotted against the pH it will be found that it increases slowly from a pH of 7 to 9. This is followed by a very rapid rise between a pH of 9 to 11 and reaches a constant value between a pH of 11 to 14.

This is precisely the type of result obtained by Bradfield[11] for the minimum potassium ion concentration required for the coagulation of a clay suspension at different pH values. At high pH values it was immaterial whether the base

or its salt was used as the coagulating electrolyte. In Bradfield's experiment the sudden increase in electrolyte requirement took place between pH values of 6 and 8; this indicates, on the theory, that the dissociation constant of the clay acid is in the neighborhood of $10^{-7}$.

The foregoing results have shown that the theory offers a natural explanation for the more characterisitc behaviour of colloids towards acids, alkalies and salts of the alkali metals.

The effect of the valency of the ion has not been considered. Loeb showed that the Donnan equilibrium predicts that the ions of higher valency should be more effective in depressing the P.D. The ratio of the P.Ds. for uni-valent, di-valent and tri-valent ions at the same concentration and pH should be in the ratio of 2; 3; 4. Loeb showed this held for uni-valent and di-valent ions with proteins. Usually the precipitating power of polyvalent ions is too great to be accounted for solely on these lines. The high precipitating power may be accounted for on the hypothesis that the surface ionisation of their compounds is much less than that of the corresponding alkali metal compound. Much of the data has, however, been obtained without control of the hydrogen ion concentration.

Many exceptions may be found to the behaviour of colloids outlined in this paper, but these are not necessarily irreconcilable with the notion of surface ionisation. Sols which can be made either positive or negative will usually be found to be of a slightly amphoteric nature, e.g. ferric hydroxide and chromium hydroxide. That is to say under suitable conditions they can be made to ionise as an acid or as a base. Metallic sols presumably form some surface compound with water or with electrolytes present during their preparation. Thus gold sol may be negative because of the surface ionisation of an auric acid complex[1]. Other metallic sols may owe their positive charge to the ionisation of a surface layer of hydroxide.[2] The sign of metallic sols may be changed by polyvalent ions because of the formation of a surface "salt" of this ion with one of its valencies, while its other valencies are free to ionise.

The peculiar base exchanging properties of zeolites, clay and artificial alumino-silicates may be attributed to the surface ionisation of the compounds of these substances with bases. The fact that calcium is held more tenaciously than sodium is in agreement with the idea that the calcium compounds are much less ionised that the sodium compounds, as has been suggested for silicic acid.

Adopting Loeb's theory as an hypothesis will at any rate serve as a guide in the making of experiments and will afford a strong reason for the control of the pH in all investigations on colloids. Its success in accounting for the behaviour of clay and proteins towards electrolytes is strong evidence for the truth of its assumptions[3].

---

[1] J. A. Wilson: Bogue's "The Theory and Application of Colloidal Behaviour", 1, (1924).

[2] Burton: "The Physical Properties of Colloidal Solutions" (1921).

[3] For application of the theory to living cell boundaries see:—Lapicque: Ann. de Physiologie et de Physicochimie biologique, 1, No. 1; Nature, 116, 150 (1925).

## The Nature of the Electrical Double Layer

In the whole of the foregoing the assumption has been made that the force on a particle during cataphoresis and its stability are proportional to the potential difference existing at its surface, and not to the charge on the particle.

This is an essential part of the theory. Thus a pure clay suspension at a low pH may cataphorese as rapidly as it does in an alkaline medium[1], although, if the clay is behaving as a weak acid, the ionisation and therefore the charge must be immensely greater in the latter case. Hitherto the assumption has always been made by writers that the force on a charged particle is always equal to the product of its charge and the potential gradient in the solution, in spite of its being recognised that the particle as a whole acts as an electrically neutral condenser whose outer charge is mobile.

This is surely a fallacy. The law $F = QV$, where $F$ = force, $Q$ = charge, $V$ = potential gradient, only applies to a charge whose potential is not modified by any other charges in its neighbourhood, even if these charges are mobile.

A truer statement is to say that the shearing force between a particle and the surrounding liquid is proportional to:—

(a) The potential gradient in the liquid.
(b) The P.D. between the particle and the liquid.
(c) The area over which this P.D. exists.

This will lead to the result that particles of the same kind but of different diameters will still have the same cataphoresis velocity. This is the result arrived at by the old assumption that the force is proportional to the charge.

Early in this paper, for the purpose of applying the Donnan equilibrium, the position of the boundary was defined as the average distance from the surface taken up by the ions as the result of a balance between the osmotic and electrostatic forces. This boundary may also be considered as the position of the outer electrical layer. The inner layer is formed by the bound ions on the surface of the particle.

We will consider the behaviour of this double layer under two conditions:—

(a) When the P.D. remains constant but the ionisation, and therefore the charge on the two layers is increased. This corresponds to the conditions dealt with in section (3), when small quantities of sodium hydroxide are added to the pure colloid.

Since the charge on the two oppositely charged layers is greatly increased, the only way for the P.D. to remain constant is for the distance between them to decrease. This at first sight may seem strange as the repelling force due to osmotic pressure is also greatly increased, but it will be shown that the attractive electrical force increases to a much greater extent.

The resultant osmotic pressure tending to make the ions within the boundary diffuse throughout the solution is proportional to the difference in the total ionic concentrations on the two sides of the boundary.

Assuming the osmotic pressure due to the anions bound on the surface is negligable, the resultant pressure is proportional to $z + 2y - 2x$.

Referring to Table II:—

| $y$ | $z + 2y - 2x$ |
|---|---|
| $10^{-7}$ | $9.8 \times 10^{-4}$ |
| $10^{-5}$ | $9.7 \times 10^{-2}$ |

In changing the OH-concentration, $y$, from $10^{-7}$ to $10^{-5}$ there is a hundred-fold increase in the resultant osmotic pressure on the outer layer, tending to drive it further away from the surface of the particle.

The electrostatic attraction between the two layers is, however, proportional to the *square* of the charge on either layer i.e. it is proportional to $z^2$.

Hence for the same example:—

| $y$ | $z^2$ |
|---|---|
| $10^{-7}$ | $10^{-6}$ |
| $10^{-5}$ | $8.3 \times 10^{-3}$ |

Thus there is an eight thousandfold increase in the attractive force.

The two electrical layers will therefore be closer together the greater their charge, and by this means the P.D. can remain constant.

(b) When the ionisation and therefore the charge on the two layers remains constant, but the P.D. is diminished.

These conditions correspond to a case in which the OH-concentration near the surface of the particle is by some means kept constant while the P.D. is diminished by the addition of a neutral electrolyte.

In this case the electrostatic attractive force remains constant but the *resultant* repulsive osmotic force is decreased by the neutral electrolyte. (When the P.D. is completely suppressed there is no resultant osmotic force.) The two electrical layers therefore approach very close together and by this means depress or eliminate the P.D. between them.

Since existing formulae for the charge and P.D. of particles based on data from cataphoresis or endosmosis experiments are, on this view untenable, it becomes desirable to look for other means of measuring these quantities.

When colloidal particles are charged and also move under an electric field (the two terms are not necessarily synonimous, as shown above) they must always possess an electrical conductance of their own.

This conductance must be regarded as being made up of two parts:—

(a) The conductance due to the electricity carried by the particle itself i.e. the charge on the inner electrical layer.

(b) The conductance due to the electricity carried by the ions forming the outer electrical layer. This charge is equal and opposite to that on the surface itself, and moves in a direction opposite to that of the particle. As fast as these ions leave the particle they are replaced by other ions from the solution.

The specific conductance of any substance is equal to the quantity of electricity conveyed per second through unit cross section of the substance under unit potential gradient. Therefore in cataphoresis experiment with unit potential gradient

If k = specific conductance due to the colloid alone in 1 c.c. of the solution.
$V_1$ = velocity of the particles themselves.
$V_2$ = velocity of the outer layer of ions relative to the electrodes.
Q faradays = charge of one sign carried by one particle.
n = number of particles in 1 cc. of the solution.
F = number of colombs in one faraday.

Then $k = nF(QV_1 + QV_2)$

Now if we suppose the force on the particle is also equal to the force on its outer layer, that is to say if we suppose the two forces are related as action and reaction, then the force on one ion of the outer layer will equal 1/Q of the force on the particle. Let us also assume that the velocity of a particle or ion is proportional to the force acting on it, as in Stokes' law.

Then if $f_1$ = force on the particle.
$f_2$ = force on one ion in the outer layer.
$V_1 = K_1 f_1$ and $V_2 = K_2 f_2$, where $K_1$ and $K_2$ are constants.
but $f_2 = f_1/Q$ and $f_1 = V_1/K_1$
therefore $V_2 = K_2 V_1/K_1 Q$ and $k = nF(QV_1 + K_2 V_1/K_1)$

From which the charge in coulombs carried by the particles in 1 c.c. of solution is given by:—

$$FnQ = (k/V_1) - nF(K_2/K_1)$$

The ratio $K_2/K_1$ represents the ratio of the velocity of an ion to that of the particle itself when both are subjected to the same driving force. Its value is therefore quite unknown.

$V_1$ can be measured from a cataphoresis experiment.

k, the conductance due to the colloid alone might be obtained by measuring the conductance of the colloidal solution before and after careful filtration through an ultra filter of sufficient fineness to retain the colloidal particles. The difference would give the conductance due to the colloid alone. Then the ratio, $k/V_1$ would be proportional to the charge on the colloid. Its variation in the presence of electrolytes, specially alkalies, should help to test the theory.

## Summary

1. The theory of surface ionisation has been developed to explain the charge on colloids.

2. By combining the equation for the Donnan ionic equilibrium with that for the dissociation of weak acids or bases, Loebs views have been developed to give a rational explanation of the general behaviour of colloids towards acids, bases and salts.

3. It has been pointed out that R. Bradfield's work on the behaviour of clay suspensions agrees closely with that predicted by the theory.

4. Rational deductions from the theory have been made as to the nature of the electrical double layer of colloids.

5. The present method of measuring the charge on colloids is adversely criticized and an alternative is suggested.

*Wellcome Tropical Research Laboratories,*
*Khartoum,*
*Jan. 20, 1926.*

# AQUEOUS SOLUTIONS OF SODIUM SILICATES. PART III. SODIUM ION ACTIVITY

BY R. W. HARMAN

## Introductory

The problem of the nature of the ions and their respective concentrations in aqueous solutions of sodium solicates cannot be determined solely by measurements of the total number of ions, say by means of vapour pressure or freezing point measurements and by measurement of the extent of the hydrolysis of these solutions. The number of ions deduced, assuming the laws of ideal solution to apply, from freezing point measurements (as will be seen from the discussion of those measurements in a paper to be communicated soon) is not in agreement with that which would correspond to the percentage hydrolysis if hydrolysis only took place. Hitherto, the silica in solution derived from the dissociation of silicate solutions has been considered colloidal, and the suggestion has been put forward that complete hydrolysis takes place, the low value found for the degree of hydrolysis being only apparent, since such degree of hydrolysis has been computed from the 'free' hydroxyl ion concentration (as measured by the hydrogen electrode), whereas the silica may be colloidal and may adsorb hydroxyl ions. If such were the case, then the hydroxyl ion concentration plus the sodium ion concentration should equal the total ion concentration as found by freezing point measurements. However, both conductivity and transport number experiments[1] give evidence of silicate ions or complex ionic aggregates being present in solution. If this is so, and the sodium ions are equivalent to the sum of the silicate and hydroxyl ions, and the sum of these three ions is equal to the total ion concentration, then correct conclusions can be drawn as to what really takes place in solution, the extent of both hydrolytic and ionic dissociation can be determined, and the question of the existence of colloidal or crystalloidal silica may be definitely settled. Hence the importance of determining the concentration of either the sodium or the silicate ions.

The concentration of the silicate ions is not capable of direct measurement, although a colorimetric method is useful whereby the amount of crystalloidal silica in solution may be deduced in very dilute solution. Experiments relating to the concentration and diffusion of the silicate ions are in progress and will be communicated in a later paper.

The sodium ion activity can be measured directly by means of the sodium amalgam electrode devised by G. N. Lewis, and from this we can get a fair conception of the sodium ion concentration, in fact, a correct measure of the concentration in very dilute solution; and if the assumption be made that the

[1] "Aqueous Solutions of Sodium Silicate," Parts I and II: J. Phys. Chem., 29, 1155 (1925); 30, 359 (1926).

laws of ideal solution apply, as is usually done with the hydrogen electrode, i. e. that the ion activity gives a measure of the ion concentration, we can determine the sodium ion concentration in the more concentrated solutions.

## Experimental

The technique of measurements with the alkali amalgam electrode first used by Lewis and Kraus[1] has since been developed and perfected by Lewis and by MacInnes and their co-workers, until now, the E. M. F. between a sodium amalgam electrode and a solution containing sodium ions is capable of very accurate and reproducible measurement, providing care is taken with the preparation of the amalgam, with the preparation of the solution to be experimented upon, and with the design and operation of the cell.

*Preparation of Amalgam:*—The mercury was purified according to Hulett's method by running it several times in a very fine spiral spray through 5% mercurous nitrate solution acidified with $HNO_3$, and then twice distilling it in a current of air at a pressure of 25 mm., the resulting scum of oxides (very little in the second case) being separated by filtration. The sodium amalgam was prepared in vacuo by a method similar to that employed by MacInnes and Parker.[2] As pointed out by these authors, the method is quite simple and very convenient but care must be taken in melting the sodium, as the capillary on the side tube through which the molten metal filters from the oxide is apt to become blocked and may cause an explosion.

*The Amalgam Electrode:*—The cell used was somewhat similar in design to that used by Lewis and Kraus.[1] It was found necessary to have the platinum contact with the amalgam sealed in the capillary tube without distorting the capillary and to have the platinum bent down into the capillary about 5 mm. to prevent the amalgam thread breaking when it was allowed to run out during an experiment.

The electrode vessel was filled by sealing it to the amalgam preparation vessel, evacuating with the vacuum pump and then allowing the amalgam to run down into the electrode vessel. The amalgam preparation vessel was then replaced by a $P_2O_5$ tube. By this means dry air, which has no effect on the amalgam, replaces the amalgam as it is used during the course of an experiment.

*Design and Operation of the Cell:*—Two side reactions interfere with the complete reversibility of these amalgam electrodes, but both have been eliminated. The two difficulties are:—

(1) the side reaction

$$2\,Na + 2H_2O = 2NaOH + H_2.$$

This causes decrease of potential difference between electrode and solution owing to the concentration of the amalgam being lowered, and the ion concentration in its vicinity being increased.

---

[1] J. Am. Chem. Soc., 32, 1459 (1910).

[2] J. Am. Chem. Soc., 37, 1445 (1915).

The cell was designed so that, as the sodium amalgam flowed out of the capillary, it dropped through the silicate solution and out of contact with it, by passing through a tap through which, of course, some silicate solution also passed. In this manner fresh silicate solution is always continually passing the fresh amalgam surface. By this means very reproducible results were obtained, the P. D. remaining constant to within 0.1 millivolt for 20-30 readings.

(2) the side reaction:—

$$4Na + O_2 = 2Na_2O.$$
$$Na_2O + H_2O = 2NaOH.$$

due to dissolved oxygen in the solution. This also lowers the P. D. This difficulty was eliminated by preparing the solutions free from oxygen in the following way. A 300 to 400 cc. portion of concentrated solution of the desired ratio, made up from freshly distilled air-free water, had pure nitrogen bubbled through it for a couple of hours, and was then left in a flask tightly stoppered with a cork carrying an inlet and an outlet tube. This stock solution was accurately analysed and hence its concentration found. From this stock solution more dilute solutions were prepared by forcing a little of it out into a weighed flask by applying a pressure of nitrogen, weighing, and then adding freshly distilled water, prepared air-free by the same means, and weighing again. Any air in the flask above the solution was replaced by nitrogen. The solution so prepared was allowed to stand overnight, and when required for use in an experiment the requisite amount was driven over into the electrode vessel by applying a pressure of nitrogen.

Connection was made with the normal calomel electrode used to complete the cell by having some of the same silicate solution that was being investigated in a connecting tube dipping into a small beaker of the same silicate solution. The side limb of the calomel cell also dipped into this beaker.

The normal calomel electrodes used were very carefully made up from purified materials and they agreed with one another and with other calomel electrodes made up by different investigators in this laboratory to within 0.1 millivolt. The tap on the side limb of the calomel cell was kept closed during a measurement but some KCl was run out through this limb just before and after any series of measurements were made.

The whole apparatus was kept in an air thermostat electrically heated and regulated to 25°C ±0.01.

The measurements were made on a Cambridge and Paul potentiometer with two standardised Weston cells in series balanced against two accumulators, so that the readings in volts on the scale had merely to be doubled to get the observed E. M. F.

*Concentration of Amalgam:*—A weighed quantity, about 20 gms., of the sodium amalgam was run out of the electrode vessel into a porcelain dish and was left overnight, with occasional stirring by means of a platinum wire, in contact with a considerable excess of standard HCl. When complete decomposition had taken place the remaining HCl was titrated with NaOH. Two quantities of amalgam were prepared at different times, and both were

analysed twice, once when the electrode vessel was nearly full and once when nearly empty. The concentration of the amalgam was found to be,—

1. 0.06057.
   0.06055%
2. 0.07090
   0.07091%

## Calculation of Results

If we know the electrode potential between a sodium amalgam electrode and a solution of known sodium ion activity then it is easy to calculate the sodium ion activity of any other solution containing sodium ions, from the E. M. F. observed with the same sodium amalgam electrode in this particular solution. So measurements were first made of the E. M. F. due to the sodium amalgam in a standard solution of NaOH, i. e. of the following combination,—

(1) Na amal. | NaOH | N.KCl. $Hg_2Cl_2$ | Hg.

and then the following was investigated,—

(2) Na amal. | Na sil. | N.KCl. $Hg_2Cl_2$ | Hg.

varying the concentration and ratio of the sodium silicate in (2).

Now,—

$$(1)\quad E_{\text{amal. | NaOH}} = E_o - RT/nF \ln a_{Na} \text{ (in NaOH)}$$

$$(2)\quad E_{\text{amal. | Na sil.}} = E_o - RT/nF \ln a_{Na} \text{ (in Na sil.)}$$

Hence,

$$E_{\text{amal. | Na sil.}} - E_{\text{amal. | NaOH}} = RT/nF \ln \frac{a_{Na} \text{ (in Na sil)}}{a_{Na} \text{ (in NaOH}}$$

The concentration of the first preparation of sodium amalgam was 0.06056%, and the E. M. F. observed between this amalgam and a 1.0N.NaOH, corrected for the liquid potential difference 1.0 N.NaOH | 1N.KCl, calculated by means of the Henderson formula, was 2.1035 volts. The activity coefficient[1] $\gamma$ of 1.0 N.NaOH was taken as 0.75 whence $a_{Na}=0.75$. This $\gamma(=0.75)$ is the mean activity coefficient of the ions; so, to get the activity of the sodium ion the assumption is made that the sodium and hydroxyl ion coefficients are equal. Hence, for the series of measurements made with the sodium amalgam whose concentration was 0.06056% we get the working formula,

$$E_{\text{amal. | Na sil.}} - 2.1035 = 0.5911 \text{ Log } a_{Na}/0.75.$$

For the second preparation of amalgam used in the latter part of the measurements, the concentration of the amalgam was 0.0709%, the NaOH was 0.6708N, whence $a_{Na}$ in NaOH=0.5031, and the E. M. F. (corrected for liquid potential difference) was found to be 2.1142 volts.

[1] See Harned: J. Am. Chem. Soc., 47, 676 (1925).

Values for $a_{Na}$ for the same silicate solution, obtained by the amalgams of the first and second preparations, agreed within 0.1%.

*Liquid-Liquid Potential Difference:*—The values of E. M. F. given in Tables I-II have been corrected for the P. D. between the sodium silicate solution used and N.KCl, by making use of the P. D. found between these silicate solutions and saturated KCl by the Bjerrum extrapolation method, and of the P. D. between saturated KCl and N.KCl calculated by means of the Henderson formula.

## Results

TABLE I

| $N_w$ | E. M. F. | $A_{Na}$ | $\gamma = a_{Na}/N^w$ |
|---|---|---|---|
| | Ratio 1 : | | |
| 0.832 | 2.1196 | 0.4006 | 0.481 |
| 0.373 | 2.1436 | 0.1573 | 0.422 |
| 0.111 | 2.1750 | 0.04629 | 0.417 |
| 0.043 | 2.1956 | 0.02166 | 0.504 |
| 0.020 | 2.2042 | 0.01485 | 0.739 |
| 0.00823 | 2.2200 | 0.008021 | 0.974 |
| | Ratio 1 : 2 | | |
| 0.8486 | 2.1330 | 0.2331 | 0.275 |
| 0.5408 | 2.1428 | 0.1623 | 0.300 |
| 0.2056 | 2.1596 | 0.08433 | 0.410 |
| 0.084222 | 2.1788 | 0.03992 | 0.474 |
| 0.0403 | 2.1960 | 0.02043 | 0.507 |
| 0.02296 | 2.2090 | 0.01233 | 0.537 |
| 0.01349 | 2.2160 | 0.009374 | 0.695 |
| 0.002519 | 2.2500 | 0.002493 | 0.980 |
| | Ratio 1 : 3 | | |
| 1.073 | 2.1520 | 0.1122 | 0.105 |
| 0.3829 | 2.1604 | 0.08175 | 0.213 |
| 0.1142 | 2.1788 | 0.04062 | 0.356 |
| 0.05454 | 2.1942 | 0.02239 | 0.411 |
| 0.01671 | 2.2150 | 0.009917 | 0.594 |
| 0.006594 | 2.2320 | 0.005135 | 0.779 |
| | Ratio 1 : 4 | | |
| 0.7039 | 2.1766 | 0.04426 | 0.063 |
| 0.3215 | 2.1770 | 0.04358 | 0.135 |
| 0.09517 | 2.1916 | 0.02468 | 0.259 |
| 0.04479 | 2.2080 | 0.01582 | 0.353 |
| 0.01685 | 2.2220 | 0.007492 | 0.445 |

TABLE II

$\gamma$(Activity Coefficient) for Ratios

| Conc. ($N_w$) | 1 : 1 | 1 : 2 | 1 : 3 | 1 : 4 |
|---|---|---|---|---|
| 1.0 | — | 0.265 | 0.105 | 0.050 |
| 0.80 | 0.475 | 0.275 | 0.145 | 0.060 |
| 0.50 | 0.440 | 0.310 | 0.185 | 0.090 |
| 0.40 | 0.425 | 0.335 | 0.210 | 0.110 |
| 0.20 | 0.415 | 0.410 | 0.295 | 0.185 |
| 0.10 | 0.425 | 0.460 | 0.365 | 0.250 |
| 0.05 | 0.500 | 0.500 | 0.425 | 0.325 |
| 0.025 | 0.700 | 0.525 | 0.480 | 0.405 |
| 0.01 | 0.975 | 0.850 | 0.700 | 0.550 |

These results are shown graphically in Fig. 1, where $\gamma$ is plotted against the concentration.

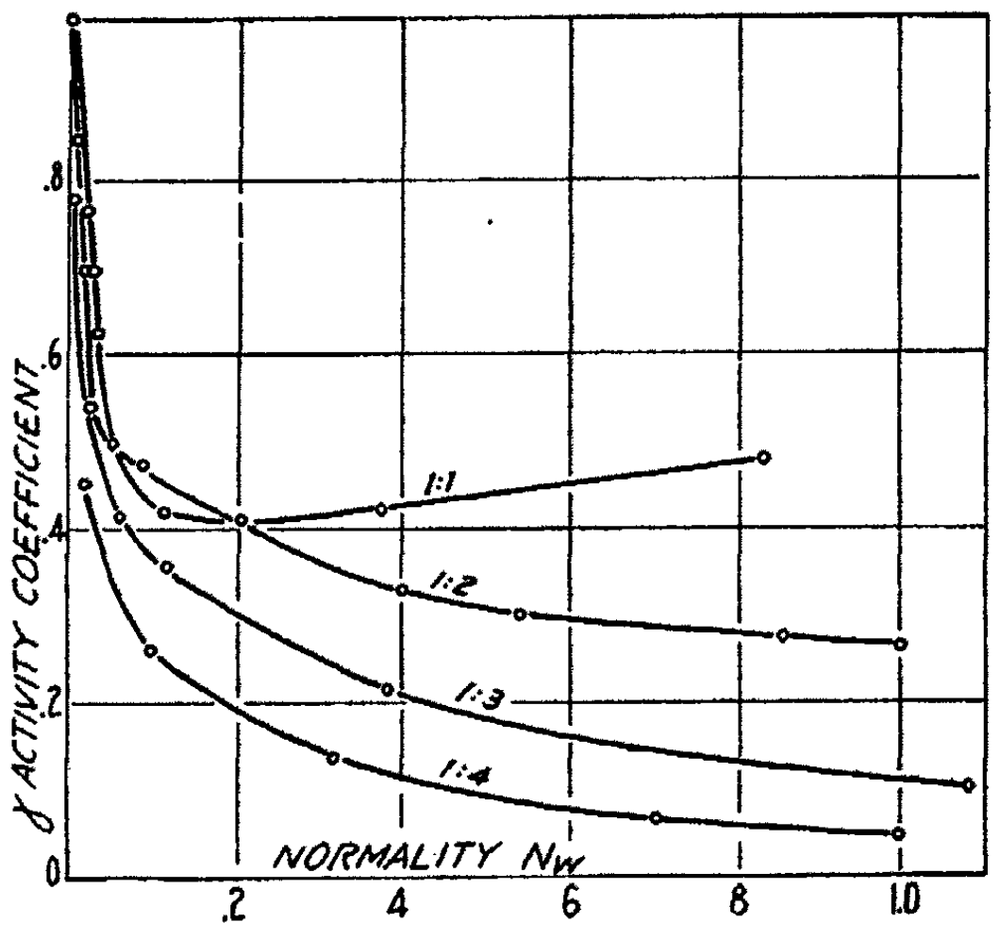



FIG. 1

Sodium Ion Activity $\gamma$ against Concentration

## Discussion of Results

The values for $\gamma$, the activity coefficient of $Na_2SiO_3$ (i. e. ratio 1:1) show that in concentrated solution as much as 40% of the total sodium exists in the active ionic state, while in dilute solution practically all the sodium exists so. The most remarkable feature is that $\gamma$ for ratio 1:1 passes through a minimum at concentration $0.2N_w$, while none of the other ratios exhibit such a minimum. It is not unusual to find this minimum in $\gamma$ for strong electrolytes in concentrated solution, and this has been shown by Debye and Hückel[1] to have a theoretical basis when the inter-ionic forces are taken into account.

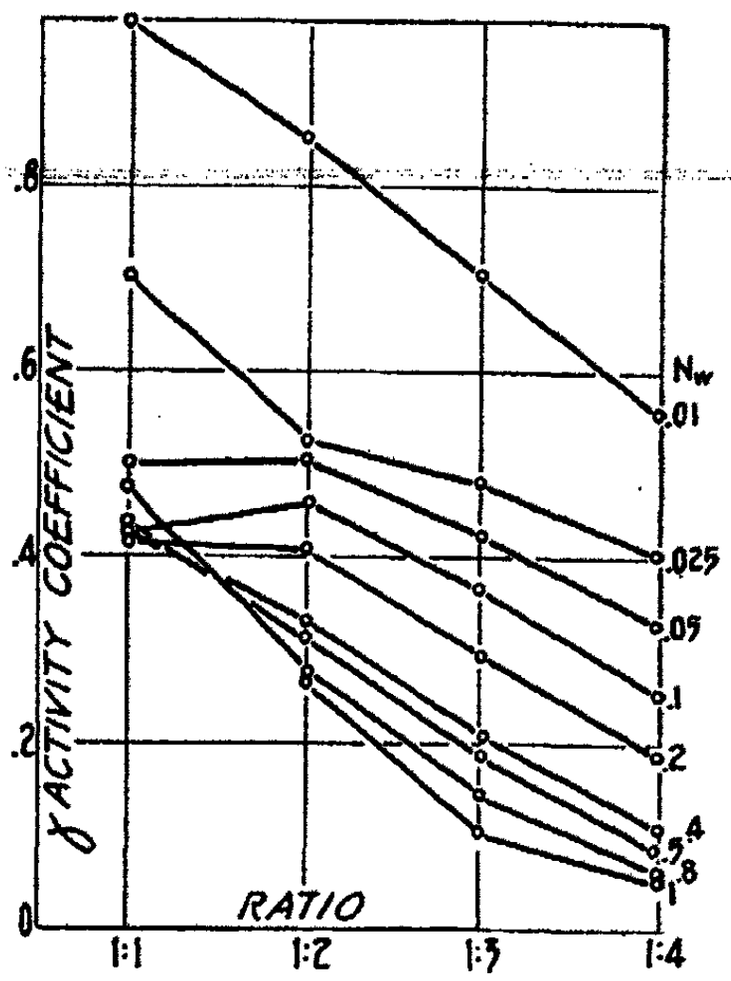



FIG. 2
$\gamma$ against Ratio

In ratio 1:3 and 1:4, the values of $\gamma$ are very low in concentrated solution and even in dilute solution are still comparatively low, indicating that all the sodium in solution does not exist as sodium ion, or if so, the silica present has considerably affected and reduced its activity.

When $\gamma$ is plotted against the ratio, as in figure 2, then for $0.1N_w$ solution, the decrease in $\gamma$ is quite regular as the proportion of $SiO_2$ increases.

The decrease in $\gamma$ is also regular for the higher concentrations beyond ratio 1:2, but owing to the fact that $\gamma$ for 1:1 passes through a minimum, and is even lower than $\gamma$ for 1:2 at concentrations near $0.1-0.2N_w$, the changes of direction in the curves above 1:1 are varied and probably have no special significance.

[1] Physik. Z., 24, 185, 334 (1923).

The general conclusion may be drawn however, that both increase of concentration for any given ratio, and increase of ratio for any given concentration, have a very marked effect on the activity of the sodium ion, so reducing it, that in concentrated solutions of ratios 1:3 and 1:4 it is remarkably low.

## Summary

(1) Measurements of sodium ion activity by means of a sodium amalgam electrode have been made for ratios 1:1, 1:2, 1:3, and 1:4, at concentrations ranging from 1.0-0.01N.

(2) The activity coefficient $\gamma$ has been plotted against the weight normality, $N_w$, and against the ratio $Na_2:SiO_2$.

(3) The curve of $\gamma$ against $N_w$ for ratio 1:1 passes through a minimum at a concentration lying between $0.1\text{-}0.2N_w$. The other curves show no minimum.

(4) In very dilute solution $\gamma$ is high, but not so high as in corresponding concentrations of NaOH, whereas in concentrated solutions of higher ratios $\gamma$ is abnormally low.

I wish to thank the Commissioners of the 1851 Exhibition for a research scholarship which has enabled me to carry out this work, and to express my gratitude to Prof. Donnan at whose suggestion this investigation was undertaken, for his constant kindly interest and advice.

*The Sir William Ramsay Laboratories of Physical and Inorganic Chemistry,*
*University College,*
*London,*
*April 7, 1926.*

16584
9,3-26

# THE ELECTRODEPOSITION OF RADIUM D AND RADIUM E

BY JOHN P. McHUTCHISON

As the result of much investigation mainly by Hevesy and his co-workers, the chemical identity of the radio-elements with their isotopes, both amongst the ordinary elements and also amongst the radio-elements themselves, has been found to extend to their electrochemical behaviour.[1] In another series of experiments von Hevesy[2] proved that electrodeposition of radio-elements is possible when the E. M. F. employed is lower than the decomposition potential of their ordinary isotopes, and that "every metal is capable of causing the deposition of every radio-active body to a greater or less degree." He emphasized the fact that the main consideration is not the voltage nor the current density, but the potential of the electrode. The single electrode potential method had been previously employed by von Lerch,[3] who obtained deposits of radio-elements by dipping metallic plates in salt solutions containing radioactive matter. The extension of this last principle by von Hevesy established the most important fact that the ratio of the B- to the C-members of a radioactive series deposited on a metal plate depended on the E. M. F. Metal | Solution. He found that when the definite potential of a metal is +0.5 or greater (measured against the calomel electrode) a certain ratio is very high, and that this ratio diminishes as the potential becomes more negative, being about 7 for 0.0 volt, about 1 for −0.6 volt, and about 0.2 for −2.0 volts. The ratio referred to is the quantity of the isotope of bismuth to that of the isotope of lead deposited on a plate dipped into a solution containing these isotopes in radioactive equilibrium.

The present set of experiments is concerned with the deposition of the radio-elements, radium D and radium E, on metallic plates in neutral aqueous solutions, that is for the case of the indefinite E. M. F. Metal | Water. Such indefinite E. M. F.'s were included by Hevesy in his generalisation that every metal is capable of causing the deposition of every radioactive body: and the same investigator also measured the indefinite E. M. F. Copper | Water, and found it 0.7 volt more negative than the definite E. M. F. Copper | N-Copper sulphate, and from the present extension of von Hevesy's work, this last result appears to be of general application.

## I.

## Metallic Deposition of Radium D and Radium E in Pure Aqueous Solution

The active solution dealt with contained radium D, radium E, and radium F in radioactive equilibrium, and was obtained by dissolving in pure con-

[1] Paneth and von Hevesy: Monatsheft, 34, 1593, 1605 (1913); Wien. Ber., 123, 1909 (1914).
[2] Von Hevesy: Phil. Mag., (6) 23, 628 (1912); 25, 390 (1913).
[3] Ann. Physik, (4) 12, 766 (1903); Jahrb. Radioakt., 1905 II, 471.

centrated nitric acid the active deposit as formed on old radon tubes. The acid extract was evaporated to dryness in a platinum basin, and the active matter dissolved off in distilled water of conductivity standard. Thus a solution was obtained of these radio-elements as nitrates in pure water. The electroscopic measurements were performed with a beta-ray electroscope through one thickness of gold-beater's skin and two centimetres of air, so as to cut off all the alpha-radiation from radium F. The experiments described, therefore, are concerned only with radium D and radium E.

Plates of the metals shown in Fig. 1, as pure as could be obtained, were immersed in quantities of the active solution for one hour at room temperature, and therefore, (except in the case of magnesium), for one hour or more at boiling point. When the solutions had cooled, the plates were removed, washed free of adhering solution by being dipped twice in pure water and once in alcohol. Measurements of the activity of the deposits on the plates were made regularly, and the results are shown in Table I.

Activities are expressed in arbitrary units, namely divisions of electroscope scale per minute. A quantity of active solution equal to that used in each case was evaporated to dryness, and gave an activity of 165.

TABLE I

| Metal. | Initial Activity | Activity after 4.9 days | Percentage of radium D extracted. | Percentage of radium E extracted. | Remarks |
|---|---|---|---|---|---|
| (*I*) | | | | | |
| Magnesium | 46 | 46 | 28% | 28% | Magnesium acted on by water. |
| Aluminium | 51 | 26 | 0% | 100% | Almost pure radium E extracted. |
| Zinc | 95 | 130 | 100% | 58% | $\frac{\%\text{ D extracted}}{\%\text{ E extracted}}=1.7$ |
| Nickel | 68 | 34.5 | 0% | 100% | Almost pure radium E extracted. |
| Tin | 37 | 25 | 8% | 20% | $\frac{\%\text{ D extracted}}{\%\text{ E extracted}}=0.4$ |
| (*II*) | | | | | |
| Lead | 60 | 50 | 24% | 36% | $\frac{\%\text{ D extracted}}{\%\text{ E extracted}}=0.6$ |
| (*III*) | | | | | |
| Copper | 66 | 44 | 13% | 43% | $\frac{\%\text{ D extracted}}{\%\text{ E extracted}}=0.3$ |
| Silver | 14 | 9 | 2.5% | 8.5% | $\frac{\%\text{ D extracted}}{\%\text{ E extracted}}=0.3$ |
| Platinum | 27 | 15 | 2% | 16% | $\frac{\%\text{ D extracted}}{\%\text{ E extracted}}=0.1$ |

The metals in (*I*) are more electropositive than lead or bismuth, the isotopes of radium D and radium E, while those in (*III*) are more electronegative.

The period of radium E is taken as 4.9 days (c. f. part 2 of this paper.)

Parallel experiments gave very similar results, and experiments involving immersion of the plates for twenty-four hours or longer were unsuccessful in extracting appreciably greater quantities of the active matter.

In Table I, the deposits obtained on the various metals are greatly different. First, whereas the rest of the metals extract radium D and radium E in other than their equilibrium proportions, magnesium extracts about 3/10ths of the equilibrium quantity of each, possibly an anomalous effect caused by the chemical action of the water on the plate. Second, the deposit on a zinc plate contained radium D in excess of its equilibrium quantity of radium E. The activity on an iron plate, which was also tested, was practically nil, since rust was formed and all the activity was adsorbed by it. It is worthy of notice that both aluminium and nickel extracted practically radium E alone, and use has been made of this to redetermine the half-life period of radium E. In the case of the more electronegative metals, it is clear that the ratio of radium D to radium E extracted becomes smaller with increase in electronegativeness, which was also the result obtained by Hevesy in 1912 for definite potentials.

Another observation made by von Hevesy for definite potentials is also proved by the above results to hold for indefinite potentials: namely, that the more electropositive metals replace the active isotopes of lead and bismuth in quite an anomalous way to what might be expected from their properties in replacing their ordinary isotopes in molecular solution.

A comparison of the results shown in Table I for indefinite potentials, and those obtained by von Hevesy for definite potentials, leads to the interesting conclusion for all the metals tested, except in the case of zinc, that indefinite potentials are more negative than definite ones. In the particular case of copper this was found to hold by Hevesy as already indicated; but the data given in Table II definitely suggest the general applicability of the result. The values of the indefinite potentials shown have been deduced from the results shown in Table I, using the curves given by von Hevesy[1] showing the percentage of the isotope of bismuth and lead respectively of the total quantity deposited on the electrode, and the potential required to bring about deposition.

TABLE II

| Metal. | Zinc. | Tin. | Lead. | Copper. | Silver. | Platinum. |
|---|---|---|---|---|---|---|
| Normal potential (against calomel electrode.) | −1.05 | −0.43 | −0.41 | +0.06 | +0.51 | +0.6 |
| Indefinite potential Metal \| Water deduced from von Hevesy's curve from results of Table I. | −0.69 | −0.50 | −0.59 | −0.42 | −0.41 | +0.01 |
| Difference in Volts. | +0.36 | −0.07 | −0.18 | −0.48 | −0.92 | −0.59 |

[1] Phil. Mag., (6) 23, 637 (1912).

## II

### Re-determination of the Half-Life Period of Radium E

This re-determination was considered advisable in view of the fact that Bastings[1] in 1924, obtained the value 4.98 days, which differed very appreciably from the commonly accepted value 4.85 days as obtained by Thaller[2] in 1912, and suggested that the earlier value of 5.0 days as determined by Antonoff[3] was the correct one. It was therefore thought desirable to re-determine the period, and the above experiments involving electrodeposition on metallic plates suggested a suitable method of obtaining radium E in a state of purity. Recently, however, Fournier[4] has published his determination of the period as 4.86 days, also confirming Thaller's value: but since the experiment described in this paper, although akin in nature to Fournier's method, was undertaken before Fournier's results were advanced, and since the two determinations agree well, it may be useful to give a few details.

It was remarked above that the deposit obtained on a nickel plate consisted of practically pure radium E, and it was thought that if to the active solution a quantity of lead nitrate were added, the lead would mask the slight deposition of any radium D, and so a very pure deposit of radium E would be obtained.[5] This proved to be the case, and nickel plates so treated, measured after the lapse of two months were quite inactive, proving that radium E alone has been deposited.

In the active solution a quantity of lead nitrate was dissolved, and the pure nickel plate boiled with this solution for two hours, the plate being afterwards washed in water and then in alcohol to remove any adhering solution. Measurements of the activity were made as before with a beta-ray electroscope. The usual precautions of daily standardisation with a constant betaray source, and checking of the constancy of the natural leak were observed. The electroscopic measurements are considered to have an accuracy of about 1 in 300. Three determinations were made: two of these gave a value of 4.9 days to the degree of accuracy indicated, while the other, for which the electroscope was most thoroughly cleaned, and the insulation renewed, gave the value 4.87 days, which is in striking agreement with Fournier's value of 4.86 obtained by measurement with an accurate piezo-electrometer. Details of this last experiment are given in Table III, in which column A gives the activities as measured and column B contains those calculated on the basis of a half-life period of 4.87 days. The agreement between the experimental and theoretical values is very good.

---

[1] Phil. Mag., (6) **48**, 1075 (1924).
[2] Wien. Ber., **121**, 1611 (1912).
[3] Phil. Mag., (6) **19**, 825 (1910).
[4] Compt. rend., **181**, 502 (1925).
[5] Cf. Meyer and von Schweidler: Jahrb. Rad. Elektron, 3, 381 (1906); 4, 112 (1907).

TABLE III

| Time in days | Activity in arbitrary units. A. Experimental. | B. Theoretical for period of radium E 4.87 days. |
|---|---|---|
| 0.0 | 35.0 | 35.0 |
| 0.92 | 30.6 | 30.7 |
| 1.93 | 26.5 | 26.6 |
| 2.96 | 22.7 | 23.0 |
| 3.71 | 20.6 | 20.6 |
| 4.71 | 18.1 | 17.9 |
| 5.92 | 14.9 | 15.0 |
| 7.96 | 11.3 | 11.3 |
| 14.0 | 4.8 | 4.8 |
| 46.0 | nil. | nil. |

It is therefore evident that the above results, taken along with Fournier's work, indicate that Thaller's value of 4.85 days as the half-life period of radium E is the most accurate value yet available.

## Synopsis

The results enumerated in this paper may be summarised as follows:—

1. The work of von Hevesy on the deposition of radioactive isotopes of bismuth and of lead on metals when the metals are dipped into solutions containing their own ions, has been extended to the case of metals dipping into pure water. The isotopes of bismuth and of lead used were radium E and radium D respectively. It has been found that these isotopes are deposited on metals irrespective of whether the latter are more electropositive or electronegative than bismuth or lead. It has also been found that the ratio of radium D to radium E deposited on metals decreases with the increasing electronegativeness of the metals, which is in qualitative agreement with Hevesy's results for definite potentials.

2. Aluminium and nickel, when boiled with pure neutral solutions of radium D and radium E, extracted radium E practically pure.

3. A re-determination of the half-life period of radium E has been made, and the value 4.87 days obtained, which confirms Thaller's value of 4.85 days.

*The Radiometric Laboratory,*
*The University,*
*Glasgow.*
*February 2, 1926.*

# THE TRANSITION POINTS OF SALT HYDRATES IN NON-AQUEOUS SOLVENTS*

BY WALTER W. LUCASSE AND JOHN McARTHUR HARRIS, JR.

A number of methods have been used to determine the transition points of various systems, the methods depending both upon abrupt changes and upon identity of certain properties at this point. For individual cases an especial method may be particularly applicable. Electrical methods have certain advantages[1] and have been used in a number of types of systems.

Electromotive force methods may depend in part either upon the difference in the ionic concentration in the saturated solution of the substance in the two phases or upon the change in the sign of the electromotive force while the system passes thru a series of temperatures where first the one and then the other phase is stable. Conductance methods may depend either upon a difference in the conductance of the two phases or upon a change in conductance due to a difference[2] in the solubility of the two phases. These methods, first used by Cohen, have recently been extended by Mason and Mathews[3] to non-aqueous systems where solvates are formed such as those with copper chloride and cadmium chloride in pyridine. In the case of salt hydrates we may take advantage, also, of the difference in conductance in a non-aqueous and in a mixed solvent. The results of such a study are given in the present paper.

## Apparatus, Materials and Method

The cell used, except for certain preliminary runs and for the determinations with barium acetate, was in the shape of a large U-tube. In one arm the electrodes were permanently fixed while the other bore a thermometer, calibrated to tenths of a degree, which had been checked with a standard thermometer. This arrangement permitted the cell to be shaken without danger of changing the cell constant due to changing the relative position of the thermometer and electrodes.

The absolute alcohol was prepared by allowing ordinary commercial alcohol to stand over freshly broken lime for about two weeks during which time it was shaken several times each day. It was then distilled over a slow water bath, only the middle portion being retained. The salts used were all high-grade products and no attempt was made to further purify them.

In making a determination an excess of the salt was shaken with a quantity of the absolute alcohol at room temperatures. After being allowed to settle completely, the supernatant liquid was poured into the cell. The cell was then placed in a water bath which had been brought up to a temperature a

*Contribution from the John Harrison Laboratory of Chemistry of the University of Pennsylvania.

[1] Van't Hoff-Cohen: "Studies in Chemical Dynamics"; Findlay: "The Phase Rule."
[2] Svedberg: Ann. Physik, (4) **49**, 437 (1916); Cohen: Z. physik. Chem., **14**, 53 (1894).
[3] Mason and Mathews: J. Phys. Chem., **29**, 1507 (1925).

few degrees below the transition point of the salt. The temperature of the bath was raised at the rate of about eight degrees an hour, and frequent readings of the resistance were made, the cell and contents being thoroughly shaken before each. The reading of the thermometer within the cell was noted simultaneously with the taking of the resistance.

## Results

In Table I are given the results obtained with calcium chloride showing the

TABLE I

$CaCl_2.6H_2O = CaCl_2 . 4H_2O\beta + 2H_2O$

R = Resistance

| Series 1 | | Series 2 | | Series 3 | | Series 4 | |
|---|---|---|---|---|---|---|---|
| Temp. | R | Temp. | R | Temp. | R | Temp. | R |
| 26.7 | 23.29 | 23.4 | 41.78 | 24.2 | 167.0 | 25.2 | 328.7 |
| 27.2 | 23.01 | 24.2 | 41.20 | 24.7 | 166.0 | 25.8 | 327.0 |
| 27.5 | 22.77 | 24.8 | 40.69 | 25.4 | 165.0 | 26.3 | 325.5 |
| 27.9 | 22.45 | 25.5 | 40.11 | 26.1 | 163.8 | 26.8 | 323.8 |
| 28.5 | 22.07 | 26.2 | 39.55 | 26.9 | 162.3 | 27.4 | 322.4 |
| 29.2 | 21.70 | 26.8 | 39.23 | 27.4 | 161.1 | 27.6 | 321.5 |
| 29.5 | 21.41 | 27.4 | 38.77 | 28.2 | 159.7 | 28.3 | 319.9 |
| 30.0 | 21.03 | 28.1 | 38.23 | 29.4 | 158.2 | 28.8 | 318.3 |
| 30.5 | 20.83 | 28.8 | 37.73 | 29.8 | 157.3 | 29.2 | 317.0 |
| 31.0 | 20.56 | 29.2 | 37.47 | 30.4 | 156.5 | 29.6 | 316.1 |
| 31.5 | 20.34 | 29.5 | 37.24 | 31.2 | 155.4 | 30.1 | 315.2* |
| 32.1 | 19.99 | 30.0 | 36.93 | 31.6 | 154.6 | 30.9 | 313.0 |
| | | 30.4 | 36.71 | 32.3 | 153.7 | 31.4 | 311.5 |
| | | 31.1 | 36.30 | 32.9 | 152.7 | 32.0 | 310.1 |
| | | 31.8 | 35.81 | 33.8 | 151.7 | 32.6 | 308.5 |
| | | 32.1 | 35.64 | | | | |
| | | 32.7 | 35.25 | | | | |
| | | 33.2 | 34.97 | | | | |
| | | 33.6 | 34.86 | | | | |
| | | 34.1 | 34.46 | | | | |

values of the resistance at the respective temperatures. In the first series are given the results obtained by using a solution made up as described above. Series 2 gives the results from a solution made up in the same manner but which was evidently slightly less concentrated. The third and fourth series give results from solutions which were made up by diluting with absolute alcohol portions of the same solution as used in Series 2, the former in the ratio of one part solution to three parts absolute alcohol, and the latter, one part solution to nine parts absolute alcohol. These results are plotted in Fig. 1 where the ordinates give the resistances and the abscissas, the temperatures. In each case a solid straight line is drawn thru the points below and above the transition point. In order to make the change more apparent the former

is continued above the transition point as a broken line. While the individual points fail to lie as closely upon the curves in some cases as might be desired, there can be no doubt considering all of the points that such a break occurs and that it takes place at about the accepted transition point. The deviations are due, no doubt, to the method of temperature control. In certain prelimi-

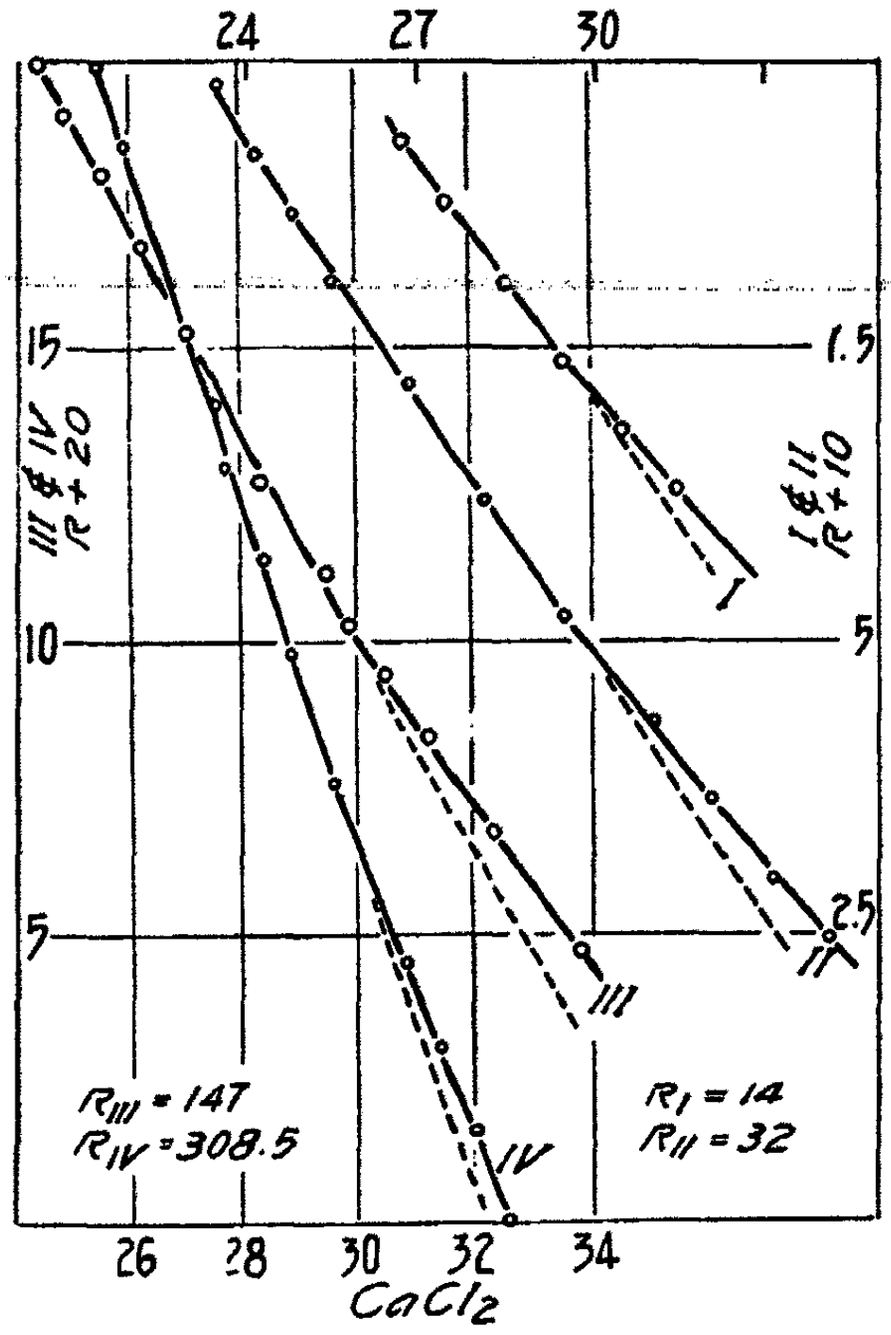



FIG. 1

nary determinations where the solution was very concentrated or not made up immediately before carrying out the measurements an additional break seemed to appear at about 32°. This may have been due to experimental error or to the results of compound formation between the solvent and solute.

In Table II are given the results with lithium nitrate, the first series being those from a saturated solution made up as described above and the second from a solution made up by diluting one part of the saturated solution with three parts of absolute alcohol. The difference in the resistance temperature

## TABLE II

$$LiNO_3 . 3H_2O = LiNO_3 . \tfrac{1}{2}H_2O + 2\tfrac{1}{2}H_2O$$

R = Resistance

| Series 1 | | Series 2 | |
|---|---|---|---|
| Temp. | R | Temp. | R |
| 24.1 | 35.28 | 25.0 | 51.57 |
| 24.8 | 34.79 | 25.6 | 51.14 |
| 25.7 | 34.33 | 26.2 | 50.63 |
| 26.3 | 34.03 | 26.7 | 50.19 |
| 27.2 | 33.49 | 27.1 | 49.85 |
| 27.9 | 33.04 | 27.7 | 49.31 |
| 28.7 | 32.50 | 28.5 | 48.71 |
| 29.3 | 32.00* | 29.1 | 48.32 |
| 30.2 | 31.58 | 29.5 | 47.91 |
| 30.9 | 31.10 | 30.1 | 47.46 |
| 31.6 | 30.65 | 30.6 | 47.08 |
| 32.1 | 30.27 | 31.1 | 46.74 |
| | | 31.6 | 46.48 |
| | | 32.2 | 46.07 |
| | | 32.7 | 45.66 |
| | | 33.2 | 45.17 |
| | | 33.8 | 44.94 |
| | | 34.2 | 44.60 |

## TABLE III

$$Ba(C_2H_3O_2)_2, H_2O = Ba(C_2H_3O_2)_2 + H_2O$$

R = Resistance

| Series 1 | | Series 2 | |
|---|---|---|---|
| Temp. | R | Temp. | R |
| 25.4 | 39920 | 31.3 | 13550 |
| 31.2 | 37520 | 32.8 | 13260 |
| 32.6 | 36780 | 35.2 | 12910 |
| 35.1 | 35760 | 38.7 | 12360 |
| 38.5 | 34490 | 40.2 | 12150 |
| 40.0 | 33660 | 40.9 | 12020 |
| 40.8 | 33260 | 41.7 | 11950 |
| 41.5 | 32990 | 42.6 | 11810 |
| 42.5 | 32730 | 43.8 | 11680 |
| 43.6 | 32070 | 44.8 | 11480 |
| 44.7 | 31810 | 47.3 | 11220 |
| 47.2 | 31050 | 49.1 | 10960 |
| 49.0 | 30180 | | |

coefficients of these two solutions as shown from the results plotted in Fig. 2 is due, no doubt, to the difference in the solvation of the ions in the two solutions. The change in the slope of the two curves upon passing thru the transition point is of about the same order of magnitude but of opposite sign. In the more concentrated solution the decrease in resistance per degree is greater above the transition point than below while in the less concentrated solution the reverse is the case. This effect of concentration does not seem to

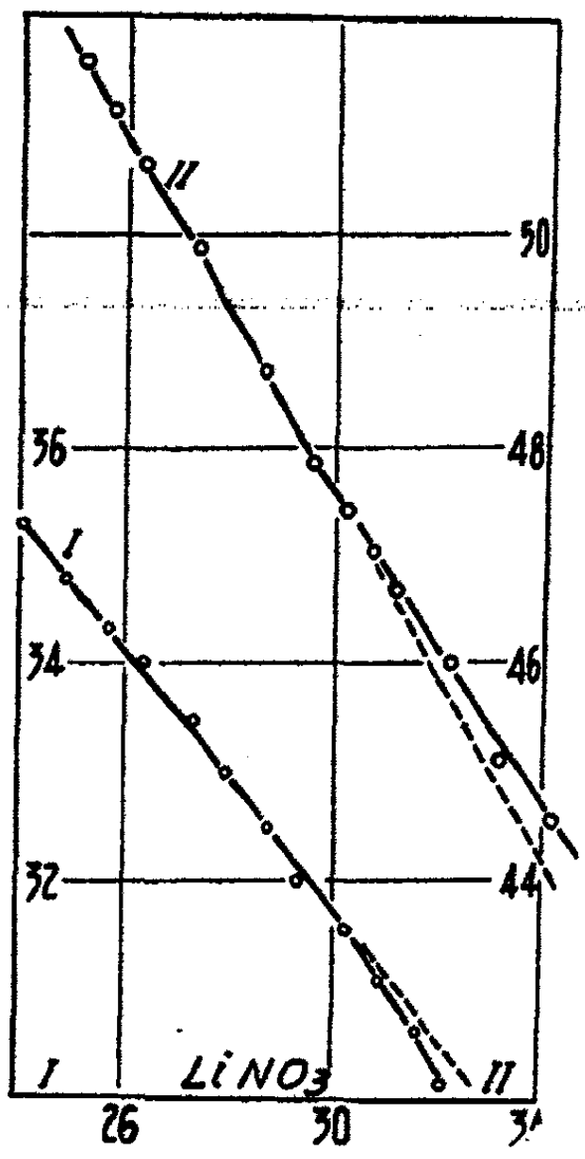



FIG. 2

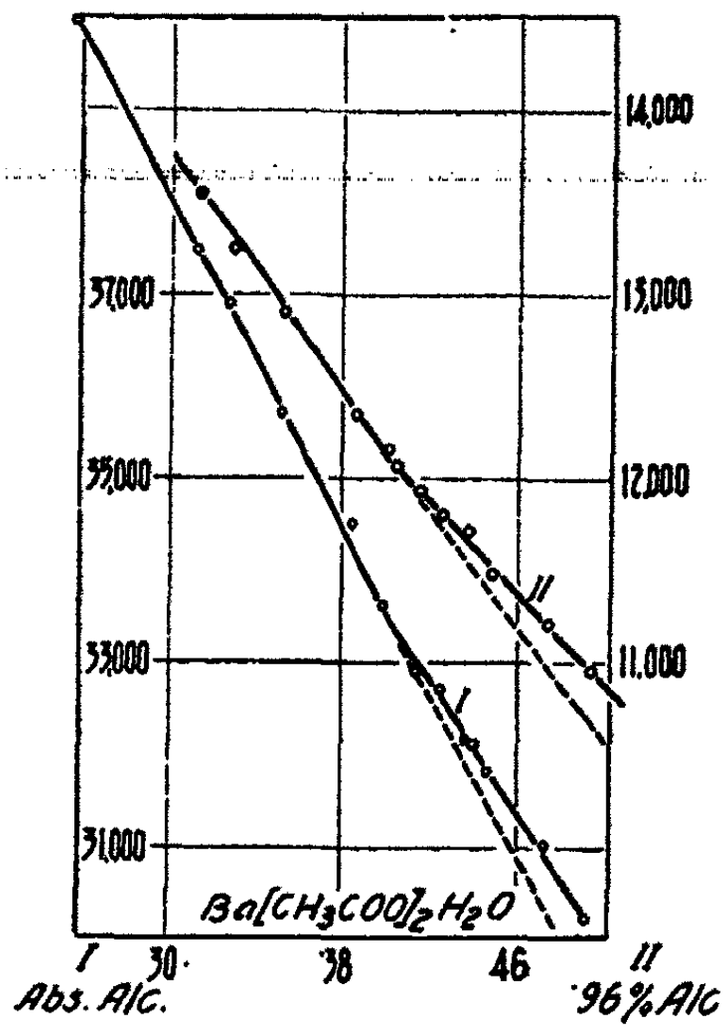



FIG. 3

exist in the solutions of calcium chloride, the difference being due, perhaps, to the different tendencies of the lithium and calcium ions toward solvation.

In Table III and Fig. 3 are given the results of saturated solutions of barium acetate in absolute and in 96% alcohol. The slight water content in the latter solution increases the solubility and thus the conductance. Altho the value of the transition point of a particular system as determined by different methods may vary considerably, it is not likely that changing the solvent or modifying it slightly as in the present case would have any marked effect. The order of accuracy obtained with this particular salt was not such as to permit any conclusions to be drawn in this respect from the different values obtained from the calculations given below.

In Table IV are given the results from saturated solutions[1] of strontium nitrate (31.3°) and calcium bromide made up in the manner described. The curves are plotted in Fig. 4 where it is seen that the intersections of the curves come at about the accepted values of the transition points.

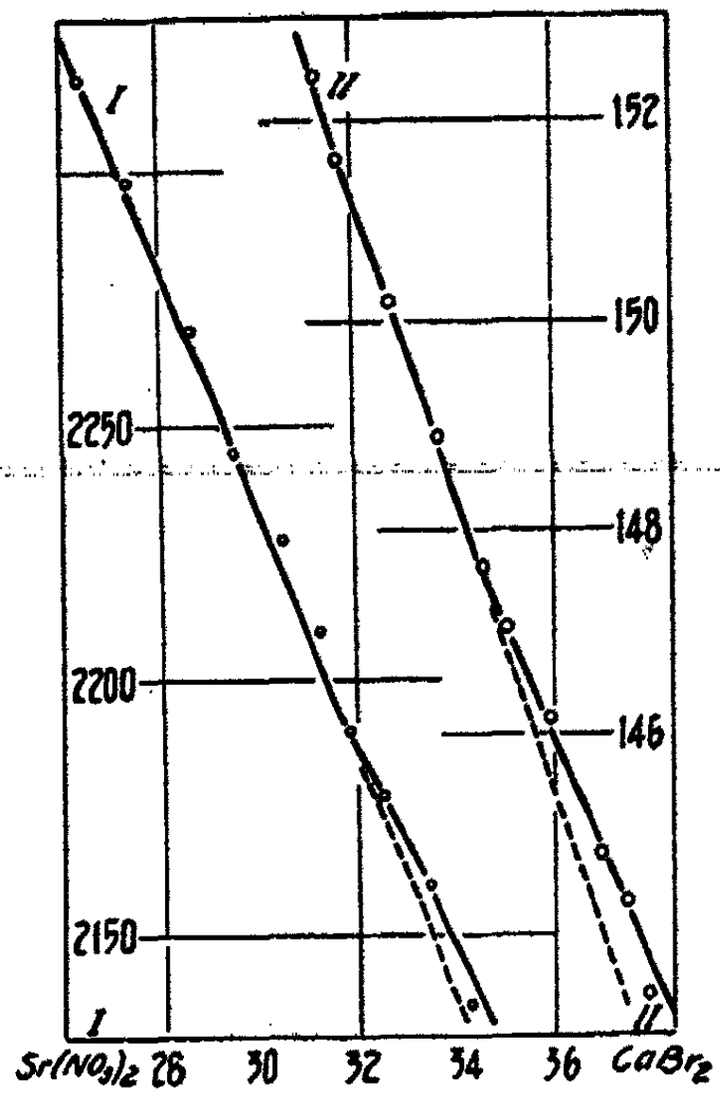



FIG. 4

TABLE IV

$Sr(NO_3)_2 . 4H_2O = Sr(NO_3)_2 + 4H_2O$ $CaBr_2 . 6H_2O = CaBr_2 . 4H_2O + 2H_2O$

R = Resistance

Series 1

| Temp. | R |
|---|---|
| 26.3 | 2318 |
| 27.3 | 2299 |
| 28.5 | 2269 |
| 29.4 | 2245 |
| 30.4 | 2228 |
| 31.2 | 2210 |
| 31.8 | 2190 |
| 32.4 | 2177 |
| 33.3 | 2160 |
| 34.2 | 2136 |

R = Resistance

Series 2

| Temp. | R |
|---|---|
| 31.1 | 152.4 |
| 31.6 | 151.6 |
| 32.6 | 150.2 |
| 33.2 | 149.3 |
| 33.6 | 148.9 |
| 34.0 | 148.6* |
| 34.5 | 147.6 |
| 35.0 | 147.0 |
| 35.9 | 146.1 |
| 36.9 | 144.8 |
| 37.4 | 144.3 |
| 37.9 | 143.4 |

[1] Mellor: "Treatise on Inorganic and Theoretical Chemistry," 3, 849 (1923).

## Calculation of the Transition Point

The curves showing the resistances of these systems as a function of the temperature are doubtlessly slightly curved rather than straight as indicated in the diagrams. However, over the small temperature range above and below the transition point, they may be considered straight within experimental error. On this assumption we may calculate the transition point by determining the equations of the two curves for each system. The intersection of the two curves gives the transition point since here the resistance becomes the same. The constants of the equations

$$R = a + bt$$

were determined by the method of least squares and are given in Table V. In the first column is given the formula of the salt followed by the reference

TABLE V

Calculation of the Transition Points

| Salt | | a | b | a′ | b′ | t | t′ |
|---|---|---|---|---|---|---|---|
| $CaCl_2$ | I, 1 | 41.04 | −0.6652 | 36.76 | −0.5216 | 29.8 | 29.2[1] |
| | I, 2 | 59.09 | −0.7419 | 55.01 | −0.6021 | 29.2 | 29.2 |
| | I, 3 | 209.1 | −1.743 | 200.1 | −1.435 | 29.2 | 29.2 |
| | I, 4 | 401.6 | −2.895 | 391.04 | −2.531 | 29.1 | 29.2 |
| $LiNO_3$ | II, 1 | 49.47 | −0.5894 | 52.10 | −0.6796 | 29.2 | 29.6[2] |
| | II, 2 | 71.93 | −0.8139 | 68.45 | −0.6973 | 29.8 | 29.6 |
| $Ba(Ac)_2$ | III, 1 | 50803.0 | −427.9 | 48152.0 | −365.3 | 42.4 | 41.0[3] |
| | III, 2 | 18408.0 | −156.1 | 17417.0 | −131.5 | 40.3 | 41.0 |
| $CaBr_2$ | IV, 2 | 196.46 | −1.418 | 189.04 | −1.200 | 34.0 | 34.2[4] |

to the table and series where the data are given from which the constants of the equation were determined. The constants *a* and *b* are given in the second and third columns and refer to the equation below the transition point. The constants a′ and b′ are for the corresponding curve above the transition point. Solution of the equations for *t* yields the values of the transition points given in column six. In the last column are given values obtained by other methods. In the tables above all points obtained in the temperature interval are given. In determining the equations of the curves, however, a few points were omitted if from the plot they were seen to be in error. This was done particularly when such a point lay at or near the end of the curve and would thus, due to the small number of points, have a considerable effect on the slope of the curve. The legitimacy of disregarding these points may well be seen from the curves with strontium nitrate. Inclusion of the points at 30.4° and 31.2° would not only wipe out the self-consistency of the earlier points but would so change the slope of the curve as to make the points at higher temperatures

[1] Bancroft: "The Phase Rule," 71 (1897).
[2] Donnan and Burt: J. Chem. Soc., **83**, 335 (1903).
[3] Walker and Fyffe: J. Chem. Soc., **83**, 173 (1903).
[4] Landolt-Börnstein Tabellen, I, 641 (1923).

without meaning. Points omitted in the calculation are indicated in the tables by an asterisk; the remaining points were given equal weight. If from the graph a point appeared to lie at the intersection of the lines it was included in the calculation of both curves.

From a study of the four curves for the different concentrations of calcium chloride it appeared that the curves intersected at about 29.5°. This point was used therefore as a basis for calculating the two curves in each case, the points lying to either side of this value being used to determine the equation. This proceedure gave values of 29.2° and 29.1° for the transition point of the three dilute solutions and 29.8° for the most concentrated solution. The transition point of the system $CaCl_2 . 6H_2O$ in equilibrium with $CaCl_2 . 4H_2O\beta$ is given as 29.2° and for $CaCl_2 . 6H_2O$ with $CaCl_2 . 4H_2O\alpha$ as 29.8°. It would appear therefore that in the less concentrated solutions, at least, it is the $\beta$ tetrahydrate which is formed. That the unstable modifidation rather than the $\alpha$ tetrahydrate is formed may be due to the solvent. It will be recalled that crystals of $Na_2SO_4 . 7H_2O$ can be obtained by adding alcohol to a mixture of sodium sulphate and water.

It may be seen from the values of the transition points given in the last two columns of the table that the values obtained by the present method agree within somewhat better than 0.3 of a degree, except in the case of barium acetate, with those obtained by other methods. This agreement is as good as could be expected in view of the order of accuracy sought. It might be advantageous to hold the system at a series of temperatures below and above the transition point, as is usually done, rather than to attempt to take instantaneous readings of the variables.

## Discussion

Preliminary determinations were made with a number of other systems and in each case the transition point came at about the temperature found by other methods. Thus, runs were made with zinc sulphate in absolute alcohol and in 96% alcohol; cadmium chloride in absolute alcohol, and sodium sulphate containing various amounts of water. The cadmium salt under certain conditions formed a gel with the alcohol and thus limited its use. The solubility of sodium sulphate in absolute alcohol is so slight that no break could be detected. With the addition of from 2 to 4% water the solubility increases sufficiently so that a change in the slope of the curve at the transition point was easily observable. With larger amounts of water the break seemed to disappear. Altho these and other determinations indicate the generality of the phenomenon, the accuracy sought was not sufficient to warrant the calculation made above.

It was hoped that the present study might throw some light upon the problem of complete and partial dissociation. In its present form, however, this does not seem to be the case. The phenomena involved are too many and too complicated to permit of ready interpretation. We may believe that the undissociated parts of dissolved salts are hydrated to about the same extent

as in the solid state at the same temperature and thus that the change in the temperature resistance curve above the transition point[1] is due to the changes in the properties of the system caused by the liberation of the molecules of water from the undissociated salt. Or, we may believe that the salt upon dissolving becomes completely dissociated and that the water molecules in part, at least, become associated with the ions, and further that at the transition point the ions become somewhat less hydrated. Thus no definite view can be formed from these experiments relative to the extent of dissociation. In either case one might expect a somewhat abrupt change in the magnitude of the conductance at the transition point after which there would appear a change in slope due to the different temperature coefficients. This, however, was not borne out, due perhaps, to the very slight change in the viscosity and dielectric constant of the solvent. Interpretation is further complicated by the presence of two molecular species either of which may contribute to the solvation of the ions.

The method might be extended to other solvents. Obviously the most advantageous system with which to work would be one in which a highly hydrated salt is very soluble in a solvent of low dielectric constant. Such a system, however, by the nature of solubility is obviously not possible to find. In general for a particular system we should expect the difference in the slopes of the curves to diminish with increasing dilution. This is seen to be the case with the results given above for barium acetate and for calcium chloride. For the four concentrations in the latter case the ratio of the slopes of the curves above and below the transition point are, with increasing dilution, 1.28, 1.23, 1.21 and 1.14.

## Summary

The above study indicates that even tho dissolved a measurable change takes place at the transition points of salt hydrates.

Values of the transition points of certain salts from a study of the resistance temperature curves of their solutions in alcohol are given.

The results were obtained by calculating the intersection of the two curves resulting from the difference in the slopes of the curves below and above the transition point.

*Philadelphia,*
*Pennsylvania.*

[1] Arrhenius: "Theories of Solutions" (1912).

# CATALYTIC AND INDUCED OXIDATION OF SOME CARBOHYDRATES, URIC ACID, AND INORGANIC SUBSTANCES

BY C. C. PALIT AND N. R. DHAR

In foregoing publications,[1] we have shown that many substances which are not ordinarily oxidised by air, are readily oxidised by air in presence of reducing agents like sodium sulphite, ferrous hydroxide, cerous hydroxide, manganous hydroxide, phosphorus, iron, cuprous oxide, stannous chloride, etc.

In a previous paper[2] we have shown that solutions of different carbohydrates can be oxidised by passing air at the ordinary temperature in presence of cerous hydroxide. We have observed that in presence of an excess of alkali, carbohydrates like starch, maltose, arabinose, laevulose, galactose, glucose, lactose and cane sugar can be completely oxidised by passing air for about five and a half hours in presence of cerous hydroxide, which undergoes oxidation. In the same paper we also published some preliminary results on the oxidation of maltose and lactose by passing air in presence of freshly precipitated ferrous hydroxide.

In this paper we have investigated the oxidation of starch, maltose, laevulose, lactose, arabinose, cane sugar, galactose and glucose by air in presence of sodium sulphite or freshly precipitated ferrous hydroxide. Moreover we have investigated the oxidation of uric acid, sodium arsenite, arsenious acid, sodium nitrite and potassium oxalate in presence of various substances.

The experimental method adopted in this communication is the same as that described in the paper by Palit and Dhar.[3] The experimental results are obtained in the oxidation of the carbohydrates are given in Tables I-III.

## (2)—Uric Acid

After having made a detailed investigation on the oxidation of carbohydrates by passing air in presence of different reducing agents, we have naturally started investigation on the oxidation of some nitrogenous matter, and the first substance chosen is uric acid. The uric acid was estimated by potassium permanganate. Standard solution of uric acid was made by weighing a known amount of the substance and dissolving it in dilute solution of caustic soda and making it up to a definite volume. 10 c.c. of this standard solution

[1] Dhar: Proc. Akad. Wet. Amsterdam, 29, 1023 (1921); Mittra and Dhar: Trans. Faraday. Soc., 17, 676 (1922); Z. anorg. Chem., 122, 146 (1922); J. Phys. Chem., 29, 376 (1925).

[2] Palit and Dhar: J. Phys. Chem., 29, 799 (1925).

[3] loc. cit.

## Carbohydrates

### TABLE I

In each of these experiments the volume of air passed was 36.5 litres in 5.5 hours and the volume of $FeSO_4$ solution used was 20 c.c.[=0.0674 grm. of $Fe(OH)_2$].

| No. of Expt. | Carbohydrate used for the experiment. | Actual weight of carbohydrate in 10 cc. of the solution taken in grm. | Amount of carbohydrate oxidised in grm. in presence of caustic soda in grm. containing | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | (1) 0.075 | (2) 0.10 | (3) 0.15 | (4) 0.20 | (5) 0.25 | (6) 0.30 | (7) 0.35 | (8) 0.40 | (9) 0.50 | (10) 0.60 | (11) 0.70 |
| 1 | Starch | 0.1027 | 0.0485 | 0.0523 | 0.0573 | 0.0636 | 0.0932 | 0.0973 | 0.1013 | 0.1021 | Complete oxidation | | |
| 2 | Maltose | 0.1097 | 0.0323 | 0.0516 | 0.0779 | 0.0829 | 0.0849 | 0.0943 | 0.0999 | — | do | do | |
| 3 | Lactose* | 0.0997 | 0.0164 | 0.0258 | 0.0388 | 0.0797 | 0.0832 | 0.0926 | 0.0992 | — | do | do | |
| 4 | Laevulose* | 0.09185 | 0.0155 | 0.0202 | 0.0345 | 0.0462 | 0.0567 | 0.0651 | 0.0756 | — | do | do | |
| 5 | Arabinose | 0.1000 | 0.0040 | 0.0138 | 0.0218 | 0.0254 | 0.0321 | 0.0411 | 0.0904 | — | do | do | |
| 6 | Cane Sugar | 0.0964 | 0.0204 | 0.0134 | 0.0185 | 0.0078 | 0.0043 | 0.0079 | 0.0281 | 0.0158 | 0.0087 | 0.0054 | 0.0016 |
| 7 | Galactose | 0.0861 | 0.00965 | 0.0112 | 0.0128 | 0.0152 | 0.0246 | 0.0349 | 0.0487 | — | 0.0703 | 0.0802 | 0.0821 |
| 8 | Glucose | 0.0962 | 0.00235 | 0.0066 | 0.0129 | 0.0172 | 0.0493 | 0.0599 | 0.0698 | 0.0768 | 0.0873 | 0.0935 | complete oxidation |

*These results have been taken from our previous publication. Palit and Dhar: J. Phys. Chem. 29, 799 (1925).

TABLE II

In each of these experiments the volume of air passed was 36.5 litres in 5.5 hours and the volume of Sodium Sulphite taken was 20 c.c.[=0.1513 grm. of $Na_2SO_3$].

| No. of Expt. | Carbohydrate used for the experiment. | Actual weight of carbohydrate in 10 cc. of the solution taken in grm. | Amount of carbohydrate oxidised in grm. in presence of caustic soda in grm. containing | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | (1) 0.00 | (2) 0.10 | (3) 0.15 | (4) 0.20 | (5) 0.25 | (6) 0.30 | (7) 0.35 | (8) 0.40 | (9) 0.50 | (10) 0.60 | (11) 0.70 |
| 1 | Starch | 0.1027 | 0.0273 | 0.0213 | 0.0221 | 0.0430 | 0.0586 | 0.0183 | 0.0214 | 0.0326 | 0.0200 | 0.0247 | 0.0231 |
| 2 | Maltose | 0.1097 | — | 0.0300 | 0.0381 | 0.0446 | 0.0501 | 0.0568 | 0.0607 | — | 0.0349 | 0.0337 | 0.0307 |
| 3 | Lactose | 0.0997 | 0.0250 | 0.0084 | 0.0116 | 0.0173 | 0.0245 | 0.0275 | 0.0305 | — | 0.0354 | 0.0345 | 0.0326 |
| 4 | Laevulose | 0.09185 | 0.0000 | 0.0007 | 0.0014 | 0.0018 | 0.0067 | 0.0194 | 0.0214 | — | 0.0256 | 0.0387 | 0.0427 |
| 5 | Arabinose | 0.1000 | 0.0096 | 0.0041 | 0.0072 | 0.0098 | 0.0252 | 0.0395 | 0.0524 | — | 0.0286 | 0.0365 | 0.0363 |
| 6 | Cane Sugar | 0.0964 | 0.0099 | 0.0034 | 0.0008 | 0.0125 | 0.0153 | 0.0146 | 0.0015 | 0.0082 | 0.0210 | 0.0232 | 0.0150 |
| 7 | Galactose | 0.0861 | 0.0104 | 0.0047 | 0.0047 | 0.0123 | 0.0318 | 0.0443 | 0.0169 | 0.0367 | 0.0660 | 0.0773 | 0.0764 |
| 8 | Glucose | 0.0962 | 0.0088 | 0.0033 | 0.0057 | 0.0062 | 0.0133 | 0.0302 | 0.0048 | 0.0217 | 0.0497 | 0.0708 | 0.0699 |

TABLE III

In each of these experiments the volume of air passed was 36.5 litres in 5.5 hours.

| No. of Expt. | Carbohydrate used for the experiment. | Actual weight of carbohydrate in 10 cc. of the solution taken in grm. | Amount of carbohydrate oxidised in grm. in presence of caustic soda in grm. containing | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | (1) 0.00 | (2) 0.05 | (3) 0.075 | (4) 0.10 | (5) 0.15 | (6) 0.20 | (7) 0.25 | (8) 0.30 | (9) .035 |
| 1 | Starch | 0.1027 | 0.0000 | 0.0310 | — | 0.0364 | 0.0241 | — | 0.0245 | — | 0.0255 |
| 2 | Maltose | 0.1097 | — | — | — | — | — | — | — | — | — |
| 3 | Lactose | 0.0997 | — | — | — | — | — | — | — | — | — |
| 4 | Laevulose | 0.09185 | — | — | — | — | — | — | — | — | — |
| 5 | Arabinose | 0.1000 | 0.0000 | 0.0109 | — | 0.0254 | 0.0365 | — | 0.0403 | 0.0485 | 0.0561 |
| 6 | Cane Sugar | 0.0964 | 0.0000 | 0.0125 | — | 0.0119 | 0.0121 | — | 0.0122 | — | 0.0120 |
| 7 | Galactose | 0.0861 | 0.0000 | 0.0017 | — | 0.0080 | 0.0169 | 0.0267 | — | — | — |
| 8 | Glucose | 0.0962 | 0.0000 | 0.0109 | — | 0.0686 | — | 0.0807 | — | — | — |

were taken in each case and mixed with freshly precipitated hydroxides of the respective metals. The results are given in Table IV.

TABLE IV

In each of these experiments the volume of air passed was 36.5 litres in 5.5 hours and the volume of uric acid added was 10 cc [= 13.0 cc. y N/10 $KMnO_4$ = 0.0975 grm of uric acid]. The different metallic salt solutions were precipitated by an equivalent amount of alkali and the resulting mixture was practically neutral.

| No. of Expt. | Substance added as catalyst. | Amount of catalyst present in grm. per c.c. | Amount of uric acid oxidised in grm. in presence of different catalysts containing the following volumes in c.c. | | | |
|---|---|---|---|---|---|---|
| | | | 10 | 20 | 40 | 50 |
| 1. | Ferrous Sulphate | 0.01 grm of salt | 0.0060 | 0.0120 | 0.0120 | |
| 2. | Manganese Nitrate | 0.0115 grm " | 0.0390 | 0.0600 | | 0.0727 |
| 3. | Cerium Chloride | 0.01 grm " | 0.00975 | 0.0210 | | |
| 4. | Cobalt Nitrate | 0.01 " " | | | 0.05325 | |
| 5. | Nickel Nitrate | 0.01 " " | | | 0.03375 | |
| 6. | Copper Nitrate | 0.025 " " | | | 0.0810 | |
| 7. | Sodium Sulphite | 0.00757 " " | 0.01275 | 0.0225 | 0.0525 | |
| 8. | Caustic Soda | 0.005 gr of NaOH | 0.0075 | 0.00975 | | |

The experimental results show that in presence of alkali, uric acid is appreciably oxidised by passing air in absence of any catalyst. In presence of hydroxides of different metals, the oxidation of uric acid is increased and the order of the accelerating effect of the different catalysts is the following:—

Cupric > manganous > cobaltous > sodium sulphite > nickelous > cerous > ferrous

### 3(a)—Sodium Arsenite

We have also determined the oxidation of arsenious acid and of sodium arsenite by passing air in presence of alkali and hydroxides of different metals. The results are given in Tables V-VII.

These results indicate that no oxidation of Sodium Arsenite or arsenious acid takes place in aqueous solution or in presence of alkali.

From our experimental results it will be seen that sodium arsenite even in presence of an excess of alkali cannot be oxidised by passing air.

TABLE V

Experiments with Sodium Arsenite in presence of several catalysts. The volume of air passed was 36.5 litres in 5.5 hours and the volume of sodium arsenite used was 10 c.c. in each case [10 c.c. of sodium arsenite solution≡10.0 c.c. of N/10 Iodine]

| No. of Expt. | Substance added as catalyst | Amount of catalyst added in grm. | Amount of caustic soda added in grm. | Volume in c.c. of N/10 Iodine required for 10 c.c. of sodium arsenite taken | Volume in c.c. of N/10 Iodine required for 10 sodium Arsenite left after the experiment | Amount of Sodium Arsenite oxidised in terms of N/10 Iodine in c.c. |
|---|---|---|---|---|---|---|
| 1 | Cobalt Nitrate | 0.20 grm. | 0.20 | 10.0 | 7.4 | 2.6 c.c. |
| 2 | Nickel Nitrate | 0.20 " | " | " | 4.6 | 5.4 c.c. |
| 3 | Manganese Nitrate | 0.230 " | " | " | 2.6 | 7.4 c.c. |
| 4 | Mercuric Chloride | 0.20 " | " | " | 0.3 | 9.7 c.c. |
| 5 | Copper Nitrate | 0.504 " | " | " | 1.9 | 8.1 c.c. |
| 6 | Lead Nitrate | 0.20 " | " | " | 2.8 | 7.2 c.c. |
| 7 | Uranium Chloride | 0.20 " | " | " | 4.8 | 5.2 c.c. |
| 8 | Mercurous Nitrate | 0.27 " | " | " | 0.2 | 9.8 c.c. |
| 9 | Ferrous Sulphate | 0.20 " | " | " | 7.6 | 2.4 c.c. |
| 10 | Ferric Chloride | 0.122 " | " | " | 8.9 | 1.1 c.c. |

## 3(b)—Arsenious Acid

TABLE VI

Experiments with Arsenious Acid in presence of several catalysts. The volume of air passed was 36.5 litres in 5.5 hours and the volume of arsenious acid used was 10 c.c. in each case [10 c.c. of Arsenious Acid≡9.55 c.c. of N/10 Iodine].

| No. of Expt. | Substance added as catalyst | Amount of catalyst added in grm. | Amount of caustic soda added in grm. | Volume in c.c. of N/10 Iodine required for 10 c.c. of arsenious acid taken | Volume in c.c. of N/10 Iodine required for arsenious acid left after the experiment | Amount of arsenious acid oxidised in terms of N/10 Iodine in c.c. |
|---|---|---|---|---|---|---|
| 1 | Cobalt Nitrate | 0.20 grm. | 0.20 | 9.55 | 8.0 | 1.55 |
| 2 | Nickel Nitrate | 0.20 " | " | " | 4.0 | 5.55 |
| 3 | Manganese Nitrate | 0.23 " | " | " | 1.5 | 8.05 |
| 4 | Mercuric Chloride | 0.20 " | " | " | 0.3 | 9.25 |
| 5 | Copper Nitrate | 0.504 " | " | " | 0.7 | 8.85 |
| 6 | Lead Nitrate | 0.20 " | " | " | 3.0 | 6.55 |
| 7 | Mercurous Nitrate | 1.024 " | " | " | 0.6 | 8.95 |
| 8 | Ferrous Sulphate | 0.20 " | " | " | 7.6 | 1.95 |
| 9 | Ferric Chloride | 0.122 " | " | " | 7.75 | 1.80 |
| 10 | Uranium Chloride | 0.20 " | " | " | 3.8 | 5.75 |
| 11 | Cuprous Chloride | 0.07 " | " | 9.55 | 0.65 | 8.90 |

## Table VII

Experiments with Sodium Arsenite and arsenious acid in presence of alkali. The volume of air passed was 36.5 litres in 5.5 hours and the volume of sodium arsenite or arsenious acid taken was 10 c.c. in each case.

| No. of Expt. | Substance used in the experiment | Volume in c.c. of the solution of substance taken | Volume of N/10 Iodine required for the substance taken | Volume of N/10 Iodine in c.c. required for the substance taken in presence of caustic soda containing in grm. (1) | (2) | (3) | (4) | (5) | Amount of substance oxidised |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Sodium Arsenite | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | Nil |
| 2 | Arsenious Acid | 10.0 | 9.55 | 9.55 | 9.55 | 9.55 | 9.55 | 9.55 | Do |

On the other hand sodium arsenite becomes oxidised when air is passed through a solution of the substance in contact with different hydroxides. The order in which the hydroxides accelerate the reaction is as follows:—

Mercurous, > mercuric > cuprous > cupric >, manganous > lead >, nickelous >, uranium >, cobalt >, ferrous > ferric.

In a recent paper Reinders and Vles[1] have shown that cupric salts act as positive catalysts in the oxidation of sodium arsenite by air. The above authors have not observed any accelerating effect of other salts.

In a previous paper Mittra and Dhar[2] have proved that the oxidation of sodium sulphite by air is retarded by the presence of sodium nitrite. In the same paper it was shown that marked retardation of the oxidation of sodium sulphite by air takes place in presence of potassium oxalate. These results are in agreement with our generalisation that reducing agents act as negative catalysts in oxidation reactions.

In a subsequent paper we[3] have attempted to induce the oxidations of sodium chromite, sodium manganite, sodium nitrite and potassium oxalate by passing air in contact with cerous hydroxide. Only sodium chromite and sodium manganite were partially oxidized to sodium chromate and sodium manganate respectively. Sodium nitrite and potassium oxalate were not appreciably oxidized. Similar results have very recently been obtained by Jorissen and van der Pol[4].

We have made further careful experiments in the oxidation of sodium nitrite and potassium oxalate by air in presence of different catalysts. The results are given in Tables VIII-X.

---

[1] Rec. Trav. chim., **44**, 29 (1925).
[2] J. Phys. Chem., **29**, 376 (1925).
[3] Palit and Dhar: loc. cit.
[4] Rec. Trav. chim., **44**, 805 (1925).

## (4) Sodium Nitrite

TABLE VIII

In this experiment the volume of air passed was 36.5 litres in 5.5 hours and the volume of $FeSO_4$ used was 20 c.c.[≡0.06476 gr. of $Fe(OH_2)$] and the volume of $Na_2SO_3$ used was also 20 c.c.≡[0.1513 gr of $Na_2SO_3$]. Also 20 c.c. of $FeSO_4$≡0.075 grm of NaOH.

| No. of Expt. | The order in which the substances were taken | Actual amount of sodium nitrite in 10 cc. of the solution | Amount of sodium nitrite in grm. oxidised in presence of caustic soda containing in grm. (1) 0.00 | (2) 0.05 | (3) 0.075 | (4) 0.10 | (5) 0.15 | (6) 0.20 | (7) 0.25 |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $FeSO_4$, $NaNO_2$, NaOH, $H_2O$ } Total volume =100 c.c. | 0.0983 grm. | — | — | 0.01145 | — | 0.0069 | 0.0060 | — |
| 2 | $FeSO_4$, NaOH, $NaNO_2$, $H_2O$ } =100 c.c. | do | — | — | 0.0017 | 0.0007 | Nil | Nil | Nil |
| 3 | $Na_2SO_3$, $NaNO_2$, NaOH, $H_2O$ } =100 c.c. | do [≡28.5 c.c. of N/10$KMnO_4$] | Nil (28.5 c.c.) | Nil (28.65c.c.) | — | Nil (28.7 c.c.) | Nil (28.9 c.c.) | Nil (28.9 c.c.) | Nil (29.0 c.c.) |

*In the case of sodium sulphite, the amount of potassium permanganate (N/10) required after the experiment is slightly greater than that required for 10 c.c. of sodium nitrite taken in a blank experiment. The figures within brackets indicate the volume of N/10 $KMnO_4$ required.

TABLE IX

Experiments with Sodium Nitrite in presence of several catalysts. The volume of air passed was 36.5 litres in 5.5 hours and the volume of sodium nitrite used was 10 c.c. in each case [10 c.c. of sodium nitrite sol. ≡ 28.5 c.c. of N/10 $KMnO_4$].

| 1 No. of Expt. | 2 Substance added as catalyst | 3 Amount of catalyst added in grm. | 4 Amount of caustic soda added in grm. | 5 Volume in c.c. of N/10 $KMnO_4$ required for 10 c.c. of nitrite | 6 Volume in c.c. of N/10 $KMnO_4$ required for the nitrite left after the experiment | 7 Difference in volume of $KMnO_4$ between the numbers (5) and (6) positive and negative |
|---|---|---|---|---|---|---|
| 1 | (a) Ferrous Sulphate | 0.05 grm. | 0.25 | 28.5 | 28.5 | 0.0 |
| | (b) do do | 0.40 " | 0.16 | do | 25.8 | −2.7 c.c. |
| | (c) " " | 0.50 " | 0.20 | do | 25.6 | −2.9 c.c. |
| 2 | Ferric Chloride | 0.0305 " | 0.25 | 28.5 | 28.7 | +0.2 c.c. |
| 3 | (a) Manganese Nitrate | 0.0575 grm. | 0.25 | 28.5 | 28.5 | 0.0 c.c. |
| | (b) " " | 0.230 " | 0.105 | do | 28.7 | +0.2 c.c. |
| | (c) " " | 0.460 " | 0.210 | do | 28.7 | +0.2 c.c. |
| | (d) " " | 0.575 " | 0.2625 | do | 28.75 | +0.25 c.c. |
| 4 | Cobalt Nitrate | 0.20 grm. | 0.0575 | 28.5 | 28.95 | +0.45 c.c. |
| 5 | Nickel Nitrate | 0.20 grm. | 0.055 | 28.5 | 28.95 | +0.45 c.c. |
| 6 | Chromium Sulphate | 0.20 grm. | 0.070 | 28.5 | 28.6 | +0.1 c.c. |
| 7 | Mercuric Chloride | 0.20 grm. | 0.060 | 28.5 | 28.9 | +0.4 c.c. |
| 8 | Copper Nitrate | 0.126 grm. | 0.25 | 28.5 | 28.8 | +0.3 c.c. |
| | (b) " " | 0.504 " | 0.215 | do | do | + do |
| | (c) " " | 1.260 " | 0.5375 | do | 28.9 | +0.4 c.c. |
| 9 | (a) Cerium Chloride | 0.40 grm. | 0.20 | 28.5 | 28.9 | +0.4 c.c. |
| | (b) " " | 0.50 " | 0.25 | 28.5 | 28.95 | +0.45 c.c. |

## (5) Potassium Oxalate

TABLE X

In this experiment the volume of air passed was 36.5 litres in 5.5 hours and the volume of $FeSO_4$ used was 20 c.c. [≡0.06476 grm. of $Fe(OH)_2$] and the volume of Sodium Sulphite was 20 c.c. [≡0.1513 grm. of $Na_2SO_3$]. Also 10 c.c. of potassium oxalate solution ≡ 10.8 c.c. of N/10 $KMnO_4$.

| No. of Expt. | Substance added as catalyst | Volume of N/10 $KMnO_4$ required in c.c. for 10 c.c. of potassium of solution | Volume of N/10 $KMnO_4$ in c.c. required after the experiment in presence of caustic soda containing in grm. (1) | (2) | (3) | (4) | (5) | (6) | (7) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Ferrous Sulphate | 10.8 | 10.8 | 10.9 | 11.0 | 11.1 | 11.2 | 11.2 | 11.2 |
| 2 | Sodium Sulphite | 10.8 | 10.8 | 10.9 | 11.1 | 11.2 | 11.2 | — | — |

N. B. In each of these experiments the amount of potassium permanganate required after the experiment is greater than that required before the experiment.

According to Gmelin-Kraut,[1] Berzelius found a direct oxidation of nitrite to nitrate with air. On the other hand, Matignon and Marchal[2] were unable to show a direct oxidation. Our experimental results show that even in presence of alkali, sodium nitrite is not appreciably oxidized by air. Reinders and Vles[3] have observed no perceptible oxidation in neutral or alkaline sodium nitrite.

From our experimental results, it will be observed that when air is passed through freshly precipitated ferrous hydroxide containing sodium nitrite appreciable quantities of sodium nitrite are oxidised. This is a typical case of induced oxidation; the oxidation of ferrous hydroxide induces the oxidation of the nitrite.

When ferrous sulphate is added to a solution of sodium nitrite and then alkali is added, the amount of the oxidation of the nitrite is greater than that obtained when the nitrite is added to ferrous hydroxide which has already been precipitated by the interaction of ferrous sulphate and alkali. This is due to the fact that on the addition of ferrous salt to a nitrite, a basic nitrite is formed and nitrous acid is set free and a part of the nitrous acid immediately oxidises the ferrous salt to the ferric state with the formation of nitric oxide which in its turn is oxidised to nitrogen peroxide by air which reacts with water and forms nitric acid and nitric oxide. Moreover free nitrous acid undergoes decomposition according to the following reaction:—

$$_3HNO_2 \leftrightharpoons HNO_3 + _2NO + H_2O$$

Hence apparently the amount of oxidation of nitrite is greater than in the previous case where the nitrite is added to the ferrous hydroxide which has already been precipitated.

We could not oxidise sodium nitrite by passing air in presence of $Fe(OH)_3$ $Cu(OH)_2$, $Mn(OH)_2$, $Co(OH)_2$, $Cr(OH)_3$, $Ni(OH)_2$, $Na_2SO_3$, $HgO$ and $Ce(OH)_3$. The hydroxides of the above metals were obtained in the freshly precipitated condition. It must be emphasised that these substances must be in the freshly precipitated condition, because we[4] have repeatedly observed that the chemical reactivity of a substance decreases with its age.

From our experimental results it will be seen that when air is passed through solution of potassium oxalate containing reducing agents, like $Fe(OH)_2$, $Ce(OH)_3$, $Na_2SO_3$, etc., there is appreciably no oxidation of the oxalate. On the other hand after removing the $Fe(OH)_3$, $Ce(OH)_4$ and unchanged $Na_2SO_3$, if the oxalate is titrated with $KMnO_4$ in presence of an excess of dilute $H_2SO_4$, greater quantities of $KMnO_4$ are required than that calculated in terms of oxalate originally taken. In the end of the titration the colour of $KMnO_4$ disappears very slowly.

Exactly similar results were obtained in the experiments on sodium nitrite in the presence of $Fe(OH)_3$, $Cr(OH)_3$, $Ni(OH)_2$, $Co(OH)_2$, $Ce(OH)_3$, $Mn(OH)_2$,

[1] Handbuch. anorg. Chem., 1 I, 271.
[2] Compt. rend., 170, 232 (1920).
[3] Rec. Trav. chim., 44, 1 (1925).
[4] Ganguli and Dhar: J. Phys. Chem., 26, 836 (1922); Chatterji and Dhar: Kolloid-Z. 33, 18 (1923); Ghosh and Dhar: J. Phys. Chem., 29, 432 (1925).

$Cu(OH)_2$ and HgO. It is difficult to explain this peculiar behaviour. It seems probable that some unstable oxidising agent like $H_2O_2$ is formed when air is passed through solutions of sodium nitrite or potassium oxalate in presence of the hydroxides and this unstable substance reacts slowly on $KMnO_4$. We are trying to elucidate the matter further. We have observed that when air is passed through solutions of sodium nitrite or potassium oxalate in the absence of the hydroxides, no such peculiar behaviour is observed.

From the foregoing results it will be observed that even in the absence of alkali all the eight carbohydrates can be oxidised by passing air through solutions of the carbohydrates in the presence of sodium sulphite or ferrous hydroxide which in its turn is being oxidised. We have also proved that in presence of an excess of alkali most of the carbohydrates can be oxidised by passing air at the ordinary temperature. When the carbohydrates are oxidised by air in presence of freshly precipitated ferrous hydroxide and when there is no excess of alkali starch is more readily oxidised than the other carbohydrates and the order in which they are oxidised in the following:— starch > maltose > lactose > laevulose > cane sugar > arabinose > galactose > glucose.

With sodium sulphite the order is starch > lactose > galactose > cane sugar > arabinose > laevulose.

From the foregoing results it will be also observed that in the presence of ferrous hydroxide the oxidation of the carbohydrates usually increases with the increase in the amount of alkali with the exception of cane sugar, in which case increase of alkali does not increase the amount of oxidation. With sodium sulphite the results are analomous; in certain cases there is an increase and other cases there is a decrease in the amount of oxidation of the carbohydrates as the quantity of alkali is increased.

In the oxidation of the carbohydrates in presence of sodium sulphite, we have determined the amount of soidum sulphite, which is oxidised during the course of the oxidation. The results are given in Table XI.

From the foregoing results it will be seen that in absence of alkalies sodium sulphite is completely oxidised when air is passed through different carbohydrates. In presence of alkali the oxidation of the sulphite is appreciably retarded and it is observed that the greater the amount of alkali added the greater is the retardation of the oxidation of the sulphite. These results seem interesting and they will be discussed later on.

In this connection it will be interesting to consider the influence of alkalies on the slow oxidation of substances in air. In the foregoing pages we have shown definitely that practically all carbohydrates can be appreciably oxidised by passing air through the solutions of the carbohydrates in presence of alkalies. Similarly we have observed that uric acid can be oxidised in presence of alkalies by passing air. Moreover it is well known that though a solution of pyrogallic acid is not oxidised by passing air, yet an alkaline pyrogallate takes up oxygen readily. Similar results are obtainable with

## TABLE XI

### Estimation of Sodium Sulphite after Oxidation

In each of these experiments the volume of air passed was 36.5 litres in 5.5 hours and the volume of sodium sulphite used was 20 c.c.[≡ 0.15 13 grm of $Na_2SO_3$].

| No. of Expt. | Carbohydrate in presence of which the experiment is performed. | Actual amount of carbohydrate in 10 c.c. of the solution. | Percentage amount of sodium sulphite oxidised in grm. in presence of caustic soda containing in grm. (1) 0.0 | (2) 0.10 | (3) 0.15 | (4) 0.20 | (5) 0.25 | (6) 0.30 | (7) 0.35 | (8) 0.60 | (9) 0.50 | (10) 0.60 | (11) 0.70 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Maltose | 0.1097 | — | — | — | — | — | — | — | — | — | — | — |
| 2 | Lactose | 0.0997 | 100 | 93.3 | 82.6 | 0 | 0 | 0 | 0 | 0 | — | 0 | 0 |
| 3 | Laevulose | 0.09185 | 100 | 74.0 | — | 25.2 | — | 12.5 | — | — | — | 0 | — |
| 4 | Arabinose | 0.1000 | 100 | 55.6 | 23.3 | 17.6 | 0 | 0 | 0 | — | 0 | 0 | 0 |
| 5 | Galactose | 0.0861 | 100 | 72.9 | 59.3 | 52.1 | 30.9 | — | 28.6 | 16.3 | — | — | — |
| 6 | Glucose | 0.0962 | 100 | 72.9 | — | 69.6 | 59.5 | 39.1 | 20.4 | 20.0 | — | — | — |
| 7 | Cane Sugar | 0.0964 | 100 | 97.0 | 31.3 | 27.8 | 0 | — | — | — | — | 0 | 0 |
| 8 | Starch | 0.1027 | 100 | 83.3 | 52.1 | — | 25.0 | — | — | — | 12.5 | 2.1 | 0 |

other hydroxy-organic compounds. It seems very likely that pyrogallate ions and ions from other hydroxy-compounds are more readily oxidised by air than the undissociated substances. Moreover, though ferrous, cerous, cobaltous, and manganous salt solutions can absorb oxygen very feebly, yet the hydroxides of all these metals readily take up oxygen from air.

In a previous paper,[1] it has been proved that the induced oxidation of nickelous hydroxide due to the oxidation of ferrous, manganous, or cobaltous hydroxides by passing air goes on increasing up to a limiting value and then it decreases as the concentration of alkali is increased. Similar results were obtained by Gire[2] in the induced oxidation of sodium arsenite due to the oxidation of $Fe(OH)_2$. Very recently Reinders and Vles[3] have obtained similar results in the oxidation of sodium arsenite in presence of cupric hydroxide.

Moreover we have proved in a foregoing paper[4] that a solution of sodium sulphite, is more readily oxidised by air or oxidising agents like $HgCl_2$ or $I_2$ than sulphurous acid of equivalent strength. We[5] have also proved that sodium formate is more readily oxidised by $HgCl_2$, $AgNO_3$, Halogens, etc., than formic acid of the same concentration. We have proved that this behaviour is due to the fact that these oxidising agents react on the formate or sulphite ions and not on the undissociated substances. On the other hand, we have proved that the oxidation of oxalic acid, formic acid, tartaric acid, sulphurous acid etc. by $KMnO_4$ or $H_2Cr_2O_7$ takes place mainly between the undissociated substances.

We are of the opinion that ferrous, cerous, manganous, and chromous hydroxides are more readily oxidised than their salt solutions because these gelatinous hydroxides with large surface can adsorb oxygen molecules readily and these oxygen molecules react with the hydroxides quickly at the surface.

From our experiments on oxidation reactions, we have proved that substances which are not ordinarily oxidised by air can be oxidised by passing air through their solutions containing reducing agents like $Fe(OH)_2$, $Na_2SO_3$, P, $Cu_2O$ etc. In this way we have been able to oxidise many substances, e. g. carbohydrates, various organic acids and their salts, nitrite, arsenite etc.

In foregoing papers[6] in discussing the results obtained by Spoehr we made the following observations:—

"Very recently Spoehr has oxidized sugars by passing air through solutions of sugars containing ferric or ferrous salts and phosphoric acid. It is well known that in presence of excess of phosphoric acid or disodium phosphate complex ferrous and ferric salts are formed. The ferrous complex can be readily oxidized to the ferric state and this oxidation induces the oxidation of sugar, starch, etc. The amount of sugar or starch oxidised will depend on the amount of ferrous salt oxidised and hence this is a typical case of induced reaction.

[1] Mittra and Dhar: J. Phys. Chem., **29**, 376 (1925).
[2] Compt. rend., **171**, 174 (1920).
[3] Rec. Trav. chim., **44**, 29 (1925).
[4] Dhar: Proc. Akad. Wet. Amsterdam, **23**, 479 (1920).
[5] Dhar: J. Chem. Soc., **111**, 707 (1917).
[6] Mittra and Dhar: J. Phys. Chem., **29**, 376 (1925); Palit and Dhar: loc. cit.

"Glucose and other hexoses are also oxidised by air in solutions containing disodium phosphate and methylene blue with the formation of carbon dioxide. This reaction is greatly accelerated by iron salts. Not only the hexose sugars are thus oxidised, but also sucrose, trehalose, mannitol, and glycerol.

"Spoehr has observed that ferric salts also are effective in the oxidation of hexoses by air, but iron in the ferrous condition is more active than iron in the ferric condition. We have already observed that complex ferrous phosphate is a very good reducing agent and that the oxidation of this substance induces the oxidation of sugar, glycerol, etc.

"With complex ferric phosphate the case is different as it cannot be oxidised further. We have observed that the complex is very slowly reduced by sugar, glycerol, etc. into the ferrous complex, which in its turn is readily oxidised to the complex ferric phosphate and this oxidation induces the oxidation of glycerol, sugars, etc., As the action of sugars, glycerol, etc. on the complex ferric phosphate is very slow, the amount of induced oxidation of sugars, glycerol, etc., is much less than the amount of induced oxidation with complex ferrous phosphate. That is why Spoehr got 0.5600 gr $CO_2$ from 1 gram ferrous sulphate and 0.5392 gr $CO_2$ from an equivalent weight of ferric sulphate using the same quantities of glucose and sodium phosphate."

In a recent paper, Spoehr has made the following statements:—

"In strongly alkaline solution, glucose is oxidised by air, but these conditions have only remote physiological influence because it has not been possible to oxidise glucose with air in solutions of hydroxyl ion (OH′) concentrations approximating those found in the living organism even in presence of iron salts or phosphates."

In view of our experimental results, the above remarks need correction, because we have been able to oxidise eight carbohydrates in practically neutral solutions by passing air through the solutions of the carbohydrates in contact with cerous hydroxide or ferrous hydroxide.

From our experimental results as recorded in this paper it will be clear that neutral solutions of eight carbohydrates, uric acid, sodium nitrite, sodium arsenite etc., can be oxidised in presence of $Fe(OH)_2$, $Ce(OH)_3$, $Mn(OH)_2$, $Na_2SO_3$ etc. by passing air at ordinary temperature. Hence the conclusion of Spoehr[1] that neutral or feebly alkaline solution of carbohydrates are not oxidised by air is not correct.

From our experimental results with arsenious acid, it will be seen that in presence of $Fe(OH)_2$, arsenious acid is more readily oxidised than in presence of an equivalent amount of $Fe(OH)_3$ because in presence of $Fe(OH)_2$, induced oxidation of the arsenite takes place and in presence of $Fe(OH)_3$ oxidation of sodium arsenite takes place only by its reaction on $Fe(OH)_3$ and this has a very small velocity. These results are exactly in the same line as those obtained by Spoehr in the oxidation of sugars in presence of ferrous and ferric salts.

[1] J. Am. Chem. Soc., 46, 1494 (1924).

It will be evident that substances which are difficultly oxidised by passing air can be usually more readily oxidised in presence of reducing agents than in presence of a feeble oxidising agent like ferric salt or cupric salt.

Reinders and Vles[1] have shown that cupric salts accelerate the oxidation of arsenites by air but we are of the opinion that cuprous salts acting as inductors will accelerate the reaction better than cupric salts as shown by our experimental results.

Titoff[2] and others have shown that cupric salts act as marked accelerators in the oxidation of sulphites. Similarly ferric salts, cupric salts are known to accelerate the reactions between $K_2S_2O_8$ and KI, naphthalene and $H_2SO_4$ etc. We are of the opinion that in all such cases feeble oxidising agents like cupric salts, ferric salts etc., react on the reducing agents very rapidly and are themselves reduced to the ferrous or cuprous salts which, in their turn, are oxidised by air or other oxidising agents. Consequently we believe that usually weak oxidising agents ought to act as accelerators in the oxidation of substances which are readily oxidised. Moreover $Ni(OH)_2$, $Co(OH)_3$, $Mn(OH)_2$ etc. can accelerate the oxidation of $Na_2SO_3$ by air. This is due to the fact that when a molecule of $Na_2SO_3$ is oxidised to $Na_2SO_4$, a molecule of the hydroxides is also oxidised due to induction and this higher oxide readily reacts on the sulphite and readily passes into the lower oxide which in its turn again passes into higher oxide and this process goes on.

In a previous paper[3] it has been observed that in the dark the reaction between potassium oxalate and $HgCl_2$ is much slower than the reaction between $HgCl_2$ and sodium formate under identical conditions. Consequently as far as $HgCl_2$ is concerned, the formate ion is a better reducing agent than the oxalate ion. Moreover in the same paper it was shown that the reaction between oxalic acid and chromic acid is much quicker than that between chromic acid and formic acid under identical conditions. This shows that undissociated oxalic acid is a better reducing agent than undissociated formic acid towards chromic acid. Exactly similar results is obtained with oxalic acid and formic acid towards $KMnO_4$. It is well known that when $KMnO_4$ reacts with formic acid, $MnO_2$ is precipitated whilst with oxalic acid, manganous salts are produced. We have also proved that manganous salts act as marked accelerators in the oxidation of oxalic acid by $KMnO_4$ or $H_2Cr_2O_7$, whilst manganous salts act as marked retarders in the oxidation of formic acid by $KMnO_4$, or $H_2Cr_2O_7$. This is most likely due to the fact that in presence of $KMnO_4$ or $H_2Cr_2O_7$ the manganese ions are converted into $Mn^{\cdot\cdot\cdot}$ or $Mn^{\cdot\cdot\cdot\cdot}$ ions which react very readily on oxalic acid producing $Mn^{\cdot\cdot}$ ions again, whilst the $Mn^{\cdot\cdot\cdot}$ or $Mn^{\cdot\cdot\cdot\cdot}$ ions which are formed by the reaction between manganous salts and $KMnO_4$ or $H_2Cr_2O_7$ cannot at all react with formic acid. Consequently a part of the $KMnO_4$ or $H_2Cr_2O_7$ is taken up by the manganous salts in their conversion to $Mn^{\cdot\cdot\cdot}$ or $Mn^{\cdot\cdot\cdot\cdot}$ ions which

[1] Rec. Trav. chim., **44**, 29 (1925).
[2] Titoff: Z. physik. Chem., **45**, 645 (1903).
[3] Dhar: J. Chem. Soc., **111**, 707 (1917).

are practically useless towards the oxidation of formic acid and it appears, therefore, that a part of the $MKnO_4$ or $H_2Cr_2O_7$ is lost as far as the oxidation of formic acid is concerned due to the presence of the $Mn^{''}$ ions; that is why manganous salts behave as negative catalysts in the oxidation of formic acid by $H_2Cr_2O_7$ or $KMnO_4$. On the other hand, $Mn^{'''}$ or $Mn^{''''}$ ions can react very readily with oxalic acid. Moreover the formation of $Mn^{'''}$ or $Mn^{''''}$ ions by the reaction between $KMnO_4$ or $H_2Cr_2O_7$ and $Mn^{''}$ ions is a very rapid process, because we know that $MnO_2$ is very readily precipitated by the interaction of manganous salts and $KMnO_4$. Thus the positive catalytic action of manganous salts on the reaction between oxalic acid and $KMnO_4$ or $H_2Cr_2O_7$ is readily explained.

The retardation in the oxidation of sodium sulphite by air in presence of alkali is probably due to the decrease in the concentration of sulphite ions due to the common sodium ions. Moreover the solubility of oxygen in water is likely to be less in presence of strong alkali.

## Summary and Conclusion

1. When a stream of air is allowed to pass slowly through solutions of carbohydrates like maltose, arabinose, laevulose, galactose, glucose, lactose, cane sugar and starch in presence of ferrous hydroxide or sodium sulphite, oxidation of the carbohydrates takes place at the ordinary temperature.

2. Uric acid is oxidised by air in presence of alkali, sodium sulphite, ferrous hydroxide, cupric hydroxide, manganous hydroxide, chromous hydroxide, cerous hydroxide, cuprous hydroxide, cobaltous and nickelous hydroxide.

3. Sodium arsenite can be oxidised in presence of the above hydroxides.

4. Sodium nitrite has been oxidised by air in presence of ferrous hydroxide only.

5. Explanation of several catalytic oxidations has been advanced.

*Chemical Laboratory,*
*Allahabad University,*
*Allahabad, India.*
*January 16, 1926.*

# ELECTROKINETIC BEHAVIOUR AND ELECTRODE POTENTIAL

BY F. L. USHER

The double layer of ions generally assumed to be responsible for electrokinetic effects is similar, electrically, to that implied in the generally accepted theory of electrode potential. The question of their identity is one of considerable importance. This identity was assumed by Billiter[1] who formed an estimate of single electrode potential by determining the concentration of a particular ion required to annul electrokinetic effects, the normal potential being then calculated by means of Nernst's formula. The value so obtained differed by about half a volt from that based on experiments with a dropping mercury electrode and on the electrocapillary behaviour of the same metal. The results obtained by Haber and Klemensiewicz[2] and by Freundlich and Rona[3] have on the other hand furnished conclusive proof that, at least in the case of the glass surfaces studied by them, electrode potential and electrokinetic potential are distinct. In view of the apparently decisive nature of these later results, it is interesting to find that the identity of the two potentials has quite recently been again assumed[4] in the case of metals.

If the outer member of the double layer which is the seat of electrode potential is mobile, this and the inner member—and with them the surfaces to which they are respectively attached—must, when exposed to a suitably oriented electric field, undergo a relative displacement which will give rise to electrokinetic effects of the kind generally observed. If, on the other hand, the two members of the "Nernst" double layer are not relatively displaced by the tangential component of an applied electric force, the theory of electrokinetic phenomena due to Helmholtz is by implication deprived of its fundamental assumption, unless we postulate the existence of a second superposed double layer similar to the first in every respect but that of the relative mobility of its components.

The former alternative, if true, requires a modification of a somewhat revolutionary character in the current theory of electrode potential, inasmuch as the magnitude and even the sign of the charge on the mobile surface of a metal can be changed by the addition of small quantities of electrolytes that can have little if any influence on the concentration of the metal ion generally regarded as the sole determinant of electrode potential. It raises the question whether electrode potential may in fact be due primarily to an electric charge imparted by an adsorbed layer of ions of any kind, rather than to the existence in the liquid of ions of one particular kind. In order to obtain information which might help in deciding between the two views just referred to, experi-

[1] Z. Elektrochem., 8, 638 (1902); 15, 439 (1909).
[2] Z. physik. Chem., 67, 385 (1909).
[3] Sitzungsber. Akad. Wiss. Berlin, 20, 397 (1920).
[4] Garrison: J. Am. Chem. Soc., 45, 37 (1923).

ments on the influence of some uni-univalent electrolytes on the electrode potential of mercury have been carried out, side by side with electrocapillary measurements. The influence of a single electrolyte, potassium chloride, on the electrokinetic properties of a positively and a negatively charged surface has also been examined.

## Experimental

The mercury used was first purified by spraying through a long column of acidified mercurous nitrate solution, and was afterwards distilled slowly in a vacuum. The electrolytes examined were lithium, potassium, and ammonium chlorides, hydrochloric acid, potassium hydroxide, and sodium citrate, in four degrees of dilution from millinormal to normal. Two of these substances, ammonium chloride and sodium citrate, are capable of holding finely divided mercury in a stable suspension, positively charged in the first case, negatively in the second. The combination whose E. M. F. was measured consisted of the mercury in contact with the solution under examination, which was connected through a saturated solution of potassium chloride with a decinormal calomel electrode, this pair of elements being connected in series with a standard cadmium cell through a reversing key. Half the difference between the readings obtained before and after the poles of the first-named pair of elements were reversed was taken as its E. M. F. The values at 25° are given in Table I.

TABLE I

| | Potential against N/10 calomel electrode at 25° | | | | | |
|---|---|---|---|---|---|---|
| Dilution | LiCl | KCl | $NH_4Cl$ | HCl | KOH | Na Citrate |
| N/1000 | 0.067 | 0.068 | 0.065 | 0.111 | −0.104 | 0.125 |
| N/100 | 0.052 | 0.051 | 0.049 | 0.049 | −0.150 | 0.073 |
| N/10 | 0.003 | 0.002 | −0.003 | −0.001 | −0.182 | 0.008 |
| N | −0.062 | −0.068 | −0.063 | −0.068 | −0.227 | −0.014 |

Four of the electrolytes, potassium chloride, ammonium chloride, potassium hydroxide, and sodium citrate, were then made up with a dilute solution of hydrazine hydrate (0.038 *N*) instead of water, and the results are given in Table II.

TABLE II

| | Potential against N/10 calomel electrode at 25° | | | |
|---|---|---|---|---|
| Dilution | KCl | $NH_4Cl$ | KOH | Na Citrate |
| N/1000 | −0.57 | −0.53 | −0.48 | −0.55 |
| N/100 | −0.56 | −0.50 | −0.57 | −0.55 |
| N/10 | −0.47 | −0.44 | −0.70 | −0.56 |
| N | −0.45 | −0.27 | −0.72 | −0.55 |

The electrocapillary curves were determined in the usual manner, and the same solutions (omitting lithium chloride) were used as for the measurements of electrode potential. The voltage corresponding to the maximum interfacial tension was obtained by adjusting the applied voltage in steps of 0.01

volt; otherwise readings were taken only for steps of 0.1 volt. The potential corresponding to the maximum tension (considered to be the natural potential) is given to the nearest hundredth of a volt, and the error is probably not greater than this for the normal and decinormal solutions, but the uncertainty in the case of the millinormal solutions may amount to as much as 0.05 volt, owing to the flatness of the curve near the maximum at great dilutions. It is unnecessary to give the full experimental readings. These were plotted, and from the smoothed curves the constants of the ascending branch of the parabolas were calculated by means of the formula $\gamma = \gamma_{max} - \frac{1}{2}CE^2$, C and E being respectively the capacity and potential of the double layer in electrostatic units. In Table III the natural potentials are given, for convenience, in volts, the other electrical quantities in electrostatic units.

TABLE III

| Solution | Natural potential (volts) | Maximum interfacial tension (dynes per cm.) | Capacity (e. s. unit $\times 10^{-7}$) | Surface density of charge (e. s. unit $\times 10^{-7}$) | Thickness of double layer (cm. $\times 10^{7}$) |
|---|---|---|---|---|---|
| KCl | | | | | |
| $N/1000$ | 0.75 | 420 | 2.34 | 5.9 | 2.7 |
| $N/100$ | 0.70 | 426 | 2.32 | 5.4 | 2.7 |
| $N/10$ | 0.62 | 426 | 2.32 | 4.8 | 2.7 |
| $N$ | 0.53 | 420 | 2.32 | 4.1 | 2.7 |
| $NH_4Cl$ | | | | | |
| $N/1000$ | 0.75 | 414 | 1.66 | 4.2 | 3.8 |
| $N/10$ | 0.63 | 426 | 2.58 | 5.4 | 2.5 |
| $N$ | 0.55 | 423 | 3.36 | 7.1 | 1.9 |
| HCl | | | | | |
| $N/100$ | 0.63 | 426 | 2.2 | 4.6 | 2.9 |
| $N/10$ | 0.60 | 427 | 2.92 | 5.8 | 2.2 |
| $N$ | 0.56 | 419 | 3.8 | 7.1 | 1.7 |
| KOH | | | | | |
| $N/1000$ | 0.60 | 421 | 1.70 | 3.4 | 3.8 |
| $N/100$ | 0.59 | 424 | 1.36 | 2.7 | 4.7 |
| $N/10$ | 0.54 | 417 | 1.30 | 2.3 | 5.0 |
| $N$ | 0.40 | 413 | 1.32 | 1.8 | 4.8 |
| Na Cit. | | | | | |
| $N/100$ | 0.67 | 423 | 2.44 | 5.2 | 2.6 |
| $N/10$ | 0.57 | 425 | 2.94 | 5.6 | 2.2 |
| $N$ | 0.42 | 414 | 4.2 | 5.9 | 1.5 |
| $N$-KCl with hydrazine | 0.42 | 434 | 2.7 | 3.8 | 2.4 |

In Table III, the interfacial tensions have been taken as proportional to the corrected measured heights of the mercury column, the factor of proportionality being obtained by measuring, in the same apparatus, the height of the column supported by solutions of hydrochloric acid of the strengths used by Lenkewitz[1] in his determinations of this constant.

The following electro-osmotic experiments were carried out in order to ascertain (1) whether potassium chloride brings about an initial increase of charge in the case of a positive as well as a negative surface, and (2) whether this effect persists in the presence of a strongly adsorbed ion having a charge of the same sign as the surface. An "alundum" thimble (made for use in an extraction apparatus) was used as the diaphragm. It was soaked for some days in concentrated hydrochloric acid in order to remove any soluble mineral matter, and then thoroughly washed with water until the electro-osmotic flow became constant. This diaphragm was negative to water, and when required as a positive diaphragm was soaked first in dilute alum solution, then in ammonia, and finally washed as before. It was found convenient to measure the pressure balancing the electro-osmotic force in the case of the negative diaphragm, and the rate of flow of liquid in the case of the positive. The inner electrode was a straight piece of stout platinum wire sealed into a glass tube at its upper end, this tube passing through a hole in the centre of a rubber stopper which fitted tightly into the top of the thimble. The glass tube was provided with distance pieces which ensured the replacement of the electrode in a central position. The outer electrode was a long spiral of platinum wire wound on a glass frame which fitted closely into the containing vessel. The thimble was replaced after each refilling in the same relative position with respect to the outer electrode by taking cross bearings on two fixed pairs of uprights.

Measurements were made of the effect of potassium chloride when the negative diaphragm was in contact with (1) water, (2) 0.2-millinormal NaOH, and (3) millinormal NaOH; and when the positive diaphragm was in contact with (1) water and (2) 0.5-millinormal $Al_2(SO_4)_3$. The potential difference between the electrodes was 22 volts, which produced an easily measurable effect, but even at this voltage the measurements at concentrations greater than six milli-equivalents per litre were unreliable. The potassium chloride solution was made up with the appropriate liquid, water, NaOH, or $Al_2(SO_4)_3$, so that the only variable concentration in any particular experiment was that of the potassium chloride. In Table IV the figures given under "relative surface charge" are proportional to the readings of pressure or rate of flow of liquid. They denote the surface density of the uncompensated electric charge, and are comparable within each series, although the numbers given in Series I are not comparable with those in Series II. In all cases the figures given represent the mean of two or more readings. The error depends on the concentration of the electrolyte. In the pressure measurements the maximum disagreement varied from three per cent. below a concentration of one milli-

[1] "Untersuchung über Kapillarität". Münster, 1904.

equivalent per litre to ten per cent. at higher concentrations; and in the measurements of electro-osmotic flow the corresponding errors were roughly twice as great.

TABLE IV

Influence of potassium chloride on electro-osmotic effect

SERIES I. Diaphragm negative.

| Milli-equivs. KCl per litre | Relative surface charge in water | N/5000 NaOH | N/1000 NaOH |
|---|---|---|---|
| 0 | 1 | 2.71 | 2.22 |
| 0.1 | 1.39 | 2.12 | 1.56 |
| 0.2 | 1.58 | 2.58 | 2.46 |
| 0.3 | 1.44 | 2.48 | 2.39 |
| 0.4 | 1.66 | — | 2.66 |
| 0.5 | 1.73 | 2.13 | 2.37 |
| 0.6 | 2.02 | — | — |
| 0.7 | 1.93 | — | 2.44 |
| 0.75 | — | 2.66 | — |
| 0.8 | 1.83 | — | — |
| 0.9 | 1.95 | — | — |
| 1.0 | 1.88 | 2.54 | 2.12 |
| 1.5 | 1.97 | — | — |
| 2.0 | 2.05 | 1.93 | 2.20 |
| 3.0 | 2.02 | 2.17 | 1.68 |
| 4.0 | 2.05 | 1.66 | 2.10 |
| 5.0 | — | 2.13 | 1.80 |
| 6.0 | 2.17 | | |
| 8.0 | 1.95 | | |
| 10.0 | 1.39 | | |

SERIES II. Diaphragm positive.

| Milli-equivs. KCl per litre | Relative surface charge in water | N/2000 $Al_2(SO_4)_3$ |
|---|---|---|
| 0 | 1 | 2.64 |
| 0.1 | 1.84 | 2.16 |
| 0.2 | 2.20 | 2.04 |
| 0.4 | 2.80 | 1.80 |
| 0.6 | 2.54 | 1.96 |
| 0.8 | 2.92 | 2.32 |
| 1.0 | 2.68 | 2.24 |
| 1.5 | — | 2.28 |
| 2.0 | 2.48 | 2.08 |
| 3.0 | — | 1.60 |
| 4.0 | 1.56 | 0.84 |
| 6.0 | 0.56 | — |

Fig. 1 shows the relative surface densities of the charge plotted against the concentrations of KCl so as to indicate the general sense of the effects in the case of the negative diaphragm, and Fig. 2 shows the initial portions of the curves with the concentration scale magnified. Figs. 3 and 4 show the corresponding curves for the positive diaphragm.

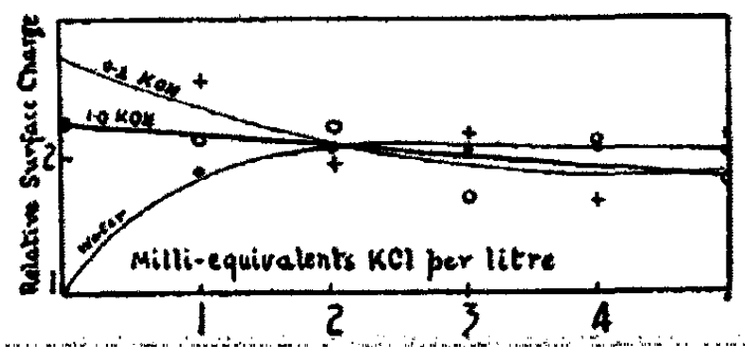



FIG. 1

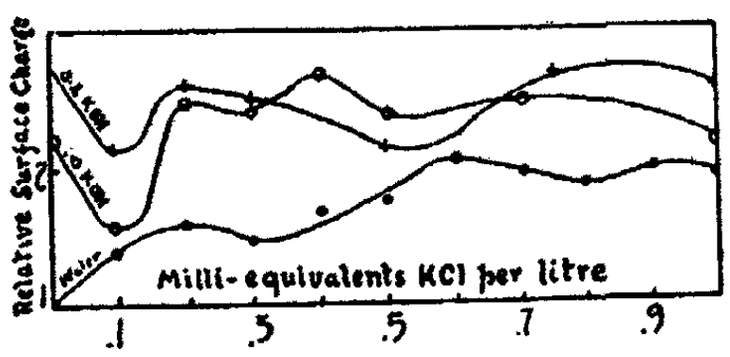



FIG. 2

## Discussion of Results

If, as it will be assumed, the liquid contact potentials between the solutions examined and the decinormal potassium chloride used in the reference electrode were eliminated by the use of the salt bridge, the measured potentials must be the algebraic sum of the potential differences across all double layers situated at the interface of the mercury and the solutions used, *minus* the sum of the corresponding potentials at the mercury-solution interface in the reference electrode. The value of the latter is not known with certainty, but is in any case constant, so that, by subtracting some constant quantity from the experimental values, it might be expected that figures would be obtained bearing some relation to the electrokinetic behaviour of mercury in the corresponding solutions. It is quite evident that no such constant quantity can be chosen so as to reveal even a suggestion of parallelism between the transversely measured potential and the electrokinetic behaviour. Finely divided mercury is known to move towards the cathode in dilute solutions of ammonium chloride, towards the anode in dilute sodium citrate, and not at all in dilute potassium chloride. On comparing the experimental values for these three salts in centinormal and millinormal solution, it is seen that, while there is very little difference between the values for potassium and ammonium chlorides, the mercury is more positive in sodium citrate than in

either of the others. Again, it is more negative in solutions of potassium hydroxide, although no stable suspension can be obtained in them. There is, in fact, a complete absence of any correlation between the transversely measured potential and the electrokinetic behaviour.

One or two points of interest emerge, however, from a consideration of the figures. It may be noticed that the potentials of mercury in decinormal solutions of the chlorides examined are substantially the same as those of the

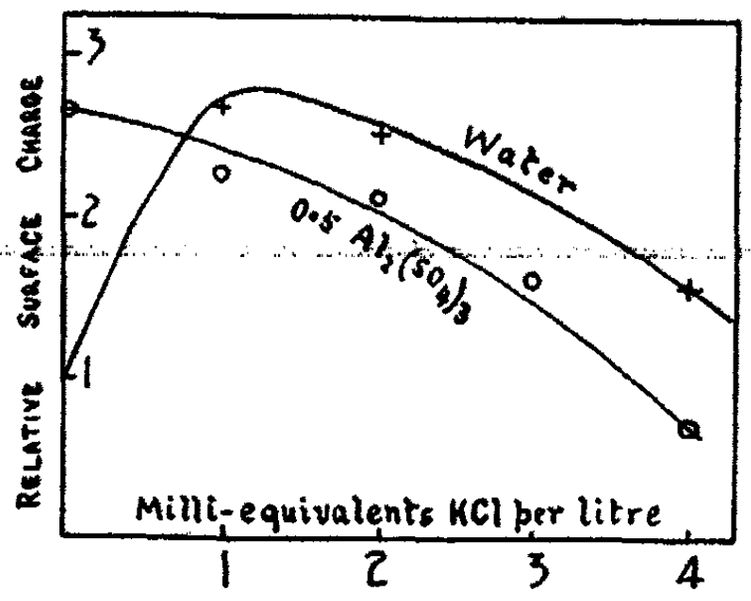



FIG. 3

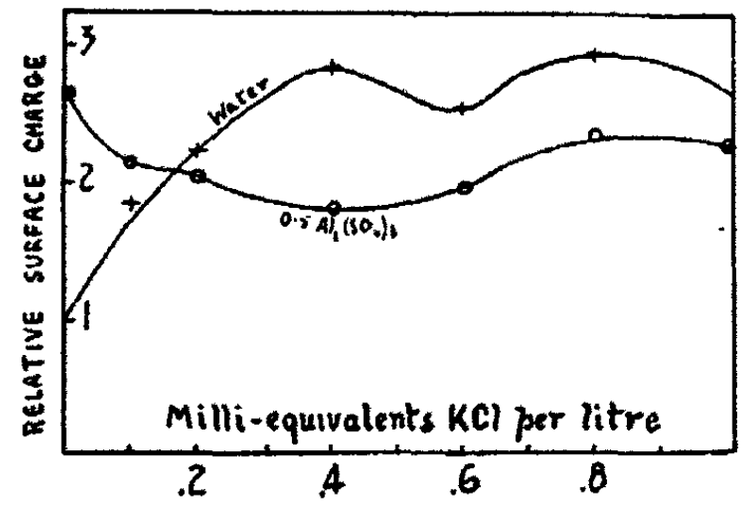



FIG. 4

mercury in the decinormal calomel electrode, and that the influence of change of concentration is, at least qualitatively, the same as in the case of a calomel electrode. This striking similarity of behaviour is not likely to be accidental, and there can be little doubt that the potential of mercury is in both cases determined by the same factor, namely, the activity of the mercurous ions in the liquid. But it was found that mercury could not be detected (by means of hydrogen sulphide) in any of the solutions used, although of course it is easily recognisable in the solution used in the calomel electrode. It would appear therefore that at great dilutions the concentration of mercurous ions at the mercury surface is almost independent of the bulk concentration, and

it is reasonable to infer that in all the solutions examined sufficient mercurous ions were formed by chemical action to provide a layer covering the mercury surface. Assuming the chemical action to be due to dissolved oxygen, one finds that only about $2 \times 10^{-8}$ gram of oxygen would be required to produce 1 sq. cm. of a unimolecular film of mercurous ions. It is obviously impracticable to carry out experiments in which so small a quantity of oxygen could be excluded with certainty, and some measurements were therefore made in presence of hydrazine hydrate which, provided the solution is alkaline, reduces mercury compounds even at very great dilution: mercuric sulphide was indeed the only compound examined which resisted reduction. As is evident from Table II, the effect of the hydrazine, which was present in the same concentration throughout, is remarkable. The potentials are given only to the nearest centivolt, since they were not reproducible with greater accuracy, presumably because the electrodes under these conditions are practically irreversible. It will be seen that the effect of changing concentration of the electrolyte is now in the opposite sense, the potential of the mercury becoming more positive with increasing concentration, except with sodium citrate and potassium hydroxide, an observation which suggests that it is no longer determined by mercurous ions. It will also be noticed that there is still little to suggest a connection between the measured potentials and the mobility of mercury in the corresponding solutions.

*Electrocapillary measurements.* The constants given in Table III are those relating to the parabola $\gamma = \gamma_{max} - \frac{1}{2}CE^2$, and were obtained by drawing the curves with the maximum interfacial tension at E=O. The "natural" potentials deduced from the electrocapillary experiments show divergencies from those reckoned from the measurements of electrode potential (taking the absolute potential of the decinormal calomel electrode as 0.61 volt) which are difficult to explain quantitatively in the present state of our knowledge, but the general results are similar. The figures are recorded here chiefly because we can deduce from them some particulars regarding the properties of the double layer responsible for the natural potential. It has been stated[1] that the relation between the interfacial tension and potential should be expressed by the equation $\gamma = \gamma_{max} - CE^2$, following a suggestion made by Krüger and Krumreich[2] that the variation of interfacial tension with surface charge should be doubled in order to include the effect of both sides of the double layer. This suggestion was originally put forward to explain a discrepancy between results obtained by two different experimental methods, but it appears to be contrary to theoretical requirements as deduced, for example, by applying the principle of Virtual Work. Thus, in a double layer of unit area, forming a condenser of capacity C, let a small positive charge, $\delta Q$, be transferred from the positive to the negative side. The work terms involved are $E\delta Q + \partial y/\partial Q \cdot \delta Q$, which, since the system is in equilibrium and the change takes place at constant temperature and volume, must be equated to zero.

[1] Freundlich: "Kapillarchemie", 395 (1922).
[2] Krüger and Krumreich: Z. Elektrochem., 19, 620 (1913).

Hence $\partial y/\partial Q = -E$, or $\partial y/\partial E = -CE$. If the capacity is assumed to be constant we obtain on integrating,

$$\gamma = \gamma_{max} - \tfrac{1}{2}CE^2,$$

without having made any assumption regarding the effectiveness of one or both sides of the double layer.

The capacity being thus determined from the electrocapillary curves, it is easy to calculate the charge per unit surface, and also the thickness of the double layer. These quantities are given in Table III, the thickness of the double layer being calculated on the assumption that the dielectric constant of the medium separating its two components is 80: the values obtained by taking it as unity are so much smaller (about $3 \times 10^{-9}$ cm.) than the normal spacing of atoms that the former alternative seems preferable.

It is interesting to find that, although potassium chloride is probably the only one of the electrolytes used which behaves in an approximately normal manner (in not giving rise to any adsorption of its ions at the electrocapillary maximum), the values for the charge per unit surface and for the thickness of the double layer are all of the same order of magnitude. Thus the surface charge (positive) in ammonium chloride is about $5 \times 10^4$ e. s. units, and in sodium citrate it is practically the same, and still positive; yet in regard to its electrokinetic behaviour mercury is positive in the former but negative in the latter.

*Effect of potassium chloride on electrokinetic charge.* The curves in Figs. 1 and 3 indicate that the general effect of potassium chloride on the electrokinetic potential of a negatively charged surface, when no other electrolyte is present, is first to increase the negative charge and afterwards to reduce it; while with a positively charged surface under similar conditions the effect is first to increase the positive charge and then to reduce it. When another electrolyte of a kind which strongly enhances the natural charge is also present, the tendency of the potassium chloride to increase it is much less marked. While these statements represent the general tendency of the electrokinetic potential under the conditions named, a closer examination of the figures for very small concentrations reveals a series of subsidiary maxima and minima in the curve, which can hardly be attributed to experimental error: the initial portions of the curves in every case have a sinuous form. It is to be noticed that the first effect of the potassium chloride is to increase the natural charge, whether positive or negative, unless this has already been enhanced by the previous addition of a suitable electrolyte.

It has been pointed out elsewhere[1] that an initial increase of surface charge may be expected to occur when the free ions produced by the dissociation of surface molecules are replaced by others which have less tendency to combine with the residual sessile ions. Thus, the addition of an alkali metal salt in sufficiently great dilution in the case of a surface giving rise to free hydrogen ions should always cause such an increase, and this is confirmed by the data so far available. But there are instances in which this explanation

[1] Trans. Faraday Soc., 21, Part 2 (1925).

is inapplicable.[1] Kruyt, in measuring the electrokinetic effect at a glass-water interface, has found that an initial increase of charge is produced not only by potassium chloride, but also by hydrochloric acid and by barium chloride. This behaviour can hardly be covered by the considerations just referred to, and may best be explained by assuming an adsorption of chloride ions at the surface of the glass. A similar assumption seems necessary to explain the results shown in Table IV and Figs. 1-4. It is evident that in these experiments two processes are at work whose effects are opposed. In the case of the "alundum" diaphragm, whose natural charge in water is negative, the potassium chloride added furnishes chloride ions which are adsorbed and thus increase the negative charge of the surface, further addition of the electrolyte then acting in the normal manner and reducing the dissociation of the surface molecules. These two effects predominate alternately, and would presumably continue to do so until the surface was fully occupied by the negative ions of dissociated and undissociated molecules—a stage which cannot be reached experimentally on account of difficulties of measurement. With an alumina diaphragm whose natural charge is positive, the cations of the electrolyte are adsorbed, and the further course of events is then much the same as before. This view of what occurs is supported by the observation that when in the first case a strongly adsorbed anion, in the second a strongly adsorbed cation, is initially present, the increase of the initial charge is either much smaller, or does not occur.

## Summary

1. Measurements of the contact potential and of the electrocapillary behaviour of mercury in solutions of different uni-univalent electrolytes indicate the absence of any direct connection between electrode potential and electrokinetic behaviour in the case of this metal.

2. A comparison of the potentials of mercury in solutions of chlorides with and without the addition of hydrazine, indicates that whenever the metal is brought into contact with such solutions, chemical action results in the production of mercurous ions which are present at the interface in nearly the same degree of concentration as if the solutions had previously been saturated with calomel.

3. Electro-osmotic experiments on the influence of potassium chloride on the surface charge of a diaphragm point to an initial adsorption of that ion which enhances the original charge, this effect being greatly reduced when a strongly adsorbed ion bearing the same charge as the surface is present.

*Department of Chemistry,*
*University of Mysore,*
*Bangalore.*

[1] Kolloid-Z., **22**, 81 (1918).

# MECHANISM OF THE CATALYTIC DEHYDRATION OF METHANOL AND SOME PROPERTIES OF THE HYDROUS ALUMINIUM OXIDE CATALYST*

BY H. C. HOWARD, JR.

Our present knowledge in regard to the mechanism of catalysis can be accurately classified under three general heads: (1) those cases in which intermediate compound formation has been definitely proven; (2) those cases in which absence of compound formation has been demonstrated; and (3) a type of catalytic reaction in which the matter of the formation of an intermediate chemical compound is still controversial, or merely a matter of definition. On this question of intermediate compound formation in catalysis, Sabatier states that "the idea of a temporary, unstable, intermediate compound has been the beacon light that has guided all my work on catalysis." Consequently, he explains such a catalytic reaction as the dehydration of an alcohol over hydrous aluminium oxide, by assuming a mechanism analogous to that assigned to the Williamson reaction. Aluminium is an amphoteric element, so that its compounds will possess both basic and acidic properties, and the analogy of the role played by the alumina catalyst, in the dehydration of an alcohol, to that of the sulfuric acid in the Williamson reaction, is most clearly brought out if the reaction over the alumina catalyst is pictured as taking place by the addition of a mol of the alcohol to the acidic form of the aluminium hydroxide, $H_3AlO_3$, or its partial dehydration product, $HAlO_2$, as shown in the following equations:

$$CH_3OH+HAlO_2 \longrightarrow CH_3AlO_2+HOH$$
$$CH_3AlO_2+CH_3OH \longrightarrow (CH_3)_2O+HAlO_2$$

Such a mechanism lays emphasis upon the acid properties of the oxide, and the following facts indicate that such properties are of importance.

(1) Only amphoteric or acidic oxides have been shown to be capable of acting as dehydration catalysts in such a reaction; that is, no exclusively basic oxide has been shown to function in this manner.

(2) The effectiveness of a given oxide as a dehydration catalyst appears in many cases to be related to its "acidity." The compounds formed by the hydration of such strongly acidic oxides as $SO_3$ and $P_2O_5$ are excellent catalysts of dehydration. The hydrous forms of weakly acidic oxides such as $Al_2O_3$ are fairly active, while those of the very weakly acidic oxides such as $Fe_2O_3$ exhibit catalytic dehydrating power to only a very limited degree, indeed.

(3) Those methods of preparation which would be expected to yield a catalyst in which the acidic form of the hydrated oxide predominated, are, in general, the methods which furnish the most active dehydration catalysts.

*Contribution from the Chemical Laboratory, University of Missouri.

(4) Chariou[1] has shown that adsorbed lime on an alumina catalyst decreases very markedly the activity of such a catalyst in the dehydration of ethyl alcohol to ether, and Taylor[2] has pointed out that Adkins' data show the adverse effect of ammonia in catalytic dehydration.

Adkins[3] questions the formation of a compound or compounds between the alcohol and the catalyst because such an hypothesis necessitates the assumption of two different types of compounds in the case of oxides which are capable of inducing two different types of catalysis. In every case it will be noted that it is an amphoteric oxide which is capable of exercising this dual function. Hence it appears possible to the writer that in the case of oxides of the amphoteric elements we *do* have two or more forms present, the relative amount of each form being determined by the method of preparation.

It is possible to make a partial test, at least, of Sabatier's hypothesis, by an application of the Phase Rule, and in this investigation such an application has been made.

If, in a system consisting of methyl alcohol and hydrous aluminium oxide, the alcohol forms a compound with the oxide and the properties of this compound are such as to render it a separate phase, we will be dealing with a three-phase, two-component system, a system having one degree of freedom. If, on the other hand, no compound is formed, or a compound which dissolves in the alumina to form a single phase, then we will have a two-phase, two-component system and two degrees of freedom. The methods used in distinguishing between these two types of system are discussed in the following paragraphs.

*Type A.* Assume a system such as $C_nH_{2n}AlO_2+HAlO_2$ (in which the compound $C_nH_{2n}AlO_2$ constitutes a separate phase), in an atmosphere of an inert gas, such as nitrogen,[4] and assume the total pressure on the system to be 760 mm. In such a system, at any definite temperature, there will be a certain equilibrium concentration of $C_nH_{2n}AlO_2+HAlO_2$ and $C_nH_{2n}$. If the temperature be raised, more $C_nH_{2n}AlO_2$ will dissociate, with the formation of $HAlO_2$ and $C_nH_{2n}$, and the pressure in the system will tend to increase, but up to a certain temperature the total pressure in the system can be held at 760 mm. (the initially chosen value) by allowing the $C_nH_{2n}$ and the nitrogen to expand, and more $C_nH_{2n}AlO_2$ to dissociate, since by this means the partial pressure of $C_nH_{2n}$ in the gas phase can be increased. Ultimately, however, if the temperature is increased sufficiently, the dissociation pressure of the compound $C_nH_{2n}AlO_2$ will become greater than the possible attainable partial pressure of $C_nH_{2n}$ in the gas phase, (in this case 760 mm. will be the limiting

[1] Compt. rend. 180, 213 (1925).
[2] J. Phys. Chem. 30, 167 (1926).
[3] J. Phys. Chem., 30, 167 (1926).
[4] The use of nitrogen introduces another component and another degree of freedom in each case, but the method of distinguishing between the two types of system is still valid. The second system still has one more degree of freedom than the first.

value) and dissociation will then continue as long as any of the $C_nH_{2n}AlO_2$ phase remains. In this type of system the vapor pressure is *not* a function of the concentration.

*Type B.* Assume a system similar in all respects to that described under Type A, except that the alcohol either does not react to form a compound, or if it does form a compound, the latter does not exist as separate phase. In this case it will be possible to maintain an equilibrium at any chosen pressure and temperature, merely by allowing the products of the dissociation

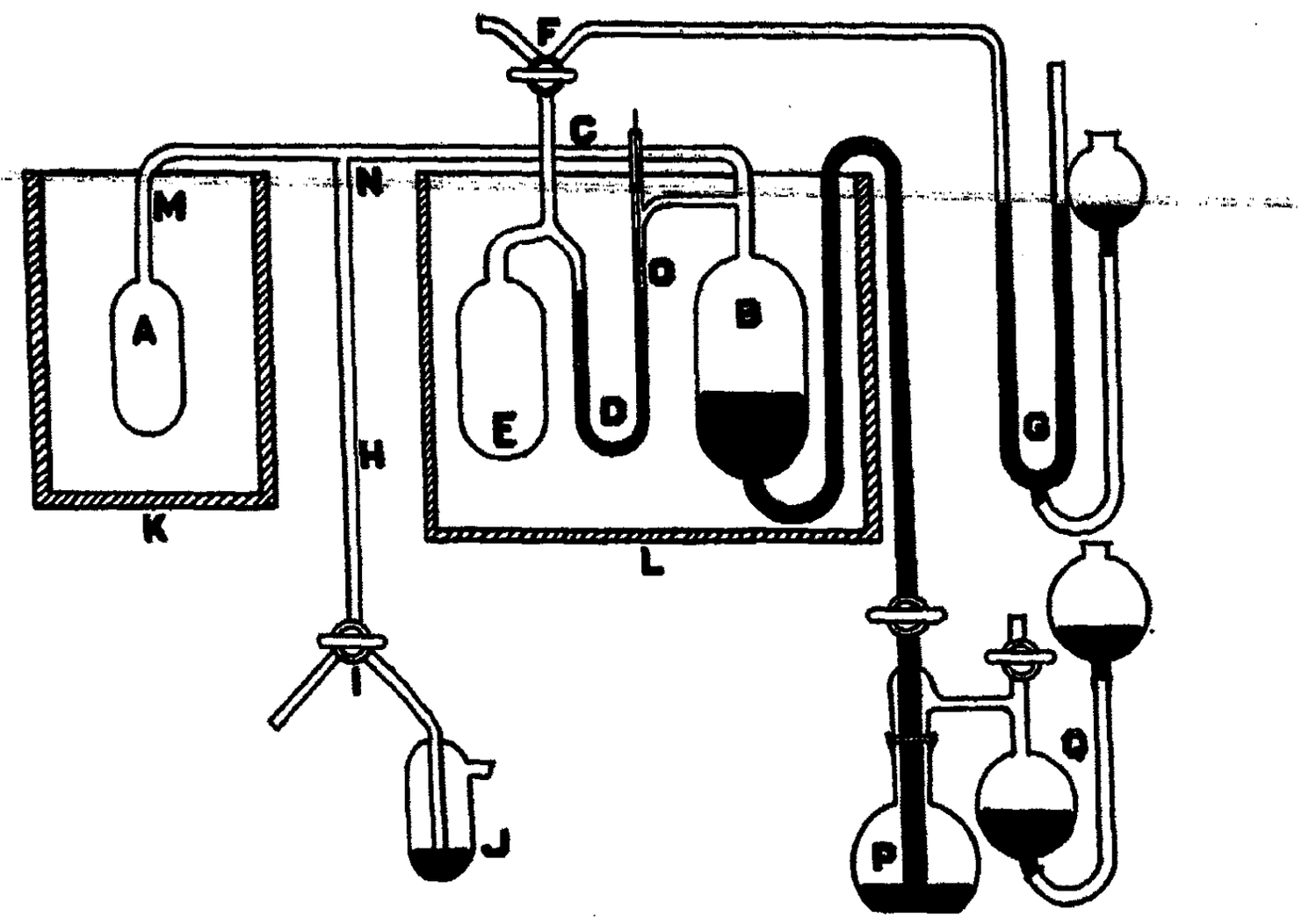



FIG. 1

to expand, by increasing the volume of the system. In other words, with this type of system there is no temperature at which dissociation is continuous. In this case the dissociation pressure *is* a function of the concentration.

## Experimental

The methyl alcohol used in this work was supplied by a large manufacturer of dimethyl aniline. It gave negative tests for aldehydes and ketones and boiled 64.40°-64.55°C. at 747 mm. (Bureau of Standards certified thermometer). It was dried in the usual manner over calcium oxide. The alumina catalysts were prepared according to the directions of Sabatier, by precipitating a solution of C. P. aluminium nitrate with a slight excess of ammonium hydroxide, washing thoroughly and drying at 300°C. The dried material was ground and screened and the particles passing a U. S. Standard screen

No. 8, and retained on a No. 16, were employed in this work. This catalytic material contained about 15% water, determined by ignition at 1000°C.

The nitrogen was prepared in the usual manner from sodium nitrite and ammonium chloride. Carbon dioxide and oxides of nitrogen were removed by sodium hydroxide, and oxygen by hot copper. It was washed with water and finally dried over phosphorous pentoxide.

The apparatus used in this study is shown in Fig. 1. It consisted essentially of a bulb "A", communicating through a capillary "C" with a weighing burette "B". The burette communicated with a small mannometer "D" and the other leg of this manometer opened into a compensating bulb "E". The latter could be connected to vacuum or pressure, or to the large constant volume manometer "G", by means of the stop-cock "F". The vertical capillary tube "H" communicated, through the three-way cock "I", either to vacuum or pressure (through the mercury trap "J") or the supply of nitrogen and methyl alcohol vapor. The baths "K" and "L" were electrically heated and fitted with automatic temperature controls. "K" was a bath of potassium acid phosphate and phosphoric acid and could be maintained at any temperature desired between 180° and 400°C. "L" was a glycerine bath and was kept at 100°C. Only about 10 cm. of the communicating capillary "C" was not immersed in either bath and this part was lagged with asbestos string.

## Method of Manipulation

The bulb "A" was filled with a sample of the catalyst and sealed to the communicating capillary "C" at some point such as "M". Bath "K" was then brought into position and maintained at 180°C. Bath "L" was brought to 100°C. and the whole system evacuated through cocks "F" and "I" until the pressure fell to a few mm. The mixture of methyl alcohol vapor and the nitrogen (the nitrogen was saturated with methyl alcohol at 25°C) was then introduced through "I" until the pressure in the system was about 10 cm. less than atmospheric, air being introduced simultaneously through "F," to maintain the pressure on both sides of the mannometer "D", approximately the same. Cock "I" was now cautiously turned to communicate with the mercury trap "J", which was open to atmospheric pressure, and mercury allowed to flow up into the capillary "H", until the point "N" was reached. Stop-cock "I" was then shut off, the column of mercury in "H" effectively sealing it. The pressure in the system was now adjusted[1] (by means of the burette "B", the weighing bottle "P" and leveling bulb "Q") to some definite value, by the indicating point shown at "O".

Several weighings of the mercury and weighing bottle were made and the average recorded. The temperature was increased by increments of approximately 20°C. Time was given for the attainment of temperature equilibrium at the end of each increment, and several weighings of the weighing

[1] For a detailed description of the method of operation of this type of burette, see J. Phys. Chem. **28**, 1082-1095 (1924).

bottle were made at definite time intervals. Data, typical of many measurements are presented in Fig. 2 in the form of a curve. Temperatures of the catalyst bulb are plotted as ordinates and weights of the weighing bottle as abscissa. The weights of the weighing bottle, or rather the changes in weight of the weighing bottle, are evidently inversely proportional to the changes in the amount of vapor in the bulb containing the catalyst and, because of the high density of mercury, very precise measurements of volume changes in the catalyst bulb could readily be made. The time interval between readings was approximately fifteen minutes.[1]

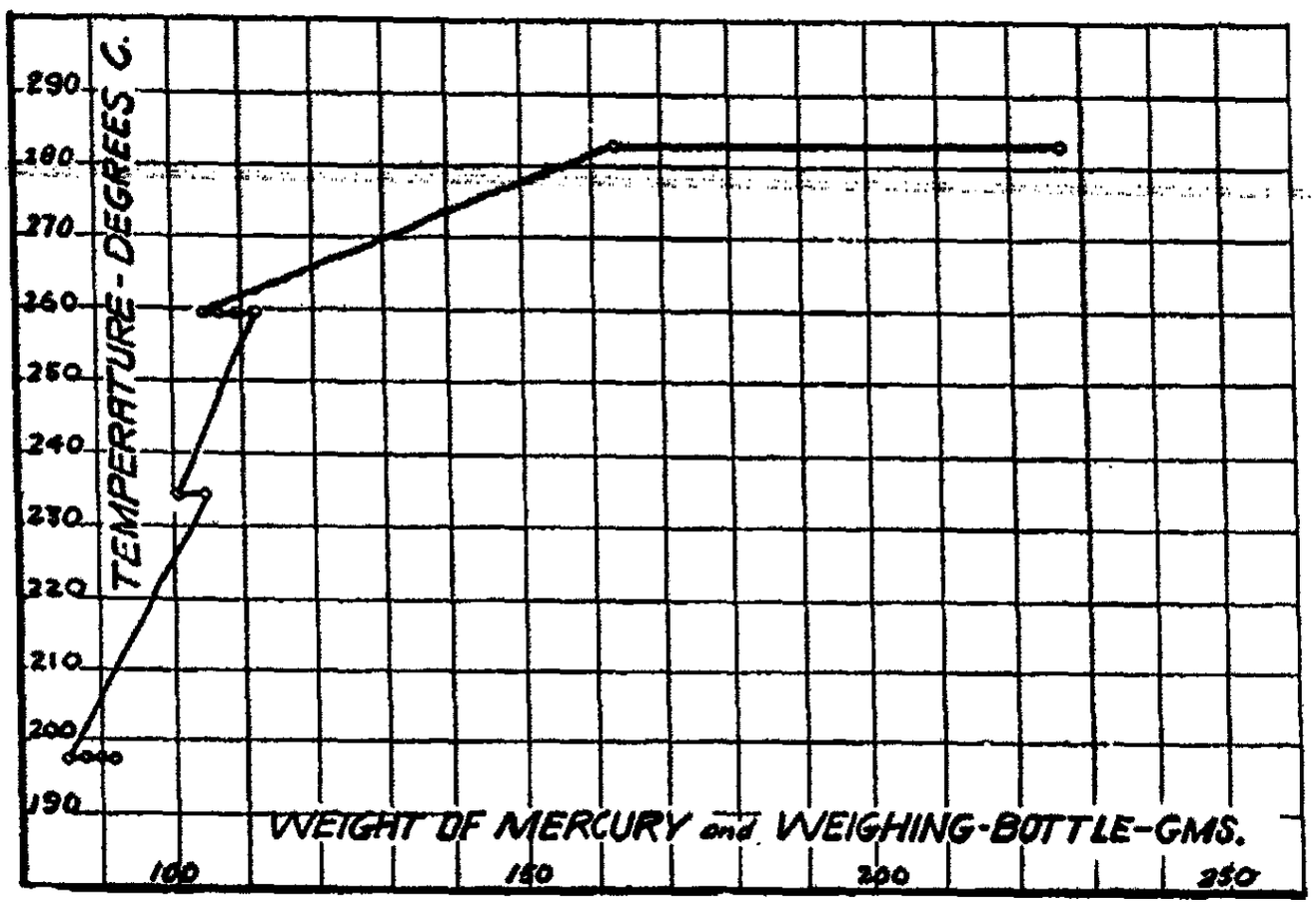



FIG. 2

At first sight it appears that this curve meets the requirements set forth under Type "A" very exactly, that is, there is a certain temperature range over which the arbitrarily chosen pressure can be maintained, merely by allowing the gas phase to expand into the burette "B", and ultimately a temperature is reached at which dissociation *appears* to be continuous A more careful analysis indicates, however, that this is a faulty conclusion. The actual change in volume over the 15 minute period at the temperature of 283°C. is approximately 0.480 cc. (the volume of 60 gm. of mercury at 100 C.). It is evident that this much vapor could evaporate from the catalyst without changing appreciably the concentration of the methyl alcohol in the alumina. That is, a flat portion to such a curve, corresponding to such a relatively

[1] An interesting feature of this curve is the evidence of "drift," or slow penetration of the gas phase into the catalyst, at the lower temperature. This "drift" is of about the same magnitude whether the gas phase is pure nitrogen or a mixture of nitrogen and methyl alcohol vapor. Thus it is evidently not specific in nature.

small evolution of vapor, is not conclusive evidence that we have to deal with the dissociation of a separate phase of constant composition. That this latter is the correct conclusion was indicated by later experiments in which the temperature at which dissociation *appeared* to be continuous was maintained constant over a period of several hours, when a very gradual, but distinct decrease in the *rate* of vapor evolution was observed. In order to fix this point still more definitely, however, the following experiment was carried out. The catalyst and the communicating system were evacuated at 250°C until the pressure fell to a few mm. The mixture of methanol and

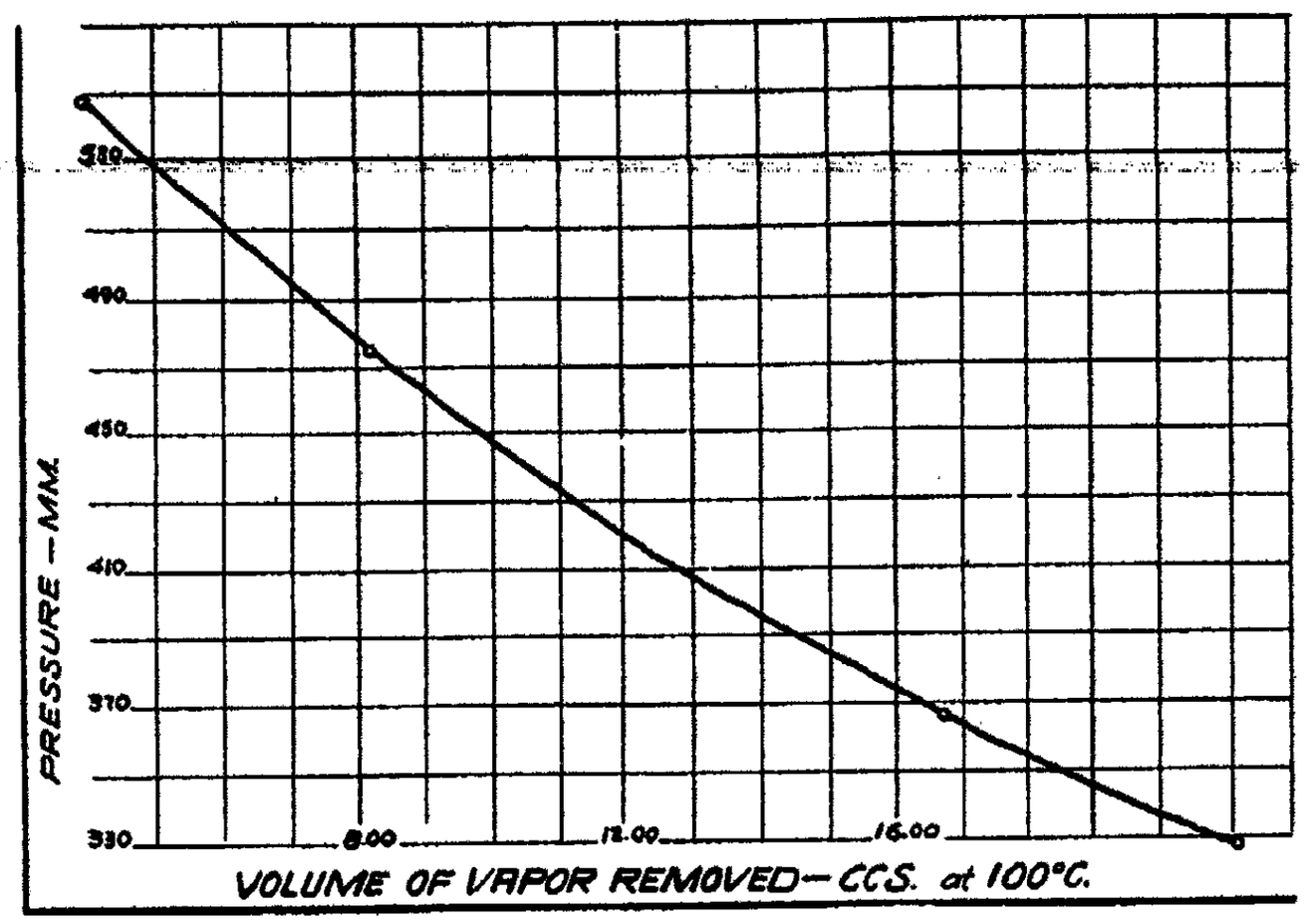



FIG. 3

nitrogen was then admitted until a pressure of about 550 mm. was reached. The pressure remained approximately constant at this value for about thirty minutes. Now, with the temperature constant, vapor was removed from the catalyst bulb by allowing mercury to flow out of the burette "B". The effect of this withdrawal of vapor, upon the pressure in the system, is shown in Fig. 3. It is evident from this experiment that the pressure in the system falls steadily, if any appreciable quantity of vapor is withdrawn, that is, the vapor pressure of the system *is* a function of the concentration of the methyl alcohol vapor. This system then evidently falls in the class of those described under "B" and hence we can state definitely that no compound, constituting a separate phase, is formed. Compound formation with subsequent solution in the catalyst (as in the case of the Williamson Reaction) is, of course, not excluded.

In order to learn the behavior of an alumina catalyst in the presence of an inert gas alone, experiments were carried out similar in every way to those already described, except that the catalyst bulb was filled with catalyst and dry nitrogen only. To our surprise, in all cases exactly the same type of curve was obtained as that shown in Fig. 2. At first this was thought to be due to traces of $CH_3OH$ or water remaining in the catalyst from previous experiments, so that a fresh sample of catalytic material was prepared, placed in a new bulb and sealed into position. Again, however, exactly the same type of curve was obtained. It was now observed that if several successive measurements, using dry nitrogen, and with intervening evacuation, were made upon

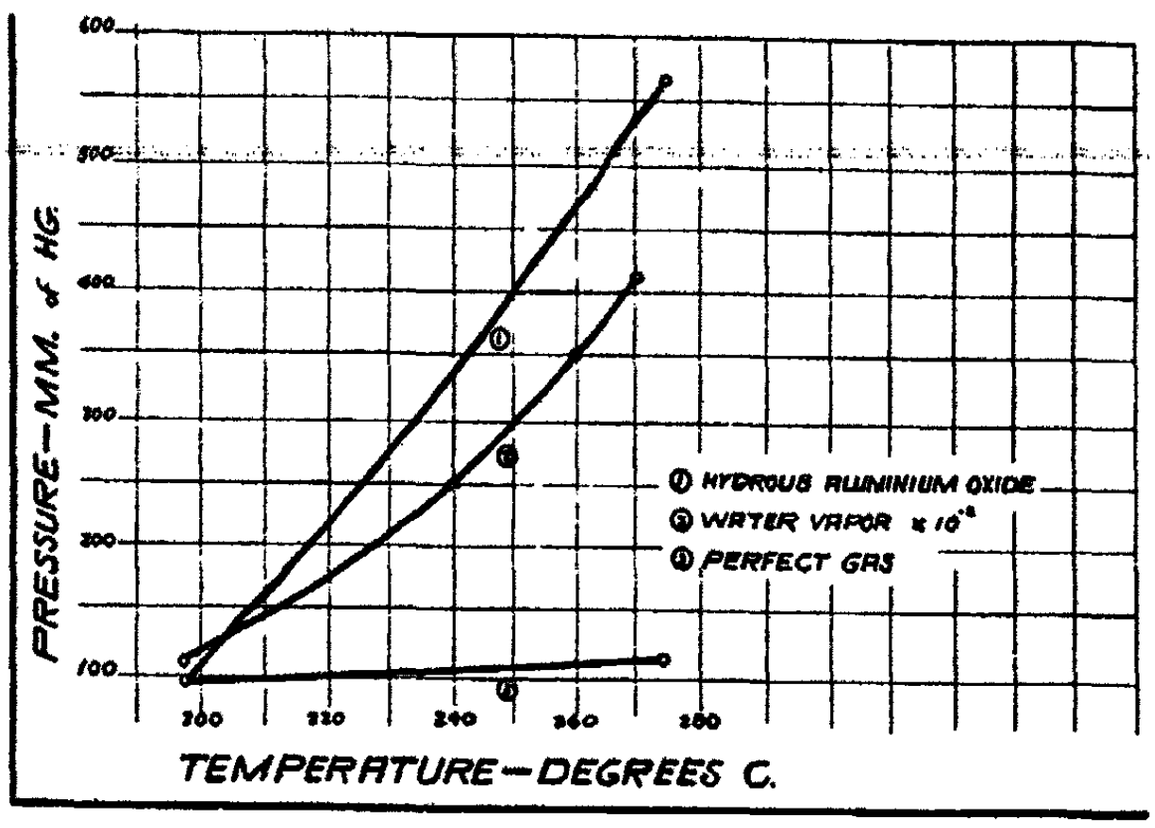



FIG. 4

the same sample of catalyst, that the temperature required to bring about rapid dissociation (indicated by the flat portion of the curve) became higher and higher. In many cases samples after having had vapor pressure measurements made upon them, were tested, qualitatively, for catalytic activity, and it was always observed that the catalysts showing a high "break" temperature were those requiring a high temperature to initiate the catalytic dehydration of methyl alcohol.

The catalytic dehydration of methyl alcohol, like many other catalytic reactions is markedly affected by rather small temperature changes. Qualitative determinations with our catalytic material indicated that below 200° the reaction is very slow, while at 250° to 275° it becomes very rapid. It was thought probable that this was due to a considerable variation, with temperature, of the vapor pressure of this aluminium oxide-water complex. To test this point the following experiment was carried out. The sample was evacuated at 197°C. until the pressure in the system had fallen to 9 mm. Water

vapor was now admitted until the pressure reached 98 mm. The supply of water vapor was shut off and the temperature raised to 275° C. In 27 minutes the pressure had risen to 420 mm., and at the end of 40 minutes the pressure was 568 mm., where it remained approximately constant for the next thirty minutes. The extraordinarily steep slope of the vapor pressure curve of this hydrous aluminium oxide catalyst is evident when comparison is made, as in Fig. 4, with the corresponding curve for water over the same temperature range. These data show the enormous effect of temperature on the vapor pressure of an alumina catalyst, and indicate that the temperature of catalysis is determined by the vapor pressure of this complex; when a temperature is reached such that the vapor-pressure of the complex is sufficiently great so that water can evaporate from the catalyst as fast as it is formed in the reaction, we have catalysis.

These experiments indicate that the catalytic dehydration of an alcohol over alumina takes place in some way through a water-aluminium oxide complex. Whether this be $Al(OH)_3$, or $HAlO_2$, a solid solution of water in $Al_2O_3$, or adsorbed water, it is impossible to say from the present data. Whatever it may be, it can be stated definitely that this complex does not constitute a separate phase.

It also appears probable that the sensitiveness to heat treatment shown by alumina catalysts, is not due, primarily, to sintering and consequent decrease of surface (change in degree of unsaturation or change in spacing) but to destruction of this complex.

It is proposed to study further the properties of alumina catalysts and to determine, if possible, the nature of this $Al_2O_3H_2O$ complex, which appears to be so essential for dehydration catalysis. In some cases alumina catalysts prepared from aluminates have been reported to be superior to those prepared in any other way. This indicates that there may be a real difference in structure between $Al(OH)_3$ prepared by precipitation by an alkali from an aluminium salt, and that produced by the acidification, or hydrolysis, of an aluminate. It seems certain at least that very different impurities would be present in the catalyst depending upon the method of preparation used.

## Summary

(1) By an application of the Phase Rule to a system containing hydrous aluminium oxide and methyl alcohol, it has been shown that over the temperature range at which the oxide functions as a catalyst, no compound between the alcohol and the oxide, constituting a separate phase, is formed. The possibility of formation of a compound, with subsequent solution in the catalyst is not excluded. Hence a mechanism such as that suggested by Sabatier, analogous to the Williamson reaction, is possible.

(2) A close relation has been found between the temperature at which the evolution of water vapor from a sample of hydrous aluminium oxide be-

comes rapid, and the temperature at which catalytic dehydration of alcohol takes place over such an oxide. This relation shows the intimate connection between the presence of water in the oxide before catalysis and the process of catalysis.

(3) The magnitude of the variation of the vapor pressure of a hydrous aluminium oxide catalyst with temperature, has been determined, and the relation between this quantity, and the effect of temperature on the catalytic dehydration of an alcohol over such a catalyst has been pointed out.

*Columbia, Missouri*
*March 24, 1926.*

# THE TERNARY SYSTEM: SILVER BROMIDE—POTASSIUM BROMIDE—WATER*

BY RAYMOND H. LAMBERT

Some idea of the solubility relation in a ternary system can be obtained from a study of the three pairs of binary systems, provided the data for the binary systems are available.[1] In the system instanced in the title such is the case and since the binary systems are very simple, it is possible to develop the entire surface between solid and liquid phases with only a very little extra data.

From the data in the literature[2], [3] the systems may be arranged as in Fig. 1. The dotted portions of the diagram indicate imaginary boundaries not existing at atmospheric pressure but real and nearly identical at sufficiently high pressures. An examination of the three pairs of binary mixtures leads to some interesting conclusions in regard to the ternary system.

At least two of the three pairs of binary mixtures i.e., systems, KBr-$H_2O$, KBr-AgBr, show distinct eutectic points, the former at 6.6 molar percentages of potassium bromide and the latter at 44 molar percentages potassium bromide. If in a ternary system each pair of binary systems contain only a single eutectic mixture, the phase diagram is very simple. For a non-variant system both temperature and concentration are fixed, this temperature being lower than for any other equilibrium mixture. At this point the liquid phase will be in equilibrium with three solid phases of the pure components.

Compound formation obviously makes the diagram more complex. Hellwig concluded that no compound or double salt between silver bromide and potassium bromide is found to exist in precipitates from water solution.[4] Reference will be made to this later in the paper. There is also no evidence of hydrates between either salt and water although many alkali halides do combine with water.

In this ternary system, the phase diagram may be even further simplified since any eutectic in the binary system, AgBr-$H_2O$, lies so very near the axis of the pure water component that it has never been detected. In any case it can be assumed to lie on the pure water axis. The lowest temperature at which equilibrium will exist between solid and liquid will then be at one of the other two binary eutectics, in this case, the KBr-$H_2O$ eutectic at $-13$°C and 6.6 molar percentages of potassium bromide.

From this assumption, one may proceed further and predict a eutectic valley leading from the AgBr-KBr side of the triangular diagram, figure 1, to the KBr-$H_2O$ side exists. This valley should be a smooth path, which on a four dimensional system, temperature being represented by height, falls in

---

* Communication No. 273 from Research Laboratory, Eastman Kodak Company.

[1] Roozeboom: "Die heterogene Gleichgewichte," 3 I.

[2] System KBr-AgBr. C. Sandonnini: Atti Accad. Lincei, 21 II, 197 (1912).

[3] Systems KBr-$H_2O$ and AgBr-$H_2O$. Landolt-Börnstein Tabellen.

[4] Karl Hellwig: Z. anorg. Chem., 25, 182 (1900).

temperature and composition from 290°C and 56 molar percentages of silver bromide and no water, the eutectic point of system, KBr-AgBr, at a continuous rate down to −13°C and zero silver bromide, the eutectic point of system, KBr-$H_2O$. For two salts in equilibrium with water, if one is extremely insoluble compared with the other, as is true with silver bromide and potassium bromide, the valley will be concave to the axis (in the triangular diagram) of the comparatively insoluble component i.e., AgBr-$H_2O$, and convex to the KBr-$H_2O$ axis. One would expect that the degree of curvature in the eutectic valley would be greater for a pair of salts whose difference in solubility, when alone in water, is greater and that for two salts equally soluble in water, the eutectic valley would approximate to a straight line in the composition diagram.

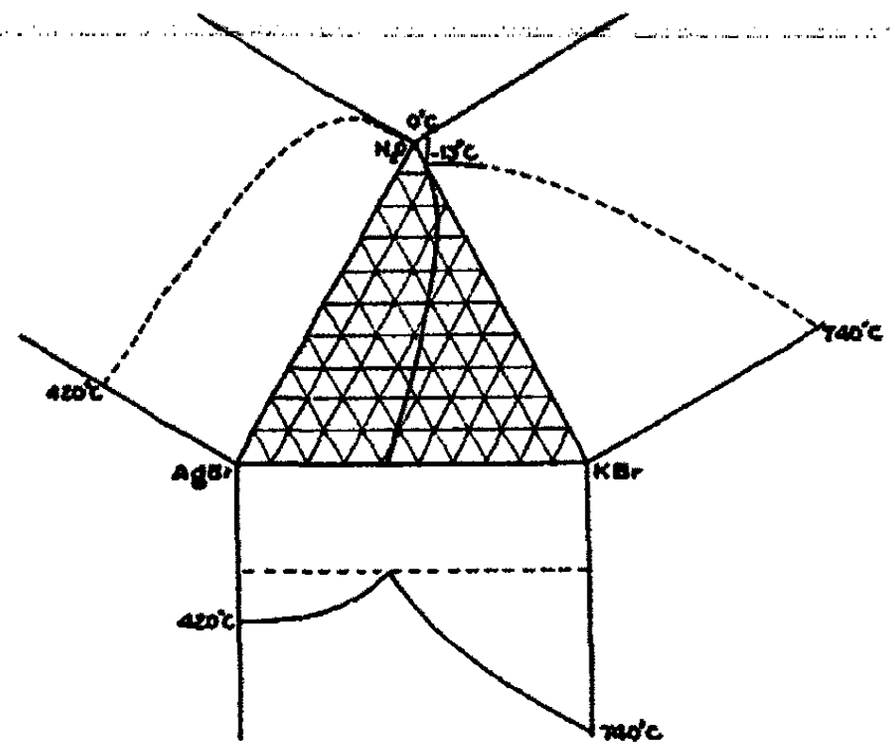



FIG. 1

Since interest lies mainly in the eutectic valley at temperatures of low vapor pressure of water, a study was made only of the solubility of silver bromide and potassium bromide co-existent in water solution in the presence of both solid salts with change of temperature up to 100°C. The method used was that suggested by Fritz Feigl[1] whereby the solution in equilibrium with solid silver bromide and potassium bromide was filtered into a porous cup which was also used as a stirrer in order to bring the system more quickly to equilibrium.

Fig. 2 is a diagrammatic sketch of the apparatus. An ordinary liquid thermostat was used. A red dye soluble in oil was added to the bath to prevent light decomposition of the silver bromide. The layer of oil prevented excessive evaporation of water from the bath at the higher temperatures. Equilibrium was obtained in about 24 hours, due to efficient stirring, after which portions of the solution were drawn off by means of a pipette which

[1] Fritz Feigl: Z. angew. Chem., **31**, 168 (1918).

several hours before sampling had been placed in the hollow glass tube to which the porous cup was fastened. This brought the pipette to the same temperature as the bath. The special pipette made of thick walled glass tubing had a very short stem so that the liquid did not leave the porous cup until the pipette was ready to be drawn entirely from the bath.

The liquid was quickly placed in tared weighing bottles and even at the highest temperatures employed little error was caused by sampling. The porous cup was alundum having the desired porosity for filtration. It was chosen from about a dozen cups.

Chemically pure potassium bromide and silver bromide were three times recrystallized together at 100°C from water solution. Samples were removed from the apparatus at ten degree intervals for increasing temperatures and at twenty degree intervals on the decreasing scale. In the latter experiments, the porous cup was not inserted until the lower temperature had been established for some time.

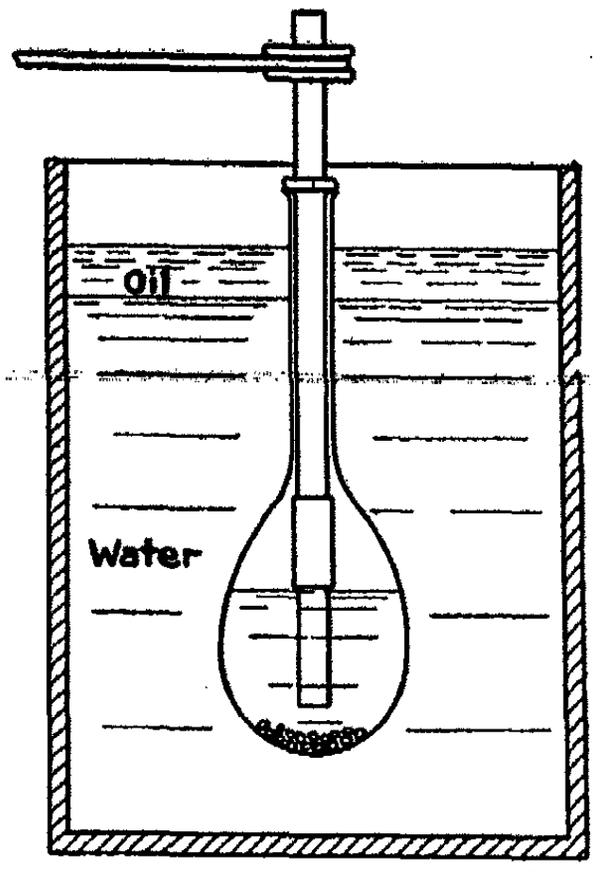



FIG. 2

TABLE I

| Temperature | Per cent by Weight AgBr | KBr | $H_2O$ | Per cent by Mol. AgBr | KBr | $H_2O$ | Ratio KBr/AgBr |
|---|---|---|---|---|---|---|---|
| −13 | 0 | — | — | 0 | 6.71 | 93.29 | ∞ |
| | 1.67 | 39.87 | 58.50 | 0.250 | 9.33 | 90.4 | 37.32 |
| 30 | 1.636 | 39.54 | 58.82 | 0.242 | 9.21 | 90.54 | 38.06 |
| 40 | 2.24 | 40.88 | 56.88 | 0.339 | 9.77 | 89.88 | 28.75 |
| | 3.25 | 43.09 | 53.66 | 0.515 | 10.78 | 88.70 | 20.93 |
| 50 | 3.12 | 42.43 | 54.45 | 0.489 | 10.50 | 89.01 | 21.47 |
| 60 | 4.20 | 44.24 | 51.56 | 0.685 | 11.42 | 87.90 | 16.67 |
| | 5.80 | 45.48 | 48.72 | 0.990 | 12.26 | 86.75 | 12.38 |
| 70 | 5.60 | 45.53 | 48.87 | 0.954 | 12.24 | 86.80 | 12.83 |
| 80 | 6.72 | 46.91 | 46.38 | 1.192 | 13.12 | 85.69 | 11.01 |
| | 8.47 | 48.15 | 43.39 | 1.580 | 14.16 | 84.26 | 8.96 |
| 90 | 9.00 | 47.98 | 43.115 | 1.687 | 14.20 | 84.11 | 8.42 |
| 100.0 | 10.55 | 48.66 | 40.79 | 2.080 | 14.98 | 82.96 | 7.27 |

Table I contains the data both in weight and molar percentages. In Fig. 3 are plotted the weight percentages of potassium bromide and silver bromide with temperature as the abscissa. The upper curve is that for the solubility of potassium bromide alone in water, the data being taken from Landolt and Börnstein's Tabellen. It is interesting to note that 10.5 per cent by weight of silver bromide dissolves in a potassium bromide solution in equilibrium with solid potassium bromide at 100°C.

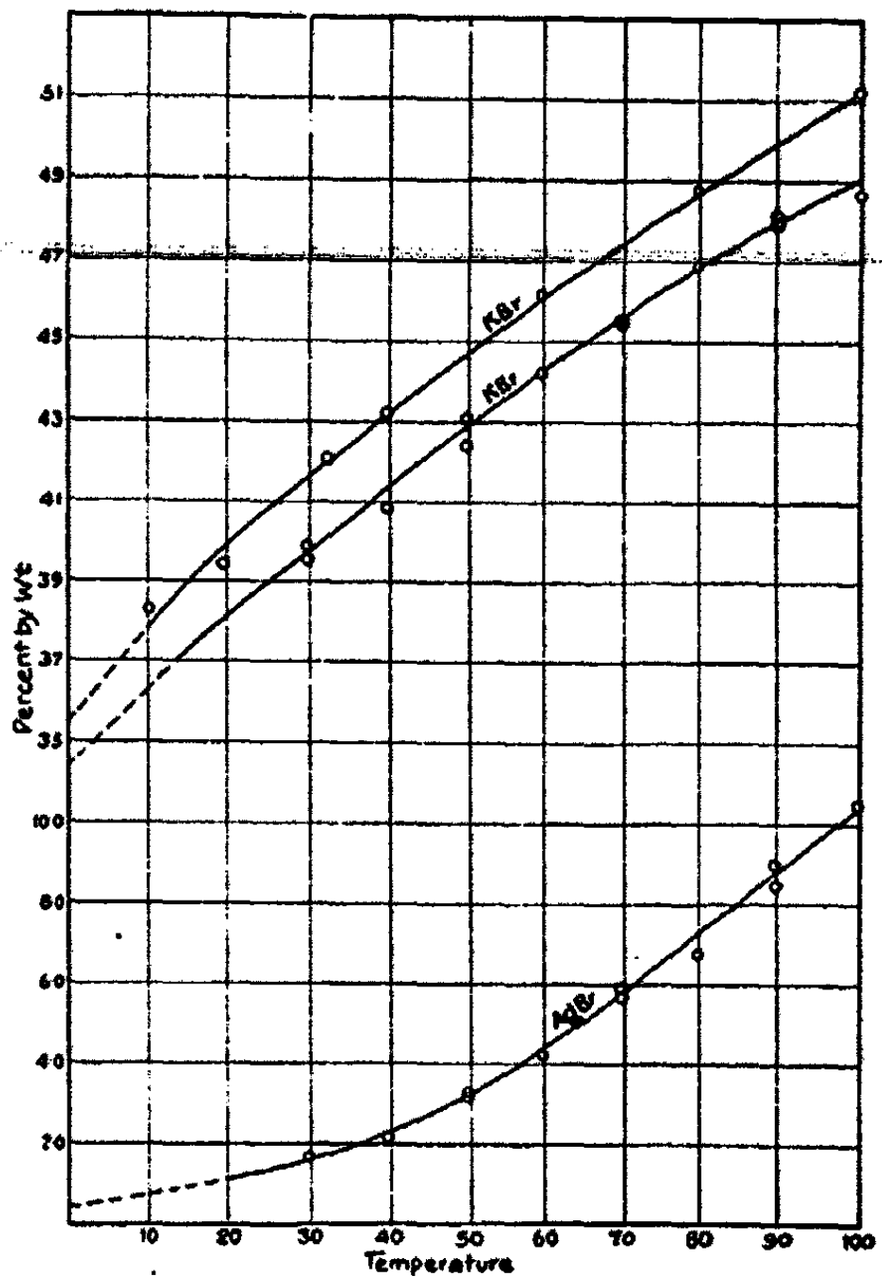



FIG. 3

The ratio of potassium bromide to silver bromide is of interest since at 290°C, Sandonnini gives the eutectic of the system, KBr-AgBr as 56 molar percentages of silver bromide. Figure 4 shows the ratio varying with temperature. The upper end of the curve should be asymptotic to the Y-axis at $-13$°C

If the eutectic valley be projected on a plane for the ternary system, the result is that shown in figure 5. Horizontal lines measure molar percentages of silver bromide with zero silver bromide on the base line. Molar percentages of potassium bromide are lines parallel to the line on which molar percentages of potassium bromide is written. The third series of lines obviously corresponds to molar percentages of water. Here check points lie on a smooth curve but

are not together. This would indicate an error in temperature reading. Extrapolation of the curve ends at the eutectic point of the binary mixture, KBr–$H_2O$, as was to be expected.

Figure 6 is an expression of the ternary system including temperature relations. The photograph is that of a plastic model and was taken expressly to show the eutectic valley. As previously stated, the system is only stable

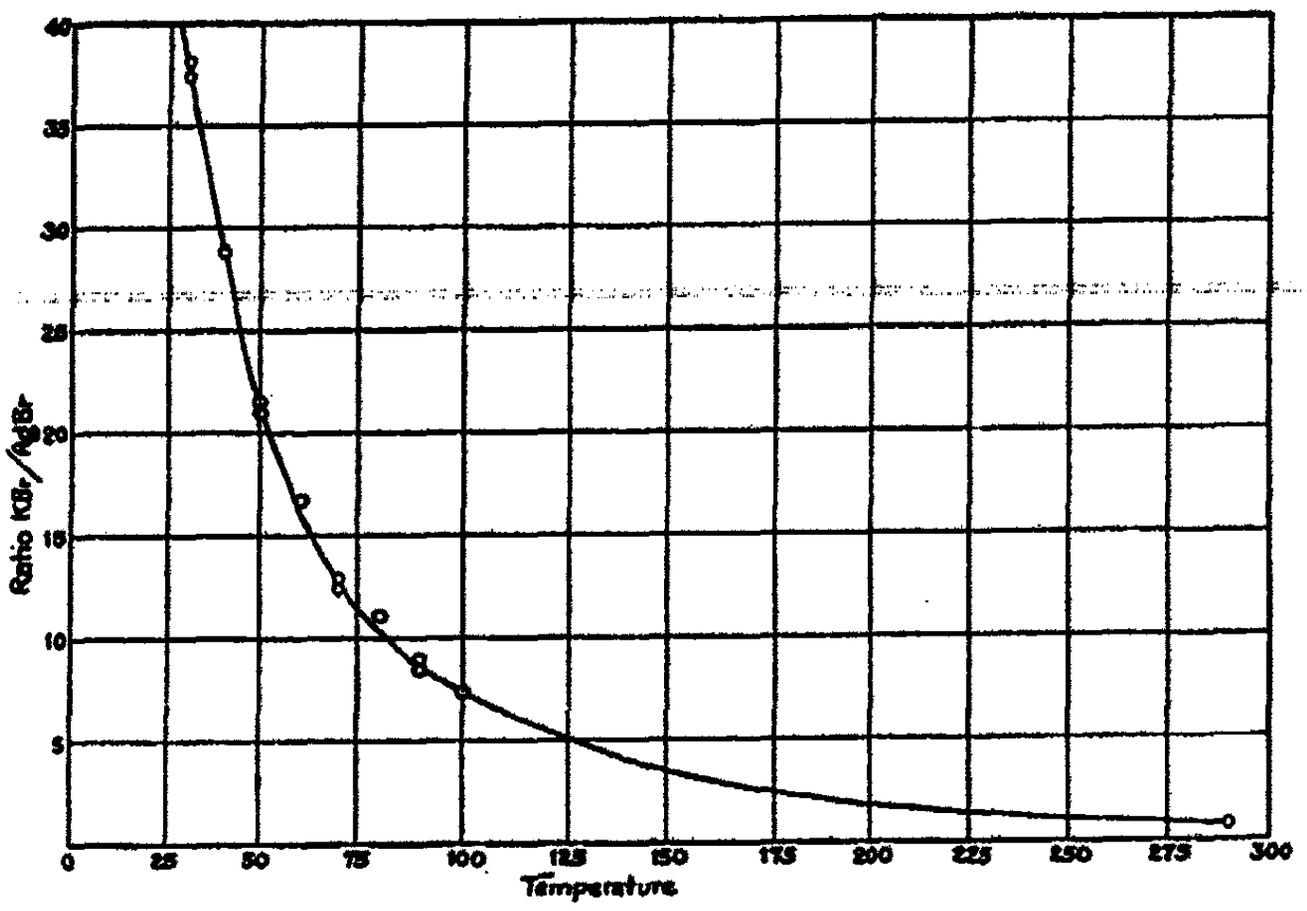



FIG. 4

for pressures greater than atmospheric since water should boil away at the high temperatures. Below 100°C, however, the model expresses actual facts.

The bend in the curve is convex to the KBr-$H_2O$ axis of the diagram as previously predicted would be the case. In order, however, to test the assertion that the curvature of the eutectic valley is greater for salts having a greater difference in solubility, an experiment was carried out with silver chloride and potassium chloride. Silver chloride is comparatively only slightly less soluble than silver bromide and therefore should not affect the

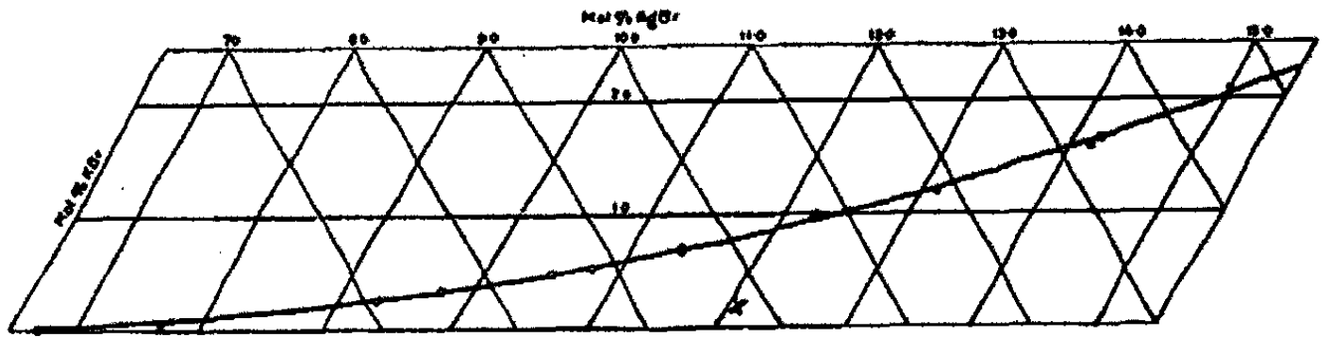


FIG. 5

shape of the eutectic valley greatly. Potassium chloride, however, is relatively much less soluble than potassium bromide and therefore this pair of salts should affect the shape of the valley greatly. Only one sample of the KCl-AgCl solution was taken and that at 90°C. Another point could be taken from Comey's tables. At 90°C the following mixture was found; 0.19 molar percentages silver chloride, 12.08 molar percentages potassium chloride and 87.73 molar percentages water. At 15°C the following results are recorded;[1]

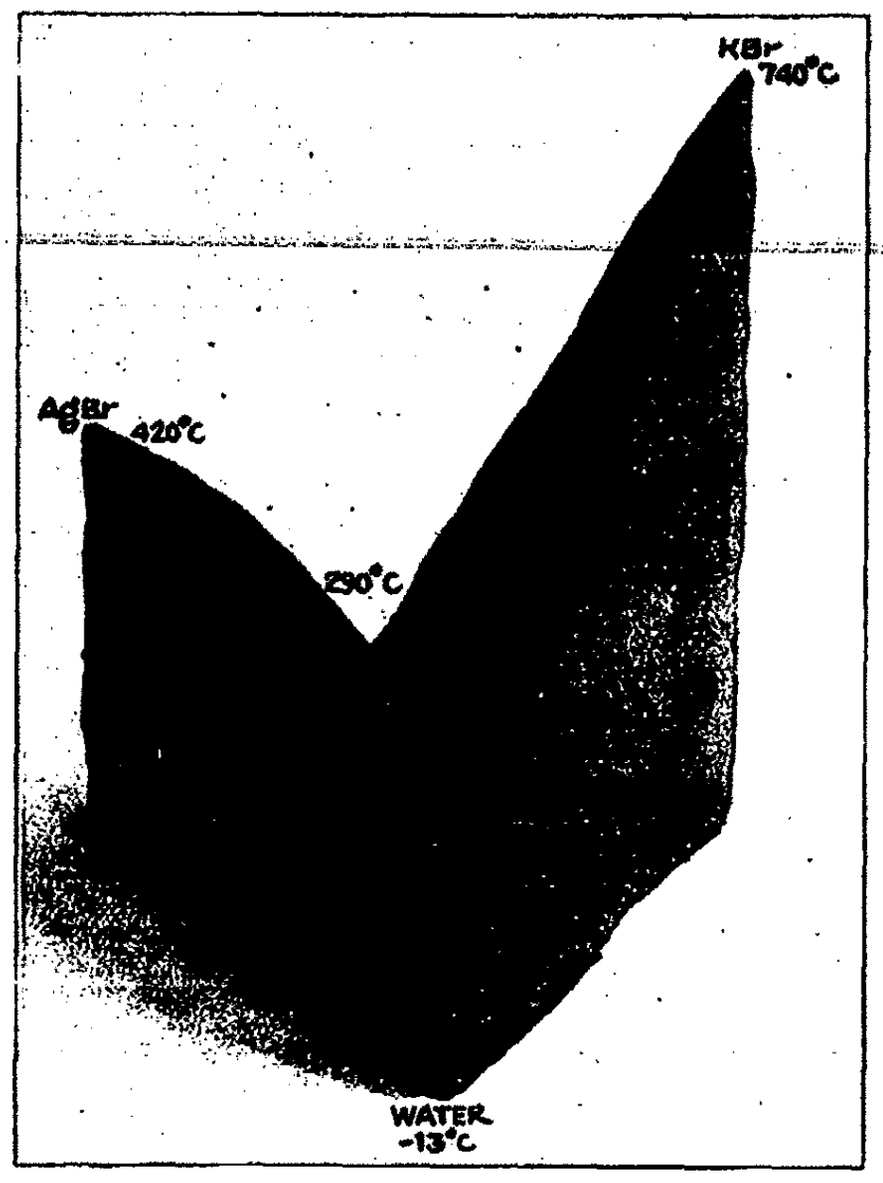



FIG. 6

0.013 molar percentages silver chloride, 7.53 molar percentages potassium chloride and 92.45 molar percentages water. These two results are shown in figure 5. The crosses are data on chlorides. The eutectic for AgCl-KCl[2] is at 70 molar percentages silver chloride and 309°C while for system, KCl-$H_2O$, it is at 5.6 molar percentages of potassium chloride and −11.1°C. The curve for the eutectic valley in the system, KCl-AgCl-$H_2O$ projected on a plane, as in figure 1, must cross that of KBr-AgBr-$H_2O$ in two places and since the curvature of the former is greater than that of the latter system, the differences

[1] K. Schierholz: Akad. Wiss. Wien, 101 IIb, 8 (1890).
[2] S. F. Shemtshuskny: J. Russ. Phys. Chem. 7, 1052-53 (1906).

in relative solubilities is not the only factor of degree of curvature. If it were the only cause, then silver chloride should be more soluble in saturated potassium chloride than silver bromide in saturated potassium bromide at any temperature.

Some predictions can be made of solubility of silver bromide in saturated lithium bromide and sodium bromide. Lithium and sodium bromide[1] form mixed crystals with silver bromide in all proportions. In both cases, however, the alkali salts form water of crystallization, thus complicating the phase diagram at low temperatures. No very distinct eutectic can exist in the ternary system with both salts present in the solid phase and therefore no constant ratio of salts exist in solution at a given temperature as shown in the system, KBr-AgBr-$H_2O$ in Fig. 4.

In order to ascertain more definitely that no compound existed between potassium and silver bromides from precipitates, powder x-ray diffraction photographs were made of the eutectic mixtures of fused silver and potassium bromides and of precipitates from saturated solutions of both salts from 100°C to 75°C, 75°C to 50°C and from 50°C to 25°C. These photographs show only the diffraction pattern of pure components, thus verifying the statement of Hellwig's previously referred to.

The author wishes to express his thanks to Mr. R. B. Wilsey for the x-ray examination of the various mixtures and to Dr. S. E. Sheppard for advice and criticism.

*Rochester, N. Y.*
*April, 7 1926.*

[1] A. Sandonnini and G. Scarpa: Atti Accad. Lincei, 22 II, 519-520 (1913).

16-85

# THE POTENTIAL OF THE IRON ELECTRODE*

BY W. H. HAMPTON

The standard electrode potentials have been accurately determined for most of the common metals from electrodes possessing a high degree of constancy and reproducibility. However, one of the greatest difficulties met in potential measurements has been to obtain such an electrode from a form of iron that will represent the most stable state of this metal and which can be used in a reversible cell. There is described in this paper a series of electrodes and equilibrium measurements from which a value has been determined for the standard electrode potential of iron. This value can hardly be in error by more than a few millivolts and is much more accurate than anything published heretofore.

There has been only a small amount of work published dealing with a direct study of the electrode potential of iron, although much discussion occurs in the literature regarding the phenomena that are observed when this metal is involved in electrolytic processes. The most important work connected with the potential measurements is that of Richards and Behr,[1] who studied the e. m. f. of the cell, $Fe|FeSO_4(0.5M), KCl(0.1M), HgCl|Hg$. They used various kinds of iron and their results varied several hundredths of a volt, depending both upon the kind of iron and its previous treatment. By the use of finely divided reduced iron, constancy was obtained within about one centivolt, but because of the large liquid potential involved and because of the unknown activity of the $Fe^{++}$ ion in such a concentrated solution, it is impossible to calculate from these measurements a value for the standard electrode potential.

## Experimental Part

The cells used in the following experiments consisted of the elements $Fe|FeCl_2$ (0.1M), $HgCl|Hg$ and contained no liquid junction. Various concentrations of ferrous chloride were employed, but, for the most part, the measurements were made in one-tenth molal solutions and, unless otherwise stated, this will be the concentration referred to.

To prevent oxidation, an H-cell was used, which could be filled and kept free from air as much as possible. The two half-cells were provided with a glass stop-cock between them. The procedure in filling was to add about an inch of mercury to the calomel side and then evacuate this portion. Ferrous chloride solution saturated with calomel together with calomel paste was added by simply letting the vacuum draw in these materials. The other half of the cell was filled under an atmosphere of hydrogen and then stoppered to exclude the air. Complete connection was now made by opening the stop-cock between the two cells.

---

*Contribution from the Chemical Laboratory of the University of California.

[1] Carnegie Inst. Pub., No. 61.

Standardized ferrous chloride solutions were prepared by dissolving powdered iron in hydrochloric acid following a similar procedure to that used by Richard and Behr in preparing their ferrous sulfate solutions. For the metal electrodes, three different varieties of iron were tried, an iron amalgam, finely divided iron and ordinary annealed iron.

*Iron Amalgam:* Measurements were made on amalgams which were prepared by electrolyzing a solution of ferrous sulfate, a method which was first discovered by Joule.[1] As iron is but very slightly soluble in mercury, it deposits as a suspended solid phase completely taken up and wetted by the mercury. Amalgam mixtures can thus be obtained varying in structure from liquid to almost completely solid in form, depending upon the amount of iron present. The iron in the solid phase is very finely divided as it gives no granular feeling whatever when rubbed between the fingers. The metal in these amalgams shows its ordinary reactivity, for on exposure to air a black film of oxide will immediately form on the surface of the mixture and, when water is present, rust will appear.

The sample for cell No. 1 was taken from an amalgam containing only a little solid phase in the liquid mercury. Cells No. 2 and No. 3 had for their electrodes amalgams of about the same consistency as soft putty, while the iron-mercury mixture for cell No. 4 was somewhat crumbly in structure.

TABLE I

Electrodes prepared from Iron Amalgams

| | Cell No. 1 | | Cell No. 2 | | Cell No. 3 | | Cell No. 4 |
|---|---|---|---|---|---|---|---|
| Time | Amalgam untouched. | Maximum after stirring. | Amalgam untouched. | Maximum after stirring | Amalgam untouched. | Maximum after stirring. | Amalgam untouched. |
| 0 | .7970 | | .8198 | | .8063 | | .8100 |
| 20 min. | | | | | | | .8147 |
| 2 hrs. | | | | | | | .8101 |
| 1 day | .7880 | | .8185 | | .8074 | | .8063 |
| 2 days | .7682 | .8012 | .8160 | | .7953 | | .8028 |
| 3 days | .7933 | .8100 | .8137 | | .7927 | | |
| 4 days | .8001 | .8106 | .8101 | | .7907 | | |
| 5 days | .7942 | .8105 | .8015 | .8084 | .7890 | .8062 | .7983 |
| 6 days | | | | .8115 | | | |
| 13 days | | | | | | | .7970 |
| 20 days | | | | | | | *.7981 |
| 40 days | | | | | | | .7994 |

*New solution added.

[1] J. Chem. Soc., 16, 378 (1863).

SAMPLE No. 5—cell on which a series of measurements were made at different concentrations

| Concentration | Potential |
|---|---|
| .0095 Molal | .830 Max. Value |
| .050 " | .8278 ± .0005 for period 15 days. |
| .0865 " | .8136 ± .0005 " " 30 " |
| .10 " | .8087 ± .0005 " " 5 " |
| .50 " | .7478 ± .0005 " " 13 " |
| 2.245 " | .6668 ± .0005 " " 6 " |
| 5.03 " | .5760 ± .0005 " " 8 " |

It can be seen that the potential fell continually in all the cells on standing. Such an action results probably from the iron being used up on the surface and on bringing fresh material to the surface layer by stirring a higher potential is again obtained. As would be expected, the e.m.f. does not fall off so rapidly with the more solid amalgams. These cells as a whole, however, show the typical variations of potential measurements of iron which are hard to fully explain. Cell No. 2 and Cell No. 3, for example, were made up to be as nearly alike as possible.

The best explanation of differences encountered above seems to be that based on solubility phenomena. As the mercury completely covers the solid phase, the activity shown must be that of the metal in solution. The surface layer must always be a saturated solution to give the true activity of pure iron. We are confronted both with the possibility of a very slow rate of solution and with the exceedingly small solubility of iron in mercury. There is no means of telling directly whether or not any particular sample has for its surface film a saturated, unsaturated, or, perhaps, a super-saturated solution of iron. However, if all of the possibilities exist, some rough equilibrium should appear from which the potentials of an unsaturated solution would gradually decrease, and those of a super-saturated solution approach that equilibrium arising from the reaction of iron with water. The experiments support this idea somewhat. From these considerations, the best sort of amalgam would be one which had as large a percentage of iron as possible with just sufficient mercury to cover the surface. To obtain this condition, a portion of the material used in cell No. 4 was heated under a vacuum, and the mercury distilled off until the residue began to assume a dark gray color differing markedly from the bright lustre of mercury. This material (sample No. 5) gave one of the best cells for reaching a constant value, and a series of measurements were made in various concentrations of ferrous chloride. The value of .8087 volts for 0.1 molal solution checks that of .8136 volts for .0865 molal solution when the potentials are calculated for the same concentration.

The results for the amalgams in general indicate that the solid phase is not any compound formation of iron with mercury but is a finely divided suspension of the former metal, since the value .8087 volts checks very closely that of iron produced by reducing $Fe_2O_3$ with hydrogen.

*Finely Divided Iron:* Table II contains a series of measurements made on electrodes prepared from finely divided iron. The samples for cells numbers 6, 7 and 8 were prepared by reducing $Fe_2O_3$ with hydrogen which had been freed of all traces of oxygen and water vapor. For the material used in cell No. 6 the reduction was carried out at about 800°C for 24 hours. The reduced iron was withdrawn from the electric furnace, crumbled up, and hurridly packed around the platinum head at the bottom of the cell. There was considerable evidence of oxidation as the e.m.f. was quite low at first and then gradually increased. This was apparently due to a thin, oxidized film formed on the metal while being removed from the furnace and placed in the cell which was slowly dissolved, though not entirely, as the cell did not reach the accepted equilibrium value of the amalgam variety.

The sample used in cell No. 7 was made by reducing $Fe_2O_3$ under the same conditions as used for cell No. 6 except that an iron wire was placed in the $Fe_2O_3$ and on reduction this held the spongy mass of iron formed. Instead of powdering this up and placing it in the bottom of the cell, it was hung from the top immediately after withdrawing from the furnace. Cell No. 7 had the exceptionally constant value of .8088 volts which did not vary more than a tenth of a millivolt for thirty days. During this time, the solution was removed over the iron three times and each solution of ferrous chloride had been separately prepared.

The electrode of cell No. 8 was a sample reduced at 850°C which gave a high initial value. Richard and Behr attribute such high initial values to an active state of hydrogen occluded by the metal. However, the potentials

TABLE II

Electrodes prepared from finely divided iron

| Time | Cell No. 6 | Cell No. 7 | Cell No. 8 | Cell No. 9 | Cell No. 10 | Cell No. 11 | Cell No. 12 |
|---|---|---|---|---|---|---|---|
| 0 | .7778 | .8017 | .8316 | .7884 | .7962 | .8390 | .8108 |
| 10 min | | | | | | .8462 max. | |
| 15 " | | | | | | | .8202 max. |
| 8 hrs. | .7942 | | | | | | |
| 1 day | .8000 | .8082 | .8216 | .8048 | .8018 | .7997 | .8102 |
| 2 days | .8026 | .8084 | .8152 | .8058 | .8024 | | |
| 3 " | .8037 | .8085 | .8115 | .8061 | .8031 | | |
| 4 " | .8042 | | .8099 | .8065 | .8035 | .7908 | .8052 |
| 5 " | .8043 | | | | | | |
| 6 " | | | .8085 | .8070 | .8048 | | |
| 8 " | | | .8086 | .8077 | .8048 | .7906 | .8032 |
| 10 " | .8047 | .8087 | | | .8052 | | |
| 12 " | .8047 | .8087 | .8090 | .8088 | | | |
| 15 " | | .8088 | | .8090 | | | |
| 18 " | | .8088 | | | | | .8062 |
| 24 " | | .8088 | | | | .8076 | |
| 36 " | | .8088 | | | | .8101 | |

given by iron produced by reducing $Fe_2O_3$ which carbon monoxide (cells No. 11 and No. 12) had similar high values at the beginning. This iron contained considerable carbon after reduction and it is not known what effect this might have had. It seems improbable that carbon thus contained would increase the potential in any way. The writer is inclined to believe that these high initial potentials are due to exceedingly small particles of iron which are used up until the variation of activity with the size of particles has become negligible, and an equilibrium value around .8090 volts is established.

The electrodes of cells No. 9 and No. 10 were a variety of Kahlbaum's C. P. iron powder which had been reduced a second time before placing in the cell. These agreed fairly well with the constant cell. Both the electrodes were of the same material and given as nearly as possible the same treatment. This again illustrates the type of differences in measurements which are constantly met and hard to account for.

*Annealed Iron:* Turning now to the series of measurements made with annealed iron as electrodes, it will be unnecessary to explain any of the experiments in detail as all the plain wire electrodes behaved similarly, giving considerably lower values than the finely divided form. No equilibrium value can be assigned to this form of iron, but, in general, the potential was about .05 volts lower than the other varieties. At times, samples approach the value of the finely divided form within .03 volts. Making the iron the cathode by simply leaving the working battery of the potentiometer slightly unbalanced against it, the e. m. f. would rise at a much faster rate than could be accounted for by polarization resulting from concentration changes, for, by placing the same electromotive force (one or two tenths of a milivolt) on several types of cells not in connection with this work, there was no effect whatever. In like manner, by making the electrode serve as an anode, the potential would decrease. This seemed to confirm the idea that iron in the annealed form has always a more or less passive state when immersed in water solutions and that the true activity may be very near that of the reduced iron. Furthermore, the same sample gave values more nearly that of finely divided iron in solutions of higher concentrations, differing .03 volts and, at times, approaching the higher value within about 01. volts.

For a final test of this idea, which seems quite conclusive, it was proposed to use some ionizing agent other than water with which the iron would not react. The only available medium was an eutectic mixture of lithium and potassium chloride. Ferrous chloride previously dehydrated and dried under an atmosphere of hydrogen chloride was added to the eutectic mixture. The resulting mixture of fused salts was further dried by first passing dry hydrogen chloride through the mixture and then hydrogen. Annealed iron wire served as one of the electrodes and finely divided reduced iron as the other. Two cells were thus made up using separately prepared electrodes. One of these showed finely divided iron to be more active by $2.3 \pm .3$ millivolts. The temperature of this cell was maintained at 380°C by a fused nitrate bath. The other showed a slightly greater difference, remaining constant at $3.3 \pm .3$ millivolts and the temperature was varied from 350°C to 450°C. We would

naturally expect to get small differences of this order of magnitude, which are attributed to the relative state of subdivision. The true activity of annealed iron is therefore very near that of finely divided iron, and the large difference shown in aqueous solutions must be due to passivity of the annealed form incurred by water.

Table III contains a series of measurements using iron wires for the electrodes. The electrode of cell No. 13 was a plain iron wire that had been heated for 36 hours at 850°C in the reduction furnace and allowed to cool slowly.

The wire in cell No. 14 was superficially oxidized by heating and cooling in air for several times and then reduced in the furnace.

The wire in cell No. 15 had been set in water until a large amount of rusting had taken place. It was then reduced by hydrogen.

The electrode of cell No. 16 was dipped in dilute hydrochloric acid for several minutes. It was then washed in 0.1 M ferrous chloride and placed in the cell.

The wire in cell No. 17 was simply sand-papered before placing in the cell.

TABLE III

Electrodes prepared from iron wire

| Time | Cell No. 13 | Cell No. 14 | Cell No. 15 | Cell No. 16 | Cell No. 17 |
|---|---|---|---|---|---|
| 0 days | .7190 | .7703 | .8052 | .7486 | .7490 |
| 2 " | .7409 | .7798 | .7797 | .7800 | .7912 |
| 4 " | .7484 | .7834 | .7773 | .7793 | .7575 |
| 6 " | .7506 | .7835 | .7773 | .7807 | .7580 |
| 8 " | | .7830 | .7774 | .7532 | .7592 |
| 10 " | | | | | .7696 |
| 12 " | | | | | .7800 |
| 16 " | .7515 | | | | .7803 |
| 24 " | .7578 | | | | .7719 |

| | Cell No. 18 | Cell No. 19 | Cell No. 20 |
|---|---|---|---|
| 0 " | .7140 | .6864 | .7475 |
| 2 " | .7095 | .7189 | .7592 |
| 4 " | .7106 | .7160 | .7492 |
| 6 " | .7153 | | .7484 |
| 8 " | .7270 | | .7484 |
| 10 " | .7330 | .7377 | |
| 12 " | .7302 | .7259 | |
| 16 " | .7350 | .7186 | |

The electrodes of cells No. 18 and No. 19 received the same previous treatment as those of No. 16 and No. 17 respectively, but the measurements were made in .500 M ferrous chloride solution.

Cell No. 20 is shown for comparison having for its electrode reduced iron oxide in .500 M ferrous chloride solution.

*Measurements at various concentrations:* Only a few cells were measured in concentrations other than one tenth molal. In all cases, the nature of the variations was the same. In the more concentrated solutions the variations as a whole were not quite so great. However, for solutions as dilute as .01 M no samples would give a constant value within any reasonable time. The tendency in dilute solutions was to decrease continually for a long period of time.

## Calculation of Results

*Choice of results for calculation:* The measurements given comprise only a small amount of the total number made, but they are selected to show the typical variations as well as to present all the peculiarities involved in this study of iron. In many ways, they duplicate the observation of others, but additional experiments were carried out to test new ideas which made it possible to arrive at a more truly representative value of the activity of iron. The most constant value given by any sample was that of cell No. 7, namely .8088 volts in .1 M ferrous chloride solution. Several cells remained constant for long periods of time within a few tenths of a millivolt of this potential. Furthermore it was approached from both directions. For constant values at other concentrations, we have the series of measurements with sample No. 5. There is no check on the results in concentration above .1 M for there are no data at hand to make the necessary calculations. However, the values for .0865 M, .05 M and .0095 M can be used and are tabulated in Table IV.

*Calculation of Results:* When two faradays of electricity pass through the cell $Fe|FeCl_2(aq), HgCl|Hg$, the following reaction takes place

$$Fe + 2\,HgCl = Fe^{++} + 2Cl^- + 2\,Hg. \qquad (1)$$

The electromotive force is given by the equation

$$E = E^\circ - RT/2F \ln 4\gamma^3 m^3$$
$$= E^\circ - 0.08873 \log \sqrt[3]{4}\,\gamma m \qquad (2)$$

in which $E^\circ$ is the potential when the activity of the ferrous chloride is unity, m is the molal concentration and $\gamma$ the activity coefficient.[1]

As there are no data at hand from which the activity coefficients of ferrous chloride can be calculated, the values for barium chloride were taken at corresponding concentrations. The justification for doing this arises from the fact that the chlorides of the bivalent salts as a class with the exception of $HgCl_2$ and $CdCl_2$ behave very similarly. For example, the solubilities of thallous chloride in .1 to .01 molal concentrations of ferrous chloride were found to be the same as that given by Bray and Winninghof[2] for barium chloride. In column 2 of Table IV are given the activity coefficients obtained by plotting the values which have been accurately calculated by Lewis and Randall for barium chloride from freezing point data against concentration and interpolating for various concentrations.

[1] Lewis and Randall: "Thermodynamics," Chapter XXIX (1923).
[2] J. Am. Chem. Soc., **33**, 1663 (1911).

TABLE IV

| m | γ | E | E° |
|---|---|---|---|
| .100 | .501 | .8088 | .7113 |
| .0865 | .516 | .8136 | .7117 |
| .050 | .563 | .8278 | .7095 |
| .0095 | .719 | .8830 | .7090 |

From a review of the discussion of the different measurements, the most probable value for E° is that calculated for .1 M and we may then write the equation: $Fe|FeCl_2$ (aq.), $HgCl|Hg : E° = .7113$ (3)

*The Normal Electrode Potential:* To calculate the normal electrode potential, we make use of the cell[1]

$$H_2|HCl\ (0.01M),\ HgCl|Hg: E = .5105 \qquad (4)$$

and using for the activity coefficient[2] of 0.01 M HCl, $\gamma = .924$ we obtain:

$$H_2|HCl,\ HgCl|Hg : E° = .2700 \qquad (5)$$

Since all the factors of equations (3) and (5) are of activity one we may write them in the form

$Fe|Fe^{++} \parallel Cl^-, HgCl|Hg$ $\quad E° = .7113$
$H_2|H^+ \parallel Cl^-, HgCl|Hg$ $\quad E° = .2700$

Combining these two equations gives

$$Fe|Fe^{++},\ H^+|H_2 \qquad E° = .4413 \qquad (6)$$

Since $(H_2|H^+)$ is taken as zero, we arrive at the value $E° = .4413$ for the normal electrode potential of iron. The reliability of this value will be discussed further after considering the results obtained by equilibrium measurements which are to follow.

## Equilibrium Measurements

Since the potential of the thallium electrode is near that of iron, it seemed possible to find some equilibrium that involved mutual oxidation and reduction of these metals. With data already at hand the equilibrium

$$Fe + 2\ TlCl = Fe^{++} + 2\ Cl^- + 2\ Tl$$

would permit an easy calculation of the iron electrode potential provided the concentration and activity of the ferrous chloride could be determined. Preliminary experiments showed that the reaction would proceed in either direction although the rate was quite slow.

From these observations, a one-liter flask was fitted with four 100 cc containers connected to the neck so that samples could be withdrawn for analysis. To the flask were added 40 grams of thallous chloride, 8 grams of powdered reduced iron, and 700 cc of water. The filling was carried out under an atmosphere of hydrogen to prevent any oxidation. The vessel was then evacuated and sealed from the air. This mixture was placed in a thermostat at 25°C and continually agitated by a mechanical shaker.

[1] Lewis, Brighton and Sebastian: J. Am. Chem. Soc., 39, 2245 (1917).
[2] Lewis and Randall: "Thermodynamics," Chapter XXVI (1923).

The sample tubes were removed from time to time and portions of the solution were rapidly weighed out and added to dilute hydrochloric acid. A titration was then made with .05 N potassium permanganate, a method used by A. A. Noyes[1] for the quantitative determination of thallium. The end point was somewhat masked by the yellow color of ferric iron but by having a comparison solution present it could be judged within two drops of .05 N potassium permanganate. Check experiments showed this method to be accurate within 0.5 per cent. This gave the total number of equivalents to oxidize both the iron and the thallium. The total chloride ion content was determined in a second portion of the solution acidified with nitric in-

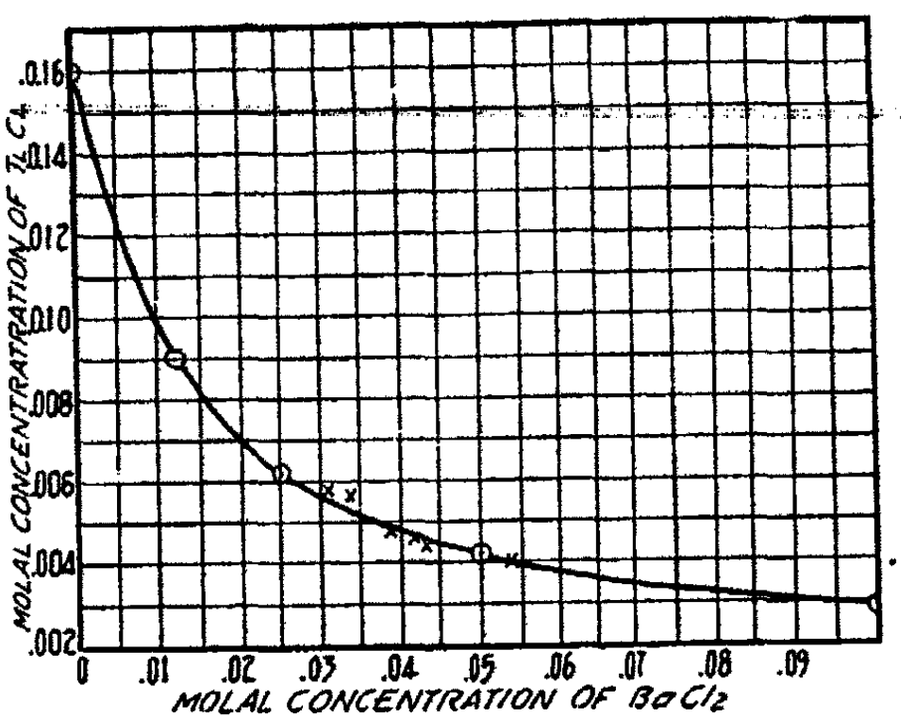



FIG. 1

stead of hydrochloric acid. From a result of these two determinations we can calculate the separate concentrations of ferrous chloride and dissolved thallous chloride from the relations:

$$2\,Fe^{++} + Tl^{+} = \text{total concentration of } Cl^{-}$$

$$Fe^{++} + 2Tl^{+} = \text{total no. of equi. } KMnO_4$$

It was found that the solubility of thallous chloride in solutions of ferrous chloride is practically the same as in solutions of barium chloride of like concentrations. The curve in Fig. 1 represents the solubility of thallous chloride in varying concentrations of barium chloride[2] and the crosses that in ferrous chloride. By the use of this curve and the titration with potassium permanganate the composition of sample portions could be determined with sufficient accuracy for calculations which are to follow later.

Table V gives a series of analyses made upon the mixture described above, and it shows how slowly the reaction proceeds toward equilibrium. Most of the reaction took place within the first nine days, at the end of which time

[1] Z. physik. Chem., 9, 603 (1892).

[2] Bray and Winninghof: J. Am. Chem. Soc., 33, 1663 (1911).

the concentration of ferrous chloride became .0306 M and only increased to .0453 M after a period of three months. When all the sample flasks had been removed from the larger vessel, the remaining contents were removed with as little exposure to air as possible and placed in a smaller container. The last two analyses were made on portions taken from this vessel when the amount of solution became exhausted. While these analyses indicate equilibrium, it is doubtful whether this point was yet reached for the shaking had been intermittent during the last period. The rate of reaction of this type depends very largely upon the agitation.

There was no exception to the behavior of iron in these experiments of showing apparently different activities as in the electrode measurements. Several mixtures in smaller amounts were made up and these behaved differently. After equal intervals of time, in some mixtures there appeared to be no reaction at all, while varying amounts of thallium were formed in others. None of these however appeared to be more reactive than the one for which the analysis is given in Table V.

There was even more difficulty in approaching the equilibrium by the reduction of ferrous chloride with metalic thallium, and, while the reaction is known to proceed, the rate is very slow. The speed of such a reaction necessarily depends to a large extent upon the amount of metalic surface exposed

TABLE V

Mixture made up with 40 grams TlCl, 8 grams iron and 700 cc water

| Time of analyses | Equi. of $KMnO_4$ per 1000 gm. sol. | Molal conc. $Fe Cl_2$ | Molal conc. Tl Cl |
|---|---|---|---|
| 0 days | — | — | .01607 |
| 9 " | .0423 | .0308 | .0057 |
| 21 " | .0437 | .0333 | .0053 |
| 31 " | .0478 | .0388 | .0047 |
| 60 " | .0507 | .0416 | .0046 |
| 83 " | .0524 | .0435 | .0043 |
| 90 " | .0531 | — | — |
| 102 " | .0533 | .0453 | .0042 |

TABLE VI

Equilibrium Measurements, $FeCl_2+2Tl$

| Sample Number 1. Time | Equi. of $KMnO_4$ in 1000 grams sol. | Sample Number 2. Time | Equi. of $KMnO_4$ in 1000 grams sol. |
|---|---|---|---|
| 0 days | .0950 | 0 days | .1010 |
| 8 " | .0865 | 6 " | .0999 |
| 15 " | .0768 | 14 " | .0968 |
| 22 " | .0710 | 21 " | .0942 |
| | | 28 " | .0920 |

and, for a soft metal like thallium, it is hard to produce a finely divided condition. Experiments were tried with small shavings of metallic thallium and a solid material from a saturated thallium amalgam. These gave only more or less qualitative results and nothing definite enough to be used in calculations. Later a method of approaching equilibrium from this direction was tried but time did not permit carrying this work to completion. Mixtures were prepared by reducing thallous chloride with excess iron powder and undissolved salt. The thallium separates out as small particles and remains for the most part in this condition. Table VI gives the results of two experiments on such mixtures beginning with one tenth molal ferrous chloride. Sample No. 1 was the residue from the run given in Table V and No. 2 was that of a separately prepared mixture. The latter was in a flask and did not permit mechanical agitation and was only shaken from time to time by hand.

It is evident that neither sample had reached equilibrium when the last analyses were made. At this time the solution over the mixture in No. 1 became exhausted and the work was discontinued.

## Calculation of Results

Equation (7) can be expressed in the following cell reaction:

$$Fe \mid FeCl_2\ (aq),\ TlCl \mid Tl$$

the e. m. f. of which is given by equation (2)

$$E = E^\circ - .08873 \log. 1.588\gamma m$$

Assuming equilibrium when the last analysis was made of the mixture given in Table V, we then have

$$E^\circ = .08873 \log. 1.588\ \gamma\ .0453 \qquad (8)$$

To determine $\gamma$ we take the activity coefficient of barium chloride of the same ionic strength as the solution of ferrous chloride and thallous chloride which corresponds to a molality of .0467. The activity coefficient for this concentration is .574. Substituting this value for equation (8) and solving for $E^\circ$ we obtain

$$Fe \mid FeCl_2\ (aq),\ TlCl \mid Tl : E^\circ = -.1228 \qquad (9)$$

Combining this with the equation[1]

$$Tl \mid TlCl,\ HgCl \mid Hg : E = .8246$$

we obtain

$$Fe \mid FeCl_2\ (aq)\ HgCl \mid Hg : E^\circ = .7022$$

Considering the equilibrium now as approached from right to left and making similar calculations for the last analysis of samle No. 1 given in Table VI, we have

$$Fe \mid FeCl_2(aq),\ HgCl \mid Hg : E^\circ = .7135$$

[1] Gerke: J. Am. Chem. Soc., **44**, 1684 (1922).

## Discussion of Results

It has been shown that the reaction expressed by equation No. 7 has been made to approach equilibrium in both directions. Assuming equilibrium at the times of the last analyses, the $E^\circ$ values for equation (3) differ by .0113 volts, but it is certain that in neither case had the reaction ceased. Furthermore, all the observed values of Table IV lie between these two. The following values have been given for comparison:

(a) From the equilibrium measurement: $2TlCl + Fe$: $E^\circ = .7022$
(b) From electromotive force: $E^\circ = .7113$
(c) From the equilibrium measurement: $FeCl_2 + 2Tl$: $E^\circ = .7135$

By examination of Table V and VI we would more likely expect the value of (c) to be too high and that of (a) to be too low. Although predictions of this kind may seem a little questionable when so many factors have to be considered as those involved in this equilibrium, nevertheless electromotive force measurements on iron in a finely divided condition, whether the amalgam variety or the reduced oxide, show quite conclusively that the value of $E^\circ$ can be but very little if any lower than that given for (b).

In round numbers, then, the normal electrode potential is taken as .4410 volts for all ordinary forms of iron, a value which is in all probability correct within three millivolts.

## Summary

The potential of several varieties of iron was measured in the cell Fe| $FeCl_2$ (aq), HgCl|Hg in which there was no liquid junction.

An amalgam variety prepared by electrolyzing a solution of ferrous sulfate, using a mercury cathode, gave .8090 volts as the best equilibrium value in 0.1M ferrous chloride.

Finely divided iron prepared by reducing $Fe_2O_3$ gave .8088 volts as the best equilibrium value in 0.1 M ferrous chloride.

Potentials of annealed iron in water solutions were much lower than those obtained with the other varieties. By measuring the potential between finely divided iron and the annealed form in a solution free from water and consisting of ferrous chloride in a fused eutectic mixture of lithium and potassium chloride it was found that there was very little difference between the activity of each. The difference in water solutions was attributed to passivity of compact iron in contact with water.

The value .4413 volts was calculated from the above measurements as the most probable value of the normal electrode potential, and it is not considered in error by more than three millivolts. Measurements made on the equilibrium $Fe + 2\,TlCl = Fe^{++} + 2\,Cl^- + 2\,Tl$ substantiated this conclusion.

# A NOTE ON THE MECHANISM OF EMULSIFICATION*

BY ALFRED J. STAMM AND ELMER O. KRAEMER**

The suggestion that the phase relations (*direction* of curvature of interface) and size of particles (*magnitude* of curvature of interface) in emulsions are determined by the orientation of *wedge-shaped* molecules of stabilizer in the interface between disperse phase and dispersion medium[1] has greatly stimulated interest in the problem of emulsions and emulsification. However, the rosy promises at first held out by this oriented wedge theory of emulsions unfortunately have not materialized. Two claims have been made for the theory: first, that it explains the decrease in the most probable size of particles with a change in emulsifying agent from sodium to potassium to cesium soaps; second, that it explains the change in phase relations upon changing emulsifying agent from an alkali soap to an alkaline earth, or an iron or aluminum soap. Neither the original evidence for the theory nor the consequences predicted by the theory have been completely confirmed. The *number*-distribution curves[2] (showing the distribution of total number of particles among the various sizes present) does not provide an appropriate basis for correlating the sizes of the particles in an emulsion with the supposed wedgeness of the stabilizing molecules. Rather, a test of the wedge theory requires a comparison of *surface*-distribution curves of emulsions with different stabilizing agents.[3] A logical application of the wedge theory would lead one to expect a decrease in the *radius of curvature* most frequently occurring in the interface with an increase in the wedgeness of the emulsifying agent molecules; and it is the maximum of the *surface*-distribution curve which defines the most probable radius of curvature of interface in the emulsion. But for practical purposes of expressing the degree of dispersion of dispersed systems, the *mass*-distribution curve[4] is usually to be preferred.[5]

Since the maximum of the surface-distribution curve corresponds to a greater radius of particle than does the maximum of the related *number*-distribution curve, the most probable radius of curvature in an emulsion stabilized by sodium oleate, as quoted by Harkins,[6] is even more than 750 times the apparent length of the oleate molecules. It therefore seems rather

*Contribution from the Laboratory of Colloid Chemistry, University of Wisconsin.

** Fellow of the National Research Council.

[1] Langmuir: J. Am. Chem. Soc. 39, 1848 (1917); Harkins: 39, 354, 541 (1917); Bogue's "Colloidal Behavior," Chapter VI (1924); Finkle, Draper and Hildebrand: J. Am. Chem. Soc., 45, 2780 (1923); Harkins and Keith: Science, 59, 463 (1924); Harkins: Paper given before Second Colloid Symposium (1924) and partially published in monograph.

[2] Finkle, Draper, and Hildebrand: loc. cit.; Keith: Thesis, Univ. Chicago, (1924); Harkins and Keith: loc. cit.

[3] Stamm: Third Colloid Symposium Monograph (1925).

[4] See earlier papers of authors.

[5] In their most recent paper, Harkins and Beeman (Proc. Nat. Acad. Sci., 11, 631 (1925)) present all three types of distribution curves; i. e., number, surface and volume (same as mass.)

[6] In Bogue's "Colloidal Behavior," p. 201.

unlikely that the oleate molecules, by virtue of *their presumed wedge-shape*, determine to any essential degree the radius of curvature of such relatively large drops.

In the second place, mass and surface-distribution curves determined by sedimentation and microscopic[1] methods have failed to reveal any significant variation in the position of the maxima for emulsions with palmitates of sodium, potassium, or cesium as stabilizers, although originally reported by Finkle, Draper, and Hildebrand, and by Harkins and Keith. This inconsistency may be due either to differences in the methods of emulsification, i.e., differences in mechanical treatment—or to inadequate microscopic measurements by the authors last named.[2] Furthermore, the total interface in the emulsions has been found to be constant, within the limits of experimental errors, for the palmitates of sodium, potassium, and cesium.[3] Other difficulties in the oriented wedge theory of emulsification have arisen. Thus, although the influence of alkali soap (univalent cation), in the presence of an excess of the corresponding alkali, upon the degree of dispersion of emulsions[4] may apparently be harmonized with the wedge theory by supposing the excess of alkali to repress hydrolysis, the same line of reasoning in the case of excess of barium hydroxide with a barium soap leads to expectations which are flatly contradicted by the facts. It seems hazardous also to suggest—as has been done—that aluminum or iron soaps function as emulsifying agents *in the form of single molecules* nicely oriented in the interface, in view of the instability of these soaps, and the observation by Briggs and Schmidt[5] that flocks of what is perhaps aluminum hydroxide exist in emulsions stabilized by the use of an aluminum soap. A similar difficulty appears in the inconsistency between facts and the wedge theory predictions concerning the relative influence of potassium palmitate and potassium chaulmoograte upon the degree of dispersion of emulsions.[6] Again, phenol gives rise to oil-in-water emulsions, contrary to what one might expect if the wedge theory is so applied as to assume the $C_6H_5$ nucleus to orient into the "oil" and the OH to enter the water phase. Likewise, on the basis of the wedge theory, there is no apparent reason for expecting or means of explaining *reversals in phase relations* in a series of aqueous emulsions of various petroleum distillate fractions (varying viscosity), stabilized by casein.[7] The usefulness of the wedge theory in other phase-relationship problems presented in this paper is also not obvious. It has not yet been shown how the oriented wedge theory of emulsions can be reconciled with *reversal of phase relations* brought about by a

[1] Kraemer and Stamm: J. Am. Chem. Soc., 46, 2709 (1924); Stamm and Svedberg: 47, 1582 (1925); Stamm: Third Colloid Symposium Monograph (1925).

[2] In a recent paper, Harkins and Beeman (Proc. Nat. Acad. Sci., 11, 631 (1925)) admit the independency of the positions of maxima in surface and mass distribution curves with respect to the soap used as emulsifier (Na, K, and Cs).

[3] Stamm: Third Colloid Symposium Monograph (1925).

[4] Harkins: loc. cit.; Stamm and Svedberg: loc. cit.

[5] Briggs and Schmidt: J. Phys. Chem., 19, 491 (1915).

[6] Harkins and Beeman: loc. cit.

[7] Seifriz: J. Phys. Chem., 29, 587 (1925).

change in the volume composition of an emulsion, even in the presence of sodium oleate,[1] or in the character of the walls of the container.[2] Even the assumption of 100% dissociation of the oriented soap molecules does not relieve the oriented wedge theory of the responsibility of predicting unequal radii of curvature with different emulsifying agents, for if such thin films (monomolecular) were directly effective in determining radius of curvature, variation in cation might be expected to so modify the "foundation" of the film[3] as to change the film properties and the normal radius of curvature.

It seems therefore that considerable experimental evidence is positively contrary to the consequences of the oriented wedge theory, as stated thus far, while direct evidence in favor of the theory is largely lacking. On the other hand, numerous observations of the influence of volume composition and methods of emulsification and homogenization upon phase relations and the degree of dispersion of an emulsion have led the authors to the suspicion that the *shapes* and *sizes* of the molecules of stabilizing agents perhaps have been over-emphasized in this connection.

It should be remembered that the phase relations and the degrees of dispersion of an emulsion prepared by dispersion are the net results of two opposing processes, namely, a pulverizing process and a coagulating process.

*The first, or pulverizing process*, is accomplished by shaking, mixing, the use of colloid mills, homogenizers, etc., and probably consists in the mutual pulverization of the two liquid phases by the formation and subsequent disruption into drops of lamellae and threads of one liquid in the other, either by flowing processes or by impact of liquid masses against each other or the walls of the container. In this stage, the dissipation of mechanical energy in the system gives rise to hydrodynamic problems of great complexity. Although it would be very difficult to correlate them quantitatively, the factors of importance may be said to be mechanical and hydrodynamic ones, and include the particular mechanical treatment, character of solid walls, volume composition, densities, viscosities, interfacial tensions and surface tensions (if a gas is present, as in shaking a partially filled bottle) of the liquids.

The relative extents to which the two liquids are drawn out into lamellae and threads in each other are probably determined principally by the volume composition, viscosities and densities of the liquids. (The interfacial tension, being the same for either phase, has a symmetrical influence upon the formation of lamellae of both liquids.[4]) This process of lamellae formation is of primary importance in determining the degree of dispersion of an emulsion. A liquid thread or lamella is unstable, however, and spontaneously breaks up into drops. Thus, a liquid cylinder is unstable when its length is greater than three times its diameter.[5] The manner in which the disruption of the lamellae

[1] Sanyal and Joshi: J. Phys. Chem., 26, 481 (1922). This type of reversal was *confirmed* in this paper.

[2] Wa. Ostwald: Kolloid-Z., 6, 103 (1910). Also confirmed in this paper.

[3] Coard and Rideal: J. Chem. Soc., 127, 1668 (1925).

[4] Compare with Donnan: Z. physik. Chem., 46, 197 (1903).

[5] Winkelmann: Handbuch Physik, I²

into drops takes place may be considered as largely dependent upon the magnitude of the lamellae and the interfacial tension and the viscosity of the lamella phase. When the interfacial tension is very high and the viscosity low, as in the case of water-mercury,[1] the dispersion of lamellae into unusually small drops is very striking. Although the interfacial tension is a factor in the disruption of lamellae, the thickness of the lamellae and the sizes of the drops make it improbable that the *shapes and sizes of the molecules* in the interface have any direct mechanical or "geometrical" bearing upon the sizes of the drops formed.

These same factors, i. e. mechanical treatment, volume composition, viscosity, density and interfacial tension, are probably involved in the dispersion of a liquid mass by impact. Impact gives rise to lamellae which break into drops. The work of disruption by impact, like the work of deformation of small drops may increase with the interfacial tension and with a decrease in a the size of the liquid mass to be broken. In this process, a decrease in interfacial tension probably facilitates dispersion—but, certainly, it is difficult to recognize how the *shapes and sizes* of molecules in the interface could directly and mechanically determine the sizes of the drops formed on such a gross scale. In the realm of magnitudes here involved, the interfacial tension is practically independent of the radius of curvature of the interface. Both phases are dispersed in the process of mixing, shaking, etc.

Simultaneously and subsequently to the pulverization process is the second major process—the coagulation or reunion of the drops of the dispersed liquids to form continuous phases. The rates of coagulation may be taken to depend primarily upon the viscosities, densities, volumes, and interfacial tensions in a fashion which cannot be accurately specified: The rates may, and usually do, differ for the two liquids, especially if an "emulsifying agent" be present. One liquid, because of a lesser degree of pulverization, a greater rate of coagulation, or both, may unite to form a continuous phase—the dispersion *medium*—in which the second liquid forms the disperse phase because of greater degree of pulverization in the first stage, or a smaller rate of coagulation in the second stage, or both. The phase relations and the degree of dispersion, or distribution of size of particle of an emulsion thus are presumed to be determined by these two opposing processes.

In the case of two pure liquids, the rates of coagulation of both may be great, and the emulsion is said to be unstable, for it more or less quickly "breaks" into two separate phases. Upon the addition of an "emulsifying agent," in moderate concentration (as a few hundredths molar soap solution) the pulverization process may not be greatly modified.[3] Only the interfacial tension is significantly changed, which means that the rates of coagulation may be most profoundly modified. Presumably, the rate of coagulation of

[1] Nordlund: Kolloid-Z., 26, 121 (1920).

[2] Hatschek: Kolloid-Z., 7, 81 (1910).

[3] Yet, *any* modification makes it impossible to preserve *uniform* and *comparable* conditions of mechanical treatment during the pulverization process—when different emulsifying agents are used.

the drops of one liquid is very much decreased, while the drops of the other liquid reunite to form a dispersion medium for the drops which are protected from coagulation by a stabilizing film of unknown nature. By virtue of the protection afforded the drops, they may "cream" without breaking, and the emulsion is said to be stable. The protecting film, to be effective, must form fairly quickly, before coagulation of the unprotected drops has progressed too far. Since the rapid formation of a film partially depends upon the tendency of the interfacial tension to be decreased by the added agent, it is clear why substances which have markedly lower interfacial tensions (as the soaps) are frequently effective emulsifying agents—or rather stabilizing agents. Thus, the stabilizing agent may influence the primary process of dispersion only indirectly by modifying what may be called mechanical or hydrodynamic factors operating during the pulverization process. The maximum degree of dispersion is fixed before the stabilizing agent steps in to protect the drops of one phase from reuniting. The greatest influence of the emulsifying agent is probably upon the coagulating process; it thus may overshadow other factors and determine the phase relationship of the final emulsion. The coagulating process in an emulsion, as that of an oil-in-water emulsion stabilized with sodium soap to which has been added $CaCl_2$, is probably very similar to coagulating processes in other suspensoids. In neither case does there seem to be any possibility of recognizing the influence of the *geometrical shapes and sizes* of the stabilizing molecules.

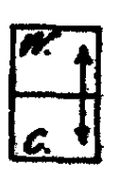
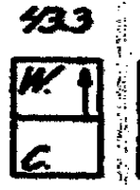
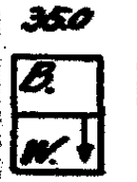
Further examples of the manner in which these factors superimpose are given in diagrammatic form in Tables I and II. Pairs of incompletely miscible liquids (1 : 1 by volume) were shaken and the phase relations of the resulting emulsions[1] observed. The denser liquid is placed below the lighter in the diagram, and the arrow indicates the direction and qualitative extent to which one liquid became dispersed in the other. One series of liquid pairs with water as a common member, and one series with glycerine as a common member are given with data on viscosities, surface tensions,[2] and interfacial tensions when available. In addition, there are given observations upon the influence of magnesium palmitate, potassium palmitate, or of oleic acid upon the phase relationship for these same liquid pairs.

In the case of the pairs in the water series, it may be noted that in each and every case examined, the less viscous liquid tended to remain dispersed in the more viscous phase, suggesting therefore either that during the pulverizing process, lamellae of the more viscous liquid were formed to a much less ex-

[1] The question may be raised as to whether such systems, usually unstable, may be properly called emulsions. It seems evident, upon consideration, that the differences between these systems and those made more stable by the addition of a stabilizing agent are differences not in kind, but only in degree. In any case, it must be admitted that the stabilized systems are more complicated, and that the factors of mechanical treatment, volume composition, viscosity, interfacial tension, etc., which play a part in determining the phase relations and size of particles in the simpler systems *without* monomolecular layers of stabilizing molecules must also be important in determining phase relations and size of particles in the systems *with* added stabilizing agents.

[2] Most of the surface tension data were taken from Harkins, Clark, and Roberts: J. Am. Chem. Soc., 42 700 (1920).

## Table I
### Water Systems.

| | Isoamyl alcohol | Isobutyl alcohol | n-Butyl alcohol | Oleic acid | Ethyl acetate | Dimethyl aniline | Nitro-benzene | Chloroform | Carbon tetra-chloride | Benzene | Heptane | Standox |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Phase relationship |  |  |  |  |  |  |  |  |  |  |  |  |
| Visible | 1 min. | 1 min. | 5 sec. | .5 min. | 5 sec. | 10 sec. | <5 sec. | <5 sec. | <5 sec. | <5 sec. | <5 sec. | 10 sec. |
| Complete separation | 15 min. | 15 min. | 2 min. | 15 min. | 1 min. | 1 min. | 1 min. | 10 sec. | 10 sec. | 10 sec. | 15 sec. | 5 min. |
| Relative viscosity | 4.58 | 4.03 | — | very viscous | 0.45 | 1.28 | 1.80 | 0.55 | 0.96 | 0.62 | .040 | very viscous |
| Surface tension | 24.1 | 22.8 | 24.5 | 32.5 | 26.5 | 38.3 | 43.5 | 26.5 | 26.9 | 28.8 | 19.0 | — |
| Interfacial tension | 4.4 | 1.8 | 0.4 | 15.7 | 18.0 | 25.8 | 25.7 | 32.6 | 43.3 | 36.0 | 50.4 | — |
| Effect of adding oleic acid |  | | | — |  |  |  |  |  |  |  |  |
| Effect of adding magnesium palmitate |  | | | — |  |  |  |  |  |  |  |  |

tent, or that the rate of coagulation of the more viscous liquid was the greater. The complexity of relationships to be met are, however, shown when reference is also made to glycerine systems; for here the very viscous glycerine became the dispersed phase in every case. These two cases of maximum simplicity (i. e., two single liquids) illustrate the complexity of the emulsification process as a hydrodynamic proposition.

Influences of volume composition upon phase relationship may be seen also in the case of two liquids. Oleic acid-water mixtures with a volume per cent of oleic acid between 5-70% were passed through the colloid mill four times. For volume compositions of 5-40% oleic acid, the oleic acid was the

*Table II*
*Glycerine Systems*

| | Ethyl acetate | Dimethyl aniline | Nitro-benzene | Chloroform | Carbon tetra-chloride | Benzene | Heptane | Stanolax |
|---|---|---|---|---|---|---|---|---|
| Phase relationship | E. / G. | D. / G. | N. / G. | C. / G. | C. / G. | B. / G. | H. / G. | S. / G. |
| Complete separation | 1 min. | 1 min. | 1 min. | 5 sec. | 5 sec. | 5 sec. | 5 sec. | 3 min. |
| Effect of adding potassium palmitate | E. / G. | D. / G. | N. / G. | C. / G. | G. / C. | B. / G. | H. / G. | S. / G. |
| Complete separation | over one month | little separated immediately remainder stood up several days | | | | | | 1 day |

*dispersed phase*. But with compositions of 45-70% oleic acid, the water was the dispersed phase.[1] It seems safe to assume that these differences indicate the influence of volume composition upon the process of lamellae formation and their disruption into drops.

It is of interest to observe the influence of benzene upon the emulsions in the region of phase reversal. To a water-in-oleic acid emulsion (45% oleic acid) 10 cc. of benzene were added and the mixture passed through the colloid mill, but without reversal. A further addition of 10 cc. of benzene and repassage through the mill gave an oleic acid-benzene-in-water emulsion just over the reversal boundary region.

Volume composition effects can also be observed with mixtures of stanolax and water, although coagulation is more rapid than in the preceding case. With 50% oil, water was the dispersed phase, but with 40% oil, the oil was

[1] Such reversals have been observed by Sanyal and Joshi, as previously cited, even in the presence of sodium oleate as emulsifier in concentrations as high as 0.075%.

the disperse phase. The latter mixture gave two layers, each with a disperse phase when the inside of the tube in which the mixture was shaken was paraffined.

The addition of a so-called emulsifying agent complicates not only the pulverization process but also the coagulation process, as before mentioned. It therefore does not seem safe to assume that the mechanics of dispersion can be preserved uniform for comparison purposes, with the use of various "emulsifying agents."

In the water series, we find oleic acid to reverse the phase relations with the alcohols, dimethyl aniline, nitrobenzene, and stanolax, and to more definitely cause carbon tetrachloride, benzene, and heptane to become dispersed in the water. The oleic acid did not completely prevent water from remaining dispersed in dimethyl aniline or nitrobenzene. In every case of the series, magnesium palmitate caused the water to become the dispersed phase. This fact suggests that the character of the film formed by the magnesium palmitate at the liquid-liquid interface is such as to protect water droplets in "oil," but not "oil" droplets in water, but the instability of oil droplets in water in the presence of magnesium palmitate is no more related to shapes and sizes of molecules than is instability of any other dispersed system in the presence of a coagulating agent.

In the glycerine series, potassium palmitate caused the phase relations to be reversed in every case, glycerine becoming the dispersion medium. In this case too, it is quite unlikely that the potassium palmitate had any marked influence upon the pulverization stage of *both* liquids (formation and disruption of lamellae), for neither the density or viscosity of the liquids or the mechanical treatment would be greatly modified. The interfacial tension, the property most changed, has a symmetrical influence upon the lamellae of both liquids and therefore has a minor influence upon the pulverization process. It only remains for the potassium palmitate to modify the relative rates of coagulation of the droplets of each phase. Empirically, it may be said that the droplets of "oil" in glycerine are stabilized or protected from coagulating, i. e., *fusing* upon encounter, whereas the droplets of glycerine in the oil are not so protected. This protection against "breaking" is usually assumed to be due to a film[1] of some kind at the interface. Although the nature and properties of this film are but vaguely understood, there seems to be no compelling reason for supposing it to consist of a simple monomolecular layer of oriented molecules, except, perhaps, when extremely small amounts of strongly polar-nonpolar stabilizers are used.[2] Even then there is no reason to believe that the *shapes and sizes* of the molecules are able to assert themselves in a mechanical or geometrical manner.

---

[1] Bancroft: J. Phys. Chem., **17**, 514 (1913); "Applied Colloid Chemistry," (1921); Clayton: "Emulsions and Emulsification, (1923).

[2] Stamm: Third Colloid Symposium Monograph (1925).

## Summary

A survey of recent studies of emulsions demonstrates that considerable of the original evidence for the "oriented wedge" theory of emulsions has not been confirmed and that the consequences predicted by the theory have not materialized. It is suggested that insufficient attention has been paid to the mechanism of emulsion formation. The formation of an emulsion by shaking, mixing, etc., may be safely considered as consisting of two stages—(1) a pulverization of both phases into lamellae and drops, and (2) a coagulation or reunion of the drops of one or both phases. The degree of dispersion (distribution of size of particle) and the phase relations of an emulsion are the net results of these two opposing processes. The function of an "emulsifying agent" is to more or less protect the drops of *one* phase already formed in the pulverizing stage from coagulating, while allowing the drops of the other phase to coagulate to give the dispersion medium. The protecting or stabilizing action is probably dependent upon the formation of a film at the interface. Although the character of such a stabilizing film is incompletely understood, it seems unlikely that the molecules in the film can determine the film properties by virtue of their *geometrical shape and size*, as suggested in the oriented wedge theory. Examples are given to demonstrate the complexity of the mechanism of emulsion formation.

# NEW BOOKS

**The A B C of Atoms.** *By Bertrand Russell. 20×14 cm pp. v + 162. New York: E. P. Dutton and Company, 1923. Price: $2.00.* The chapters are entitled: introductory; the periodic law; electrons and nuclei; the hydrogen spectrum; possible states of the hydrogen atom; the theory of quanta; refinements of the hydrogen spectrum; rings of electrons; X-rays; radio-activity; the structure of nuclei; the new physics and the wave theory of light; the new physics and relativity; Bohr's theory of the hydrogen spectrum.

There are a number of interesting passages in the book. "The chemical properties of the atom depend, almost entirely, upon the outer ring; so does the light that it emits, which is studied by the spectroscope. The inner rings of electrons give rise to X-rays when they are disturbed and it is chiefly by means of X-rays that their constitution is studied. The nucleus is the source of radio-activity. In radium and the other radio-active elements, the nucleus is unstable, and is apt to shoot out little particles with incredible speed," p. 6.

"One of the most astonishing things about the processes that take place in atoms is that they seem to be liable to sudden discontinuities, sudden jumps from one state of continuous motion to another. This motion of an electron round its nucleus seems to be like that of a flea, which crawls for a while, and then hops. The crawls proceed accurately according to the old laws of dynamics, but the hops are a new phenomenon, concerning which totally new laws have been discovered empirically, without any possibility (so far as can be seen) of connecting them with the old laws. There is a possibility that the old laws, which represented motion as a smooth continuous process, may be only statistical averages, and that, when we come down to a sufficiently minute scale, everything really proceeds by jumps, like the cinema, which produces a misleading appearance of continuous motion by means of a succession of separate pictures," p. 9.

"When I say that an electron has a certain amount of negative electricity, I mean merely that it behaves in a certain way. Electricity is not like red paint, a substance which can be put on to the electron and taken off again; it is merely a convenient name for certain physical laws," p. 25.

"It is impossible to get a ring to hold more than a certain number of electrons, though it has been suggested by Niels Bohr, in an extremely ingenious speculation, that a ring can hold more electrons when it has other rings outside it than when it is the outer ring. His theory accounts extraordinarily well for the peculiarities of the periodic table, and is therefore worth understanding, though it cannot yet be regarded as certainly true," p. 32.

"Sound-waves consist of vibrations of the air, or of whatever material medium is transmitting them, and cannot be propagated in a vacuum; whereas light-waves require no material medium. People have invented a medium, the aether, for the express purpose of transmitting light-waves. But all we really know is that the waves are transmitted; the aether is purely hypothetical, and does not really add anything to our knowledge. We know the mathematical properties of light-waves, and the sensations they produce when they reach the human eye, but we do not know what it is that undulates. We only suppose that something must undulate because we find it difficult to imagine waves otherwise," p. 41.

"All this so far is purely empirical. Rydberg's constant, and the formula for the lines of the hydrogen spectrum, were discovered merely by observation, and by hunting for some arithmetical formula which would make it possible to collect the different lines under some rule. For a long time the search failed because people employed wave-lengths instead of wave-numbers; the formulae are more complicated in wave-lengths, and therefore more difficult to discover empirically. Balmer, who discovered the formula for the visible lines in the hydrogen spectrum, expressed it in wave-lengths. But when expressed in this form it did not suggest Ritz's Principle of Combination, which led to the complete rule. Even after the rule was discovered, no one knew why there was such a rule, or what was the reason for the appearance of Rydberg's constant. The explanation of the rule, and the connection of Rydberg's constant with other known physical constants, was effected by Niels Bohr, whose theory will be explained in the next chapter," p. 48.

"It was obvious from the first that, when light is sent out by a body, this is due to something that goes on in the atom, but it used to be thought that, when the light is steady, whatever it is that causes the emission of light is going on all the time in all the atoms of the substance from which the light comes. The discovery that the lines of the spectrum are the differences between terms suggested to Bohr a quite different hypothesis, which proved immensely fruitful. He adopted the view that each of the terms corresponds to a stable condition of the atom, and that light is emitted when the atom passes from one stable state to another, and only then. The various lines of the spectrum are due, in this theory, to the various possible transitions between different stable stages. Each of the lines is a statistical phenomenon: a certain percentage of the atoms are making the transition that gives rise to this line. Some of the lines in the spectrum are very much brighter than others; these represent very common transitions, while the faint lines represent very rare ones. On a given occasion, some of the rarer possible transitions may not be occurring at all; in that case, the lines corresponding to these transitions will be wholly absent on this occasion," p. 49.

"Einstein's work has immense philosophical and theoretical importance, but the changes which it introduces in actual physics are very small indeed until we come to deal with velocities not much less than that of light. The new dynamics of the atom, on the contrary, not merely alters our theories, but alters our view as to what actually occurs, by leading to the conclusion that change is often discontinuous, and that most of the motions which should be possible are in fact impossible. This leaves us quite unable to account for the fact that all the motions that are in fact possible are exactly in accordance with the old principles, showing that the old principles, though incomplete, must be true up to a point. Having discovered that the old principles are not quite true, we are completely in the dark as to why they have as much truth as they evidently have. No doubt the solution of this puzzle will be found in time, but as yet there is not the faintest hint as to how the reconciliation can be effected," p. 57.

"A theory which explains all the known relevant facts down to the minutest particular may nevertheless be wrong. There may be other theories, which no one has yet thought of, which account equally well for all that is known. We cannot accept a theory with any confidence merely because it explains what is known. If we are to feel any security, we must be able to show that no other theory would account for the facts. Sometimes this is possible, but very often it is not. Poincaré advanced a proof that the facts of temperature radiation cannot be explained if we assume that radiation is a continuous process, and that any possible explanation must involve sudden jumps such as we have in the quantum theory. His argument is difficult, and it is possible that it may not ultimately prove wholly cogent. But it affords an instance of that further step without which scientific hypothesis must remain hypothetical," p. 79.

"Radio-activity is one of those processes of degeneration (in a certain technical sense) to which no converse process of regeneration is known. We see complex atoms breaking up, and it is natural to suppose that there are (or have been) circumstances under which they are put together out of simpler atoms. But no trace of any such circumstances has been discovered. In this respect, as in some others, the universe *seems* like a clock running down, with no mechanism for winding it up again. All the uranium in the world is breaking down, and we know of no source from which new uranium can come. Under these circumstances it seems strange that there should be any uranium. But if, like some insects, we lived only for a single spring day, we should think it strange that there should be any ice in the world, since we should find it always melting and never being formed. Perhaps the universe has long cycles of alternate winding-up and running-down; if so, we are in the part of the cycle in which the universe (or at least our portion of it) runs down. Everything pleasant is associated with this running down, because it is only this process that liberates energy for the purposes that we regard as useful. It is time, however, to return from these speculations to the mechanism of radio-activity," p. 112.

"The fact that the atomic weights are whole numbers, together with the facts of radio-activity and of Rutherford's bombardment, lead irresistibly to the conclusion that the weight

of an atom is due to helium nuclei and hydrogen nuclei which exist together in its nucleus. The over-crowding in the nucleus of a heavy atom must be something fearful. Radium C, which emits the $\alpha$-particles that Rutherford used in his experiments, has a nucleus whose radius is about three million-millionths of a centimetre (about one million-millionth of an inch). Its atomic number is 83 and its atomic weight is 214. This means that in this tiny space it must contain 53 helium nuclei and 2 hydrogen nuceli; it must also (as we shall see in a moment) contain 131 electrons. It is no wonder that helium nuclei and electrons move fast when radio-activity liberates them from this slum," p. 127.

"In the physics of the atom, as it has become in modern times, everything is atomic, and there are sudden jumps from one condition to another. The electron and the hydrogen nucleus are the true "atoms" both of electricity and of matter. According to the quantum theory, there are also atomic quantities, not of energy as was thought when the theory was first suggested, but of what is called "action." The word "action," in physics, has a precise technical meaning; it may be regarded as the result of energy operating for a certain time. Thus if a given amount of energy operates for two seconds, there is twice as much action as if it operated for one second; if it operates for a minute, there is 60 times as much action, and so on. If twice the amount of energy operates for a second, there is again twice as much action, and so on. If the energy which is operating is variable, and we wish to estimate its action during a given time, we divide the time into a number of little bits, during each of which the energy will vary so little that it may be regarded as constant; we then multiply the energy during each little interval of time by the length of the interval, and add up for all the intervals. As we make the intervals smaller and more numerous, the result of our addition approaches nearer and nearer to a certain limit; this limit we define as the total action during the total period of time concerned. Action is a very important conception in physics; from the point of view of theory it is more important than energy, which has been deposed from its eminence by the theory of relativity. Planck's quantum $h$ is of the nature of action; thus the quantum theory amounts to saying that there are atoms of action," p. 134.

"It must be confessed that the quantum principle in its modern form is far more astonishing and bewildering than is its older form. It might have seemed odd that energy should exist in little indivisible parcels, but at any rate it was an idea that could be grasped. But in the modern form of the principle, nothing is said, in the first instance, about what is going on at a given moment, or about atoms of energy existing at all times, but only about the total result of a process that takes time. Every periodic process arranges itself so as to have achieved a certain amount by the time one period is completed. This seems to show that nature has a kind of foresight, and also knows the integral calculus, without which it is impossible to know how fast to go at each instant so as to achieve a certain result in the end. All this sounds incredible. No doubt the fact is that the principle has assumed a complicated form because it has forced its way through, owing to experimental evidence, in a science built upon totally different notions. The revolution in physical notions introduced by Einstein has as yet by no means produced its full effect. When it has, it is probable that the quantum principle will take on some simple and easily intelligible form," p. 139.

"The theory of relativity has shown that most of traditional dynamics, which was supposed to contain scientific laws, really consisted of conventions as to measurement, and was strictly analogous to the "great law" that there are always three feet to a yard. In particular, this applies to the conservation of energy. This makes it plausible to suppose that every apparent law of nature which strikes us as reasonable is not really a law of nature, but a concealed convention, plastered on to nature by our love of what we, in our arrogance, choose to consider rational. Eddington hints that a real law of nature is likely to stand out by the fact that it appears to us irrational, since in that case it is less likely that we have invented it to satisfy our intellectual taste. And from this point of view he inclines to the belief that the quantum-principle is the first real law of nature that has been discovered in physics," p. 158.

*Wilder D. Bancroft*

**Regeneration.** *By Jacques Loeb. 24×16 cm; pp. 143 New York and London: McGraw-Hill Book Company, 1924 Price: $2.00.* The final revision of this book was finished by Loeb just before his death. The first part deals with mutilation and regeneration, and the chapters are entitled: introduction; general remarks about the material and the experiments; regeneration and mass relation in isolated leaves of *Bryophyllum*; the inhibiting action of the rapidly growing notches on the other notches of a leaf; the influence of gravity on the formation of roots and shoots in a detached leaf of *Bryophyllum*; why does separation of a leaf from the plant induce the growth of roots and shoots in a leaf?; the validity of the mass relation for regeneration in a defoliated piece of stem of *Bryophyllum calycinum*; the rôle of the inhibiting effect of rapidly growing parts in the regeneration of the stem.

The second part deals with polarity in regeneration, and the chapters are entitled: the influence of the leaf on the regeneration in the stem; the influence of gravity on the polar character of regeneration in a stem of *Bryophyllum* (2); the inhibitory action of apical leaves on the formation of shoots in the lower part of the stem; callus formation; inhibitory effects of a second order by an apical leaf; the inhibitory effect of an apical leaf on shoot formation in a stem suspended horizontally; the growth of the axillary shoots; some preliminary experiments on the path of the ascending and descending sap in the stem of *Bryophyllum*; concluding remarks.

"About a generation ago biologists devoted considerable time to a discussion of the vitalistic and mechanistic conception of life processes. The impulse for this discussion was given at that time by the experiments of Roux and of Driesch upon the development of eggs, parts of which had been destroyed or removed in the first stages of segmentation. It was generally or frequently observed that the development of the mutilated egg resulted in the formation of a normal organism. Driesch maintained that this phenomenon could not be adequately explained on a purely physico-chemical basis, but that in addition a metaphysical guiding principle inherent in the organism as a whole was to be postulated. The opposite view was held by Roux. The controversy was never settled, for the simple reason that on account of the microscopic size of the egg cells the experiments of both authors had to be purely qualitative. An adequate explanation of natural phenomena is possible only on the basis of quantitative experiments and such an explanation consists in the derivation of the results from a rationalistic mathematical formula (a so-called "law") without the introduction of arbitrary constants," p. v.

"The writer has for a number of years conducted quantitative experiments on the regeneration of a plant, *Bryophyllum calycinum*, which have made it possible to correlate the process of regeneration with the quantity of chemical material. By comparing the dry weight of the regenerated shoots and roots with the dry weight of the leaves or stems which were used for regeneration, it could be shown that in the presence of light the quantity of regeneration was under equal conditions of illumination, temperature, and in equal time in direct proportion to the mass of the leaves of stems from which regeneration started. If we make the legitimate assumption that the material required for the formation of new shoots or roots was under the conditions of our experiments produced by the chlorophyll contained in the leaf or stem, it follows that the quantity of regeneration is determined in this case by the mass of material available in the stem or leaf for synthetic processes. Under the guidance of this mass relation (which may be, in part at least, identical with the law of mass action), it could be shown that mutilation of the plant leads to a collection of sap in places where it would not have collected without the mutilation. This accounts for the fact that mutilation leads to growth in places of the organism where no growth would have occurred without mutilation. The process of regeneration was thus revealed as a purely physico-chemical phenomenon, leaving no necessity nor room for the postulation of a guiding principle aside from the purely physico-chemical forces," p. vi.

"It requires several weeks for a leaf or stem to produce new shoots and roots of sufficient quantity to permit exact weighings. If the time allowed for regeneration is too short, so that the roots and shoots are too small, the error made in cutting off the roots and shoots becomes considerable, since it is not possible to cut off these organs at their base with absolute accuracy. On the other hand, when the shoots reach a considerable size, they participate

to an increasing degree in the assimilation. As long as their assimilating mass is small compared with the assimilating mass of the leaf on which they grow, the error committed in neglecting this influence is small; if necessary it can be corrected by deducting the mass of the shoots from that of the leaf in calculating the influence of the active mass of the leaf on the production of roots or shoots. The writer carried on his experiments for about three or four weeks; in this time the mass of roots and shoots produced under the conditions of temperature and light prevailing in the greenhouse was sufficiently large to make the error committed in cutting off the roots and shoots comparatively small. In order to rule out accidental variations, each experiment was made on a larger number of leaves or stems, rarely fewer than six in one experiment," p. 10.

"It is obvious that the leaves suspended in air form a much smaller quantity of dry weight of shoots and roots per gram of dry weight of leaf during the same time and under the same conditions than the leaves dipping into water. Hence, if we accelerate the growth of some notches in the leaf, *e. g.*, by dipping them into water, we thereby inhibit the growth in the other notches.

"When leaves are suspended entirely and permanently in air, practically all the notches commence to form shoots and roots, but not all will continue to grow. Some notches will grow more rapidly than others and all the material will flow to the more rapidly growing notches. This explains why ultimately only a limited number of notches will continue to grow in air, usually in the more fleshy parts of the leaf.

"The fact that the sap available in a leaf flows to those notches where the growth is most rapid can be seen directly in leaves which form a purplish pigment (probably anthocyanin). This occurs only in leaves of *Bryophyllum* suspended in air, not in leaves which dip into water," p. 22.

"We now understand why the leaf of *Bryophyllum calycinum*, when it is detached from the plant, forms shoots and roots in its notches while this regeneration is inhibited when the leaf forms part of a normal plant. The leaf connected with a normal plant can be dipped into water without forming roots or shoots in its notches. All the material which might be available for shoot and root formation in the leaf is sent into the stem. During a recent visit in Bermuda, I have had a chance to examine thousands of plants of *Bryophyllum calycinum* without finding a single case where a leaf connected with a plant had formed roots or shoots. The same has been true in my greenhouse, and only recently have I had an opportunity to observe about six plants, the older leaves of which formed some tiny shoots. The plants in which this occurred were old and in two boxes containing no other plants; so that the suspicion is justified that their roots had suffered some common injury or disease. When a stem contains many leaves, and when the growth of the stem is stopped or when the sap flow has suffered, it is possible that shoots and roots may originate on leaves still connected with the stem. All that is needed for such growth is that the flow of material from the leaf into the stem should be partially or completely prevented," p. 41.

"It is the purpose of this little volume to show that a simple mass relation can be used as a guide through the bewildering maze of the phenomena of regeneration. This mass relation states that equal masses of isolated sister leaves produce, under equal conditions of illumination, temperature, etc., approximately equal masses of shoots and roots in equal time. With this relation it was possible to explain why isolation of a leaf leads to regeneration; namely, because the material available in the leaf for growth flows normally into the stem where it is used for the growth of roots, shoots, and of the stem itself. When a piece of stem inhibits the regeneration in a leaf the stem gains in dry weight to an amount equal to the diminution in the dry weight of shoots and roots in the leaf due to the stem. It was shown that this mass relation holds also for the the formation of roots and shoots in an isolated piece of the stem. Equal masses of stems produce under equal conditions of illumination, temperature, etc., approximately equal masses of roots and shoots in equal time.

"In both cases a second physiological factor was revealed which must be considered; namely, that the flow of sap in a leaf or stem is secondarily directed towards that part of a leaf or stem where the more rapid growth of shoots or roots occurs. This explains why only

some but not all of the anlagen for roots or shoots in a leaf or stem will persist in growing out; while the growth of the others will stop. This again would have remained merely a hypothesis had it not been possible to prove it quantitatively on the basis of the mass relation.

"A further complication arises in the fact of the polar character of the regeneration of roots and shoots in the stem of *Bryophyllum*. Two possibilities presented themselves for the explanation of this phenomenon: the polar character of the regeneration in the stem is either due to a difference in the chemical character of the ascending and descending sap or to a difference in the nature of the cells or anlagen which are primarily reached by the ascending and descending sap. It was possible to decide between the two hypotheses by using the mass relation, inasmuch as it could be shown that the shoots and roots formed in a piece of stem, increase with the mass of the leaf attached to the stem. Since the sap in the leaf forms shoots and roots in the same notch when the anlagen for these two organs exist closely together, the fact that shoots are formed at one and roots at the other end of a stem indicates that the ascending and descending sap of a leaf reach primarily different anlagen, and this conclusion was corroborated by two groups of facts; first, by directing with the aid of gravity the ascending sap in a stem to the tissues capable of root formation roots were produced in abundance by the ascending sap; and second, the mass of shoots produced in the basal part of the stem increased with the mass of an apical leaf. These facts seem to eliminate the idea that the polar character of regeneration is due to any chemical differences between the ascending and descending sap although such differences exist.

"The fact that certain mysterious substances like the "vitamines" or "hormones" may accelerate the rate of growth of an organ and consequently perhaps also the rate of regeneration, is neither in contradiction with the mass relation nor with its application to phenomena or regeneration. The sap sent out by a leaf contains probably all the substances needed for growth, inclusive also of "vitamines" and "hormones."

"It is quite probable that the principle of mass relation can serve as a guide in phenomena of regeneration in other organisms than *Bryophyllum*. In order to apply the principle we must be able to measure with a certain degree of accuracy the quantity of the material available for the synthetic processes underlying regeneration. This is possible in plants where the leaf is the main organ for the production of this material and where the light is the main source of energy for its production. It is also possible where we deal with definite quantities of stored material, as *e. g.*, in a potato, and where therefore the quantity of the mass of material available for regeneration can be varied at will. Unfortunately it is not easy to control the mass of available material for regeneration in animals. The material from which new organs are regenerated in animals must be furnished either by the food taken up or by the hydrolysis of material in the cells of the animal. All attempts to arrive at a rationalistic theory of regeneration in animals will have to rely on the use of organisms where the mass of material available for regeneration can be controlled as easily as in *Bryophyllum*," p. 141.

*Wilder D. Bancroft*

**The States of Aggregation.** *By Gustav Tammann. Translated by R. F. Mehl. 22×16 cm; pp. xi + 297. New York: D. Van Nostrand Company, 1925. Price: $5.00.* This is a welcome translation from the second German edition of Tammann's well-known book. The chapters are entitled: the states of aggregation; the equilibria of the states of aggregation; equilibria between vapor and liquid; the equilibrium curves; the melting curve; polymorphism; the phase diagram; the deformation of crystals and its consequences; the transition of an unstable into a stable state of aggregation; liquid crystals.

Boric anhydride appears to be a substance which does not crystallize at any temperature under atmospheric pressure, p. 38. With increasing pressure the melting-points of the tertiary alcohols are said to pass through a maximum, p. 96. From the pressure-temperature curves for the different modifications of ice, the author considers it possible that they may be isomers with a molecular weight of 54, p. 148.

"It is a fact worthy of notice that in some cases an expected transition will not occur, or will occur very irregularly, under ordinary conditions, but that in the presence of some medium the transition will take place promptly and completely. Such a case in the transition of ordinary tin into grey tin (transition point 20°) which ordinarily occurs very irregularly and with a great amount of supercooling. In contact with a solution of $SnCl_4$ the transition is regular, though requiring a good length of time for completion. Evidently the number of transition centers on the surface of the tin is greatly increased by the medium.

"The influence of dissolved admixture upon the transition point is also of interest. The crystal $Hg_6Tl_2$, m. p. 14.4°, in the pure state shows no transition point. An addition of 0.0038 percent Pb causes the appearance of a very significant transition point upon the cooling curve at 12-13°, accompanied by a discontinuous change in volume," p. 124.

"The blue earth in which diamonds are found imbedded may have worked up as olivine from a depth of 20-30 km., corresponding to a pressure of 6000-9000 kg./cm.$_2$ and a temperature of 1300°-1500°. Rapid cooling to 1000° could have produced the diamond as such. But there still remains a degree of uncertainty about the matter, for the beginning of the formation of graphite in diamond at 1000°C. is distinct after a period of twenty-four hours, whereas the half-liquid magma must have maintained a temperature above 1000° for a period considerably greater than twenty-four hours after the pressure had fallen to small values, and yet no paramorphs of graphite or of diamond have been found in the blue earth. Laboratory experience has shown that the important factor in the production of a new crystalline form is the temperature to which the original crystalline form is allowed to fall. At a definite temperature, in the course of the cooling, the number of crystallization centers increases very greatly, and in view of this fact it may be seen that a diamond crystal that had been once cooled would be much less stable at a temperature of 1300°-1500° than one that had never been permitted to cool.

"With respect to the artificial preparation of diamond it may be said that the transformation velocity of diamond decreases rapidly with the temperature upon a steep transformation curve, as, for example, upon the transformation curve of Ice I into Ice II. Experimental difficulties are multiplied by the fact that cylinders made of material with the greatest strength at high temperatures are likely to expand so greatly at a temperature of 1000° with pressure as low as 3000 kg. that the desired pressure rise of 6000-10,000 kg. becomes impracticable. Whether or not the transformation velocity of graphite into diamond at 1000° is noticeable cannot be said. At best such an artificial production of diamond would produce no large crystals but only a fine-grained crystalline conglomerate which could find use as an abrasive," p. 185.

"If a slowly increasing force be allowed to work upon a cube cut from a plastic crystalline conglomerate, such as copper, there will be seen upon microscopic investigation of the polished plane of the crystal parallel to the direction of pressure, fine, dark, parallel lines, in the individual crystallites. These gliding-lines are the traces of gliding-planes upon which the portions of each crystallite are displaced with respect to each other, and are so oriented to the direction of pressure that they exert a minimum of resistance to permanent deformation. The pressure at which the gliding-lines appear corresponds to the elastic limit, which may be exactly determined in this way. The elastic limit obtained for the operation of a pressure agrees with that found upon the application of tension. If the pressure be raised further, these gliding-lines appear in other crystallites, and with increasing pressure the angle of the gliding-line with the direction of pressure becomes sharper, and finally new sets of gliding-lines appear in the crystallites, intersecting the original set of parallel lines.

"The explanation of the fact that the gliding-planes do not form in all crystallites at the same pressure (with copper the first gliding-lines appear at 203 kg./cm.$_2$, and the last at 2000 kg./cm..) lies in the fact that the force at which gliding takes place in a crystal depends in great degree upon the orientation of the crystallites with respect to the direction of the force.

"Accordingly, all crystallites are finally divided by several systems of gliding-planes, and in this condition each crystallite can endure further deformations of a much greater magnitude. The piece, now divided into numberless small elements—as high as 1000 to

1,000,000 elements have been counted in a single crystallite—has obtained the ability to flow. With copper, the pressure at which flow begins, lies at about 2780 kg./cm.., and therefore exceeds the elastic limit thirtyfold." p. 200.

"Cold work upon a piece of metal causes the formation of laminated fragments to take place within the metal. With sufficient temperature increase very small, new crystallites appear at the boundaries of the laminated fragments, and these new crystallites increase in size until finally the whole piece consists of well-developed grains. Corresponding to the structural changes there also occur changes in the physical and chemical properties of the metal. In metallography this process is termed *recrystallization*. A somewhat similar process takes place in the union of the particles of amorphous bodies, and in the combination of liquid droplets to larger drops, but between the agglomeration or coalescence of isotropic particles and the union of anisotropic particles, a difference exists with respect both to the beginning of the process and to the structure of the end-product. At the beginning of the combination of anisotropic fragments there are formed, as has been shown with iron and copper, minute new grains at the boundaries of the fragments, whereas in the combination of amorphous fragments the process consists merely in a combination of *two or more grains into a larger grain. The end-product of recrystallization is a crystalline* conglomerate, the crystallites of which are separated from each other either by voids or by layers of varying thickness made up of non-isomorphous admixtures, whereas the combination of isotropic surfaces of the same composition leads to a physically homogeneous mass.

"The process of recrystallization plays a dominant rôle in many geological processes, such as the formation of glaciers, the production of marble from limestone, and the formation of crystalline schists. The process is of importance in the technology, not only of metallography, but also of ceramics. Unfortunately the workers in fields differing so much as these have little opportunity for the exchange of observations, and the valuable facts known to the one group have often remained unknown to the other," p. 205.

"The weight of many layers of snow deposited upon glaciers causes the snow crystals to form a grain-like glacier ice. In time this coarsely crystalline aggregate becomes clear, and in the coarse of years the size and character of the grains alter considerably. Accordingly, the undermost ice at the end of the glacier is made up of grains quite different from the grains formed first. Besides the grains of the sizes of a pin-head and a hazel-nut present in old glacier ice, there are frequently found gigantic grains 10 cm. in diameter. The grain-like structure of artificial ice of the clear glacial ice formed first upon the compression of the snow crystals is quite easily seen, especially when the grains in the ice are displaced relatively to one another by compression. In the new glacier ice the grains are generally irregularly oriented with respect to one another. In time, however, in addition to the growth of the grains, a re-orientation takes place so that in large masses of ice all of the grains have parallel optical axes. Investigation of this at different points upon Alpine glaciers has given different results with respect to the spreading of the sphere of similar grain orientation. E. v. Drygalski observed in old inland ice and in the deeper layers of icebergs of the antarctic the presence of grains varying in size from that of a pinhead to that of a hazel nut, which were optically similarly oriented," p. 217.

Tammann notes, p. 235, that a beautiful blue glass can be obtained by a suitable heating of difficulty fusible Jena glass. Since he does not add a black background, he has no real conception how beautiful these blues may be.

"If a liquid consist of two or more kinds of molecules, polymers, or isomers, and if the equilibrium between these molecules be dependent upon the temperature, the crystallization velocity can then be independent of the temperature only in the case where the equilibrium characteristic to the melting-point produces itself very rapidly, when the liquid is warmed to the temperature of the melting point," p. 270.

On p. 290 is the statement that the bright colors observed when cholesterol esters solidify slowly depend on the size of the spherulites suspended in the melt. This is inaccurate. The colors are a Christiansen effect and vary with the temperature.

*Wilder D. Bancroft*

# A RELATIONSHIP BETWEEN ATOMIC NUMBERS AND THE PROPERTIES OF IONS IN THE CRYSTAL LATTICE*

## III. The Metallic State—A Preliminary Study

BY ARTHUR F. SCOTT

The fundamental principle known as the Periodic Law carries the implication that the chemical characteristics of the elements are reflected in the physical properties of the solid state. The significance of this implication becomes more definite if it may be restated as follows: The physical properties of the elements in the solid state, say, the atomic volumes, are controlled by the identical factors that control the chemical behavior of the elements. Obviously, if we had a precise expression of this generalization, we should have information of value to our understanding both of chemical phenomena and of the crystalline state. But to demonstrate this assumption would necessitate not only a detailed knowledge of the structure of complex atoms but also a rather complete theory of the solid, metallic state. Both of these requisites, unfortunately, are wanting. Nevertheless it may be hoped that the general theory of the atom as developed by Bohr as well as the picture of the crystalline state afforded by X-ray analysis, will furnish a basis for a preliminary analysis of the problem, yielding, at the best, empirical results. Two attempts along these lines have already been made by the author, and the present study is a continuation of them. For the sake of simplicity the present analysis will be confined to the spatial distribution of atoms, which may be taken as typical of the physical properties of elements in the solid state.

In taking up this study it will be convenient to restrict ourselves at the outset to those elements whose ions have electronic structures similar to the corresponding inert gases and which form crystals of the so-called metallic nature. Furthermore, before starting out on an investigation of this limited and relatively simple group of elements, it will be necessary to formulate some concept of the metallic state. For this purpose we shall make certain postulates which, we have sufficient reasons for believing, are not incompatible with the actual conditions. We shall assume that metals consist of ions and "free" electrons, the latter being what we ordinarily consider valence electrons. The ions are bound together by electrostatic forces and are repelled by forces which are not purely electrostatic in nature. We may easily believe that the positions which the ions take in the crystal lattice and even the type of lattice depend in general on the action of these two forces. Hence, if we are to search for the determining factor of the lattice distance, we must discover the law of force which describes the net effect of these attractive and repellent forces. But this law of force is unknown; and further an understanding of the exact nature of the two forces of which it is a composite is complicated by several factors of which we shall mention two which are very important. First, the

*Contribution from the Department of Chemistry of Reed College.

repellent force is without doubt closely associated with the electronic structure of the ion and of this relationship atomic theory has thus far offered us no satisfactory explanation. And second, these forces cannot be separated from their dependence on the "free", valence electrons, concerning which we have no accepted hypothesis when they are in the crystal lattice. If, therefore, a knowledge of these two factors is vital to an understanding of the spatial properties of lattice structures, we may commence our analysis with an examination of the scant data available concerning them.

Regarding the ions themselves we have very little quantitative information. The elaborate theory of Bohr gives us a fairly good idea as to what quantum orbits the electrons occupy in the various ions. Our information does not go far enough, however, to give us the diameters of these ions, or rather of the orbits of the outermost electrons. If we take the distance from the center of the ion to the outermost point through which an electron passes, we may assume this distance to be the radius of domain of the ion, or conversely, if we know the radius of this domain we may assume that we have some measure of the extreme orbits of an ion. Some such arbitrary definition of ionic dimensions is necessary if we are to consider the atom to be a dynamical system. Now, Grimm[1] has computed the radii of domain of a number of ions after a method suggested by Fajans and Herzfeld,[2] and we may employ his data (Table I) to give us an idea as to the size of the orbits.

TABLE I

Ionic Radii and Values of f

| Valence | − − | − | o | + | ++ | +++ | ++++ |
|---|---|---|---|---|---|---|---|
| | | | He | Li | Be | B | C |
| $f \times 10^6$ | | | 2.32 | 5.8 | 12.9 | 23.2 | 38.6 |
| | O | F | Ne | Na | Mg | Al | Si |
| $r \times 10^8$ cm. | 0.89 | 0.75 | 0.63 | 0.52 | 0.39 | | |
| $f \times 10^6$ | 0.66 | 1.85 | 4.63 | 9.27 | 16.0 | 27.3 | 46.3 |
| | S | Cl | A | K | Ca | Sc | Ti |
| $r \times 10^8$ cm. | 1.09 | 0.95 | 0.87 | 0.79 | 0.67 | | |
| $r \times 10^6$ | 0.31 | 0.53 | 1.10 | 2.08 | 3.43 | 4.78 | 6.72 |
| | Se | Br | Kr | Rb | Sr | Y | Zr |
| $r \times 10^8$ cm. | 1.15 | 1.02 | 0.97 | 0.91 | 0.87 | | |
| $f \times 10^6$ | 0.28 | 0.38 | 0.73 | 1.29 | 2.06 | 1.78 | 2.28 |
| | Te | I | Xe | Cs | Ba | La | Ce |
| $r \times 10^8$ cm. | 1.24 | 1.12 | 1.10 | 1.07 | 1.07 | | |
| $f \times 10^6$ | 0.19 | 0.25 | 0.445 | 0.74 | 1.08 | 1.16 | 1.52 |
| | | | $Zn^{++}$ | $Cd^{++}$ | | | |
| $f \times 10^6$ | | | 16.0 | 1.90 | | | |

[1] Grimm: Z. physik. Chem., 98, 353 (1921).
[2] Fajans and Herzfeld: Z. Physik, 2, 309 (1920).

It should be noted, however, that Grimm's figures have no validity as absolute values and are probably too small because of the simplifying assumptions on which they are based; but there is considerable support for their relative magnitudes. One fact is obvious from these data: For a series of iso-electronic[1] ions the radius decreases with increasing nuclear charge, the atomic number.

If we are going to interpret this information by imagining the decrease in the domain of an ion with increase in nuclear charge to be brought about by a tightening of the electronic orbits about the nucleus, we must also believe the electrons in these orbits to be bound more and more firmly. As a measure of the firmness with which an electron is held in its orbit, we have the constraint, $f$, which is the restoring force when an electron suffers a displacement of one centimetre, assuming the force to be proportional to the displacement. Although this assumption would doubtless be incorrect for displacements of so great a magnitude as one centimetre, we may safely assume that it is true for the small displacements which do occur.

Smyth[2] has shown how this constraint may be calculated from the refractive index of the ions according to the formula:

$$f = \frac{4\pi N_o n e^2}{3M_\infty} \qquad (1)$$

in which $N_o$ is Avogadro's number, $6.061 \times 10^{23}$; n is the number of displaceable electrons per ion; e is the electronic charge; and $M_\infty$ is the molecular refraction for light of infinite wave-length. By making use of the data for the molecular refraction for the D-line of the individual ions obtained by Fajans and Joos, and Wasastjerna, Smyth has computed $f$ for various ions. These values are included in Table I. "In calculating $f$," says Smyth, "it was assumed that all the electrons in the outer layer of the atom or those whose orbits extended farthest out from the nucleus were capable of suffering displacement and thus contributing to the refraction, the others being too rigidly bound to have an appreciable effect upon the refraction." In spite of the fact that the values for $f$ presented in Table I are sufficiently accurate for the purpose they will serve, it must, nevertheless, be pointed out that the ingenious method employed in this determination of the refractivities of individual ions introduces certain errors which limit their validity.

A scrutiny of the data in Table I shows at once that in a series of iso-electronic ions the constraint increases as the radius decreases, which is the expected result. Moreover since both of these quantities depend ultimately upon the effective nuclear charge, it is only natural to expect some definite connection to exist between them. What this relationship is, will appear later when the subject has been examined a little more thoroughly.

Inasmuch as the constraint factor will subsequently be shown to be of considerable significance in the theory of the crystalline state, it is advisable

---

[1] We shall use the term, iso-electronic, to signify ions with the same electronic structure; e.g., He—Li—Be—B—C.

[2] Smyth: Phil. Mag., **50**, 361 (1925).

to investigate its relationship to the effective nuclear charge more completely. The dependence of the constraint on the nuclear charge seems to follow a uniform rule. For illustrative purpose, let us take as a typical case the effect of an increase in the atomic number upon the constraints of the iso-electronic ions of the first period and compare this effect to that produced in the iso-electronic ions of the second period. If to begin with we compare the constraints on the outer group of electrons in helium with those of neon, we should naturally expect to find a difference, first, because of the difference in nuclear charge, and second, because of the screening effect in the second case. Now, if the increase in nuclear charge affects both series of ions to the same degree, we should expect corresponding ions, say, lithium and sodium, to have their constraints in the same ratio as the constraints in helium and neon. Furthermore we should expect the same rule to hold for the other series of iso-electronic ions under discussion. That this interpretation is probably the correct one can be shown by plotting the constraints of the different series of iso-electronic ions against one basic series. In doing so, however, the limitations in the accuracy of the data made it impossible to decide whether the constraint or the square-root of the constraint was proper for such a comparison. In the course of this paper substantial grounds will be indicated for the choice of the latter function. Also, because of the convenience in plotting, the square-root of the constraint was selected and the values of $f$ for the iso-electronic series of ions of the neon-type were chosen to be the determinant points on the abscissa. This rather arbitrary procedure has no effect whatever upon the interpretation which has been presented above, which essentially is that the effective nuclear charge affects the constraints acting on the electrons in the outer group in any series of iso-electronic ions in a uniform manner. No more formal statement of this relationship is possible or necessary for our purpose at this time.

The results obtained by means of the foregoing scheme are portrayed in Fig. 1. Only a few observations need be made on this diagram. We could obviously attempt to approximate constraint values for some of the ions that are not given, such as $P^+$, etc., but this is scarcely justifiable in view of the known uncertainty of the data. And for the same reasons it does not seem advisable to conjecture regarding the significance to be attached to the juncture of the lines at point a. One alteration may nevertheless be suggested. The abnormally small values for scandium and titanium and the similar abnormality appearing in the points of the corresponding elements of the following periods may be taken as following in a general sense the predictions of the Bohr theory. But there is no obvious reason why the line though the points Sr—Y—Zr should show such a marked deviation from the behavior of the two adjacent lines. If we accept this conclusion, it is possible to draw a line, such as the dotted line, which would be free from this objection. From this line we may then interpolate new values of $f$ for Y and Zr, which hereafter we will designate as the hypothetical values.

We may adduce some further evidence to corroborate the above interpretation if we reverse the procedure used in Fig. 1. Take, for instance, the alkali metals. The differences in the constraints of these ions have been

attributed to differences in the structures of the ions and also to differences in the effective nuclear charges. Our premise so far has been that an increase or a decrease in the nuclear charge affects the constraint of each type of ion uniformly. Hence, if we were to plot against the constraint values for the alkali metals the constraints of the alkaline earth metals, where the nuclear charge has been increased by one, we should expect the latter values to be related to the former by some linear function. This has been done in Fig. 2

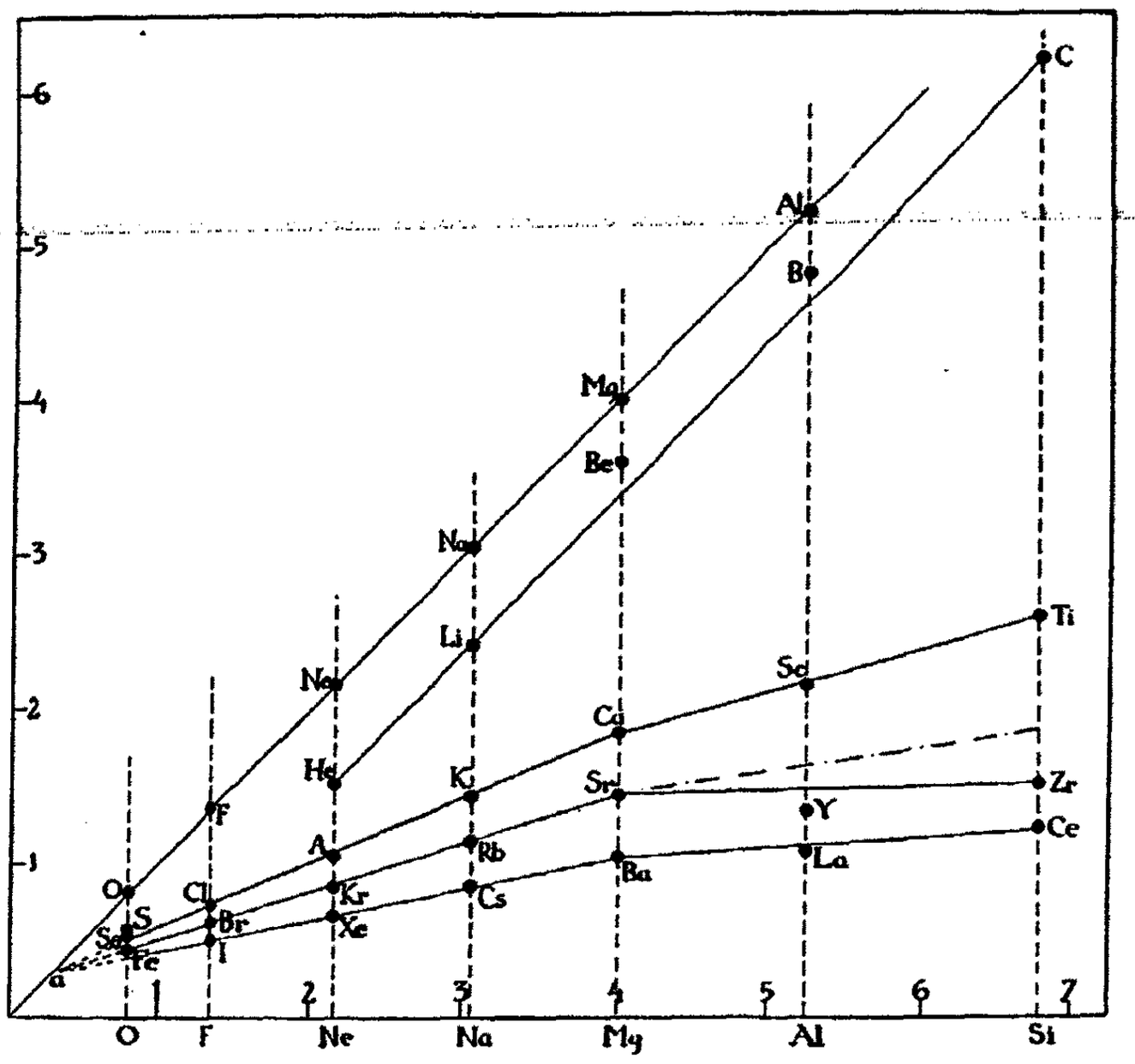



FIG. 1

Square-root of Constraint of Series of Iso-electronic Ions plotted against Square-root of Constraint of Ions of Second Period.

where the elements portrayed in Fig. 1 are plotted in this new manner, again using the square-root of the constraint. Here we find our expectations fulfilled, even to the predicted inaccuracy of the points for Y and Zr. In the present case as well as in the case to come up later, these hypothetical values (indicated by crosses in circles) obtained from Fig. 1 are found to be satisfactory. Inherent in the mode of plotting employed in both of these figures is the difficulty that if one of the abscissa points is in error, this error re-appears in all of the points plotted against it. For instance, an error in the constraint value of oxygen in Fig. 1 could be held largely responsible for the

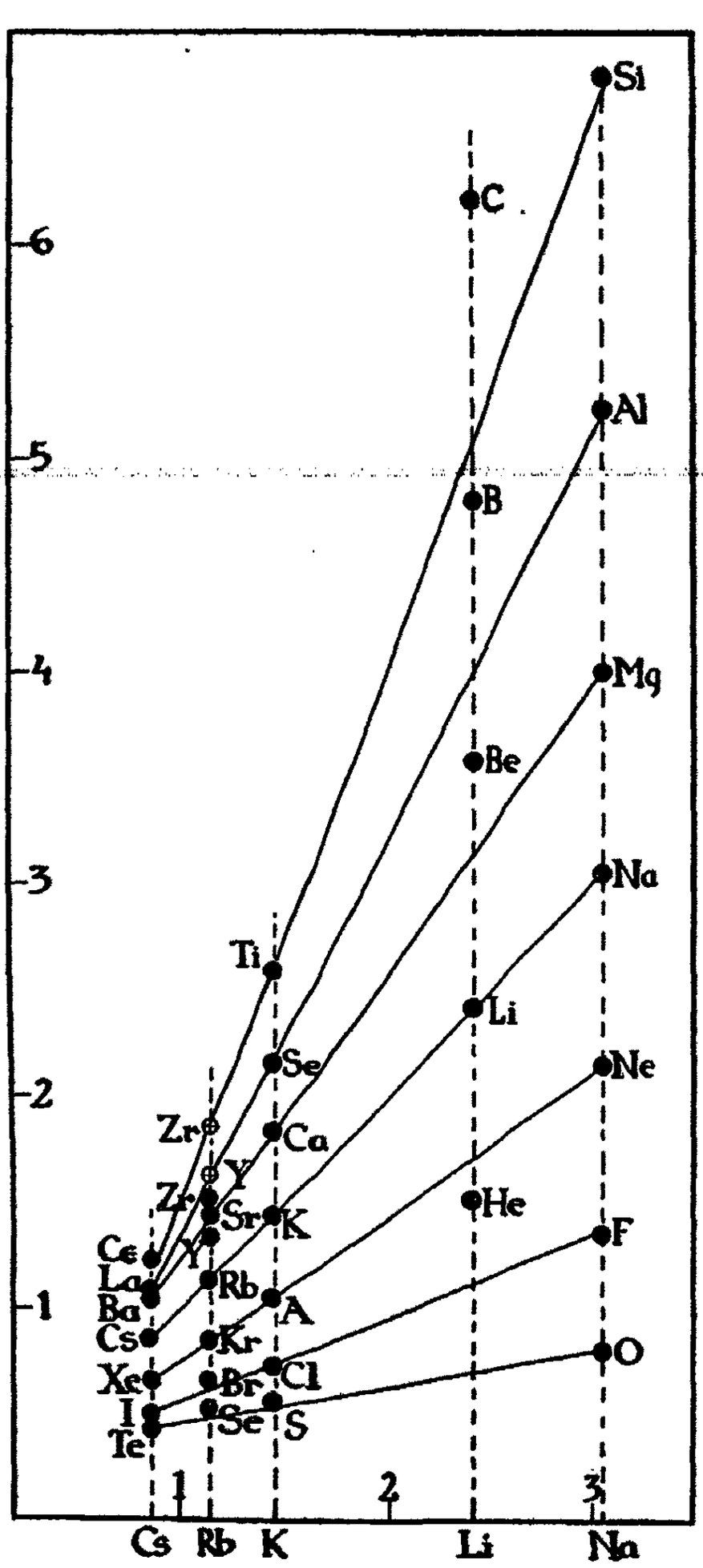



FIG. 2

Square-root of Constraint of Different Groups of Elements plotted against Square-root of Constraint of Alkali Metals.

discrepancies exhibited by the points plotted against it. Likewise, if in the same figure the silicon value were smaller, the agreement shown by the elements of the first period would be greatly improved. Again, in Fig. 2 if we could maintain that the helium point should come on the line through the points of the inert gases, the vertical line for the first period would be shifted to the left; and the point for beryllium would fall on the line of the third group elements and the boron point would come almost on the line of the fourth group elements. These last two cases are strongly suggestive of an analogous relationship well known in chemistry. But other assumptions would bring about the same results. For this reason it is easy to see the futility of attempting to reconstruct the two figures along hypothetically correct lines. Another observation which should not be ignored is the abnormal position of the points for the elements of the first period. The explanation of their unique and abnormal behavior must be sought in the great difference in the structure of these ions compared to that of ions in the other periods. It should be noted, however, that the constraints on the two electrons in this series of iso-electronic ions follow the same rule in respect to the atomic number as do the constraints in the other series of ions. Finally, from the satisfactory nature of the agreement shown in both of these figures, we may conclude that whatever the law of force is which controls the electrons in the outer group of an ion, it appears to be the same for any series of iso-electronic ions.

It has already been emphasized that the radius of domain of the ion and the constraint on the ionic electrons are both similarly dependent on the nuclear charge of the ion. Even though the exact relation is unknown in the former case just as in the second, we should naturally expect the radii to be capable of the same mode of treatment as we have used for the constraints in the first two figures. As a matter of fact they exhibit unmistakably the same characteristics. Nevertheless, corresponding representations are not given because they would not add materially to the foregoing statement, and for the further reason that the data are limited and only approximate.

Since there is no evidence to the contrary, we are justified in assuming that these two properties of ions, viz., the constraint and radius of domain, remain unaltered and follow identical rules irrespective of whether they are in solution, in the gaseous state, or in the solid state, so long as they are not subjected to any disturbing forces. But such a condition obviously cannot be realized in the crystal; for each ion must be affected to some degree by the ions which surround it and the presence of the valence electrons must likewise be of some consequence. If now we disregard the mutual influence of the ions themselves, we may obtain some information concerning the effect of the valence electrons upon the electrons in the ion by a consideration of the atom in the gaseous state. Here we have merely the atom consisting of the ion surrounded by the valence electrons. In such a case, as Compton[1] has pointed out, there is an attraction rather than a repulsion acting on the

[1] Compton: Science, 63, 53 (1926).

valence electron; and this attraction results from a distortion of the electronic shell of the ion in the field of the valence electron. In short, we see that the valence electron, although it has its own unique quantum orbit, is influenced to a certain extent by the outer group of electrons in an ion and vice versa. It is inconceivable that these influences should vanish completely when the atoms come together in a crystal lattice. A knowledge might be gained of the relationship existing between such a property as the constraint on the ionic electrons, on the one hand, and on the valence electrons, on the other, when the atom is isolated in the gaseous state. But this knowledge would be of little assistance in a study of the atom in the solid state because this latter relationship would probably be seriously modified by the added influence of the surrounding atoms.

Nevertheless, in spite of the complications introduced by the neighboring atoms, we may still expect to find some relationship between the ionic electrons and the valence electrons. Let us therefore test the suggested relationship between the constraints of these two groups of electrons. For this purpose, in addition to the data already presented in Table I for the constraints on the electrons in the outer group, we shall require values for the constraints on the valence electrons in the crystal lattice. To obtain these we need only accept Haber's "square-root" rule,[1] which is usually written:

$$\nu_v/\nu_r = \sqrt{M/m} \qquad (2)$$

Here M is the mass of an atom and m the mass of the electron. $\nu_r$ is taken to be the maximum infra-red frequency and $\nu_v$ is the "violet" frequency which corresponds possibly to the frequency of the maximum selective photo-electric effect. This is equivalent to stating that the constraints acting on the valence electrons in the crystal lattice are equal to the constraints on the ions. Now to compute the constraint acting on an ion in the crystal lattice we have recourse to the familiar formula:

$$k^{1/2} = 2\pi M^{1/2}\nu_r \qquad (3)$$

where $k$ is the constraint presumably acting on both valence electrons and ions alike in the crystal lattice; M is again the mass of the ion and $\nu_r$ the characteristic frequency. Table II contains values of $k$ computed by means of this equation. The frequencies employed in these calculations are taken from a compilation by the author.[2] In the few cases where known they are those obtained from heat capacity measurements. For the remaining cases the data are those computed by the author by means of a modification of Lindemann's melting-point formula. Finally, the mass of the ion, M, was determined by dividing the atomic weight of the element by the atomic weight of hydrogen and then multiplying this quotient by the mass of the hydrogen atom, $1.660 \times 10^{-24}$ gm.

[1] Haber: Verh. deutsch. physik. Ges., 13, 1117 (1911).

[2] Scott: J. Phys. Chem., 30, 577 (1926).

## Table II

"Nearest Approach" of Ions and Values of k

| | Li | Be | B | C |
|---|---|---|---|---|
| $k \times 10^4$ | 4.77 | 28.5 (36.6) | 77.2 | 118.6* |
| $d_o \times 10^8$ cm. | 3.03 | 2.28 | (1.86) | 1.54 |
| | **Na** | **Mg** | **Al** | **Si** |
| $k \times 10^4$ | 2.21 | 8.49 | 12.1* (17.8) | 29.1 |
| $d_o \times 10^8$ cm. | 4.00 | 3.22 | 2.860 | 2.35 |
| | **K** | **Ca** | **Se** | **Ti** |
| $k \times 10^4$ | 1.60 | 6.64 | (14.1) | 23.4 |
| $d_o \times 10^8$ cm. | 4.48 | 3.93 | (3.41) | 2.90 |
| | **Rb** | **Sr** | **Y** | **Zr** |
| $k \times 10^4$ | 1.22 | 5.61 | 10.9 | 17.0 |
| $d_o \times 10^8$ cm. | 4.93 | 4.33 | 3.75 | 3.18 |
| | **Cs** | **Ba** | **La** | **Ce** |
| $k \times 10^4$ | 0.88 | 5.24 | 8.4 | 10.6 |
| $d_o \times 10^8$ cm. | 5.34 | 4.52 | 4.0 | 3.64 |

The figures for $k$ enclosed in brackets are the hypothetical ones obtained by the author in the above-mentioned communication; the values marked by an asterisk are based on frequencies obtained from heat capacity measurements; the value of $k$ for cerium is the hypothetical one mentioned later in connection with Fig. 3. The lattice distances are taken from another paper by the author.[1] Here again hypothetical figures are enclosed in brackets. It is of interest to compare the value for diamond given in Table II with the figure computed by Smyth from refractive index measurements. The latter figure is $1.10 \times 10^6$, which is very close to the value given above.

In Fig. 6 are shown the results obtained when the constraint $k$ acting on the valence electron is plotted against the constraint $f$ acting on the outer group of electrons of the ion. A glance at this graph shows clearly that these two constraints are related by a simple linear function for each series of isoelectronic ions. A few features of the figure call for comment. The line representing the elements of the first period is drawn so that it passes through the point for diamond. In order to simplify the diagram, only the hypothetical values of $f$ for yttrium and zirconium are given and they seem to be perfectly satisfactory. The points $Be_1$ and Al are obtained by using the hypothetical values of $k$ given in Table II. The sole outstanding defect in this linear relationship is readily seen to be the point for silicon. Whether this deviation

[1] Scott: J. Phys. Chem., 29, 304 (1925).

is real and is due to a faulty value for $f$, or whether it concerns some inherent property of the ionic forces cannot be decided at this time. Nor can any explanation be offered regarding the interpretation to be placed on the exist-

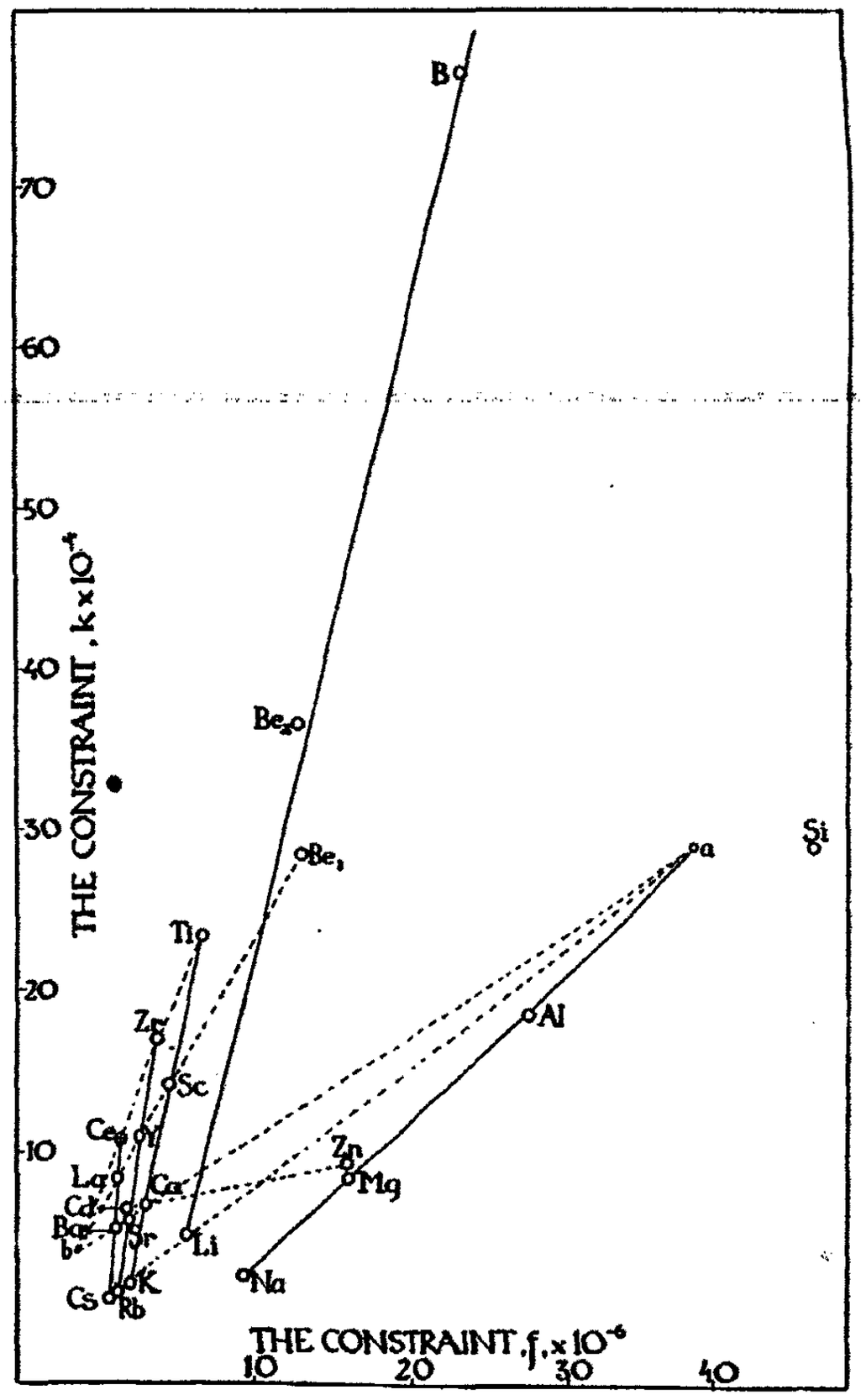



FIG. 3
Constraint on the Valence Electrons plotted against Constraint on Ionic Electrons.

ence of the two focal points, a and b. It is a suggestive fact, however, that the value of $f$ for the point a is precisely that of the carbon ion.

The correct interpretation of the results of this figure may possibly yield valuable information for the understanding of the metallic state. The obvious deductions when combined with Haber's "square-root" rule enable us

to propose a simple principle: Ions and electrons in the lattice of a metal are subject to the same forces and they are so assembled that this force, measured by their constraints, is linearly related to the constraints on the outer group of electrons of the ion when a series of iso-electronic ions is considered. If we may regard this principle as a necessary condition for the existence of a metallic crystal, we have some intimation as to the cause of the different orientations which iso-electronic ions take in the crystal lattice. For it is not easy to see how the type of lattice could be determined either by the structure or by the size of ions alone.

If the slopes of the lines in Fig. 3 are intrinsically characteristic of the structure of the ions—and this is practically the only possible assumption—, we are then in a position to make another instructive deduction: The valence electrons in the metallic state are to be regarded as still integral components of the atom and are subject to the same forces which control the electrons in the ions, namely, the so-called atomic forces. While this deduction is not very surprising, we have in it further confirmation of the evidence already accumulated against the classical theory of the "free" electron.

Verification of the conclusion that the valence electrons in the metallic state are subject to the same law of force as the more firmly bound electrons in the ions proper may be sought in still another direction. It has already been suggested that some definite relationship exists between the radius of domain of an ion and the constraints of the outer group of electrons on the grounds that they both depend ultimately on the same factors. Consequently, if our guiding idea is correct, we are justified in expecting a quite similar, if not identical, relationship to exist between the constraint $k$ and the distance between the valence electron and the center of the ion, that is, the radius of the atom. Inasmuch as the data for the solid state are on the whole more reliable than those for the ions, it seems advisable to examine the former case first in order to ascertain what the relationship actually is.

The problem of analyzing this relationship brings us back to the original object of this study—the correspondence between the spatial attributes of the elements in the solid state and their chemical properties. In order to avoid any subsequent misunderstanding we are going to make the assumption that the square-root of the constraint, $k^{1/2}$, is essentially a measure of the "affinity" of metals for their electrons. Although an indisputable proof of this assumption cannot be given at this time, a fairly sound basis can be indicated in a rather roundabout manner. Equation (2) shows that the ultra-violet frequency of the electron is proportional to the square-root of the constraint, $k^{1/2}$. Lindemann[1] has demonstrated that this ultra-violet frequency is doubtless the frequency of the maximum selective photo-electric effect. Just at present, to be sure, there is some question as to the identity of this frequency and the threshold frequency of the normal photo-electric effect. But in any case, they must be closely associated. Consequently, we are reasonably safe in supposing that the product of this frequency by Planck's constant would,

[1] Lindemann: Ber.deutsch. physik. Ges., 13, 1107 (1911).

according to the well-known equation of Einstein for photo-electric emission, give us a measure of the intrinsic potential of a metal. And this is only an indirect way of saying that the square-root of the constraint which we will employ is substantially a measure of the forces of chemical "affinity".

Now, a possible relationship between the constraint $k$ and the lattice distance $d_o$ (which, of course, is twice the radius of the atom according to our

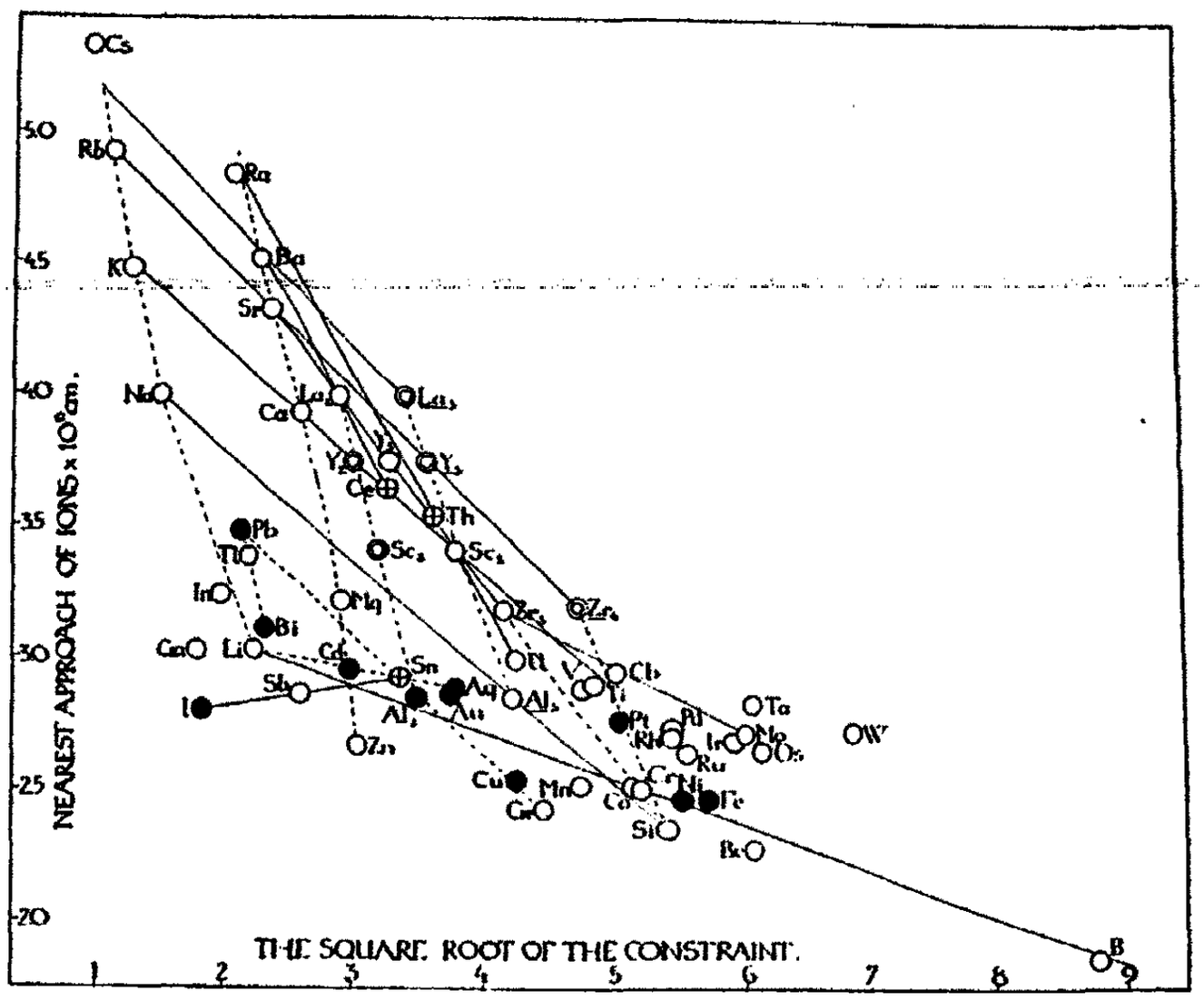



FIG. 4

Variation of Lattice Distance with Square Root of Constraint on Ions and Valence Electrons.

definition) has already been suggested by the author in the more recent communication of the two already cited. It may be expressed by the formula:

$$d_o = m\, k^{1/2} + n \qquad (4)$$

where m and n are constants for certain series of elements. To demonstrate its validity it will be advisable at this time to plot one variable against the other because nothing is known about the constraints involved. (See Fig. 4). For this purpose we shall require only the data contained in Table II. Where the data are reliable enough points for other elements than those represented in Table II have been offered (See Table III) in the hope that they may prove helpful towards an understanding of the characteristics of the graph. These additional data are from the same sources and have been computed in the same way as those contained in Table II.

## TABLE III

### Additional Values of $d_o$ and k

| Element | $k^{1/5} \times 10^2$ | $d_o \times 10^8$ cm. | Element | $k^{1/5} \times 10^3$ | $d_o \times 10^8$ cm. |
|---|---|---|---|---|---|
| Vanadium | 4.75 | 2.89 | Cadmium | 2.98* | 2.96 |
| Chromium | 5.21 | 2.508 | Indium | 1.97 | 3.24 |
| Manganese | 4.74 | 2.55 | Antimony | (2.58) | 2.87 |
| Iron | 5.70* | 2.472 | Tin | 3.37* | |
| Cobalt | 5.14 | 2.514 | Iodine | 1.82* | 2.80 |
| Nickel | 5.50* | 2.474 | Tantalum | 6.04 | 2.83 |
| Copper | 4.24* | 2.543 | Tungsten | 6.84 | 2.732 |
| Zinc | 3.04 | 2.670 | Osmium | 6.11 | 2.66 |
| Gallium | 1.77 | 3.03 | Iridium | 5.88 | 2.690 |
| Germanium | 4.46 | 2.43 | Platinum | 4.04* | 2.766 |
| Columbium | 5.00 | 2.95 | Gold | 3.74* | 2.874 |
| Molybdenum | 5.98 | 2.720 | Thallium | 2.19 | 3.38 |
| Rhuthenium | 5.52 | 2.640 | Lead | 2.12* | 3.479 |
| Rhodium | 5.42 | 2.700 | Bismuth | 2.32* | 3.11 |
| Palladium | 5.42 | 2.729 | Thorium | | 3.54 |
| Silver | 3.77* | 2.884 | Uranium | 4.23 | 2.99 |

The asterisks and brackets possess here the same significance as in Table II.

The foregoing equation (4) has been arrived at by the elimination of the logarithmic term from the following two equations, which the author in the two previous communications already mentioned has shown to be reasonably accurate:

$$d_o = a \ln (Z+e) + b \qquad 5a$$

$$k^{1/5} = a' \ln (Z+e) + b' \qquad 5b$$

Here Z is equal to the atomic number, and e the maximum number of valence electrons. The constants a, a′, b, and b′ are characteristic of certain series of ions. Obviously equation (4) will hold true only for those series of elements which are describable by both equation (5a) and equation (5b). Incidentally, the elimination of the logarithmic term furnishes a much more desirable condition for plotting, and the outcome may be used as a test of the validity of the two basic equations.

Because of the inherent uncertainties in the data, it was found necessary in constructing the graph to follow the above conditions with care. For this reason it is deemed advisable to list those series of elements for which we are justified in expecting equation (4) to hold. They are:

1. Li – Be – B – C
2. Na – Mg – Al – Si
3. K – Ca – Sc – Ti
4. Rb – Sr – Y – Zr
5. Cs – Ba – La –
6. K – Rb – Cs
7. Ca – Sr – Ba – Ra
8. Sc – Y – La

With this outline before us we may now proceed to examine the results in the individual series. The lines for Series 6, 7, and 8 are fully satisfactory,

especially when due regard is paid to the source of the data. In Series 1 (the line passes through the point for carbon) the agreement is satisfactory. The same is true of Series 2, for almost the same discrepancy in $d_o$ for magnesium appears in plotting equation (5a); further, it should be observed that the point $\underline{Al}_3$ corresponds to the hypothetical constraint value already mentioned in connection with Fig. 3. In Series 3 the slight error in the constraint value for titanium is not unexpected. But it must be made clear that the constraint values for the points $\underline{Y}_3$ and $\underline{La}_3$ were chosen arbitrarily so as to comply with the stated conditions. This action is justifiable only on the grounds that the basic measurements for these constants are hardly reliable. But such an excuse is not available for the point $Zr_4$, even if we conjecture an error in the basic measurements due to a possible hafnium contamination. Because the constraint data are most susceptible to error, we could assume provisionally the lattice distance to be correct and then determine where the point for zirconium should come on the line through the points Rb and Sr. It comes at the point $\underline{Zr}_4$, which also lies, curiously, on a prolongation of the line through the points for silicon and titanium.

The difference between the constraint values of the points $Zr_3$ and $\underline{Zr}_4$ is far too great to be attributed to experimental error. Here we encounter the first unambiguous conflict with our conditions. The error must be sought in the validity of equation (5b). It will therefore be profitable to digress at this point and examine this relationship more closely. The situation is portrayed on a large scale in Fig. 5. Here the points $Rb_1$, $Sr_2$, $Y_3$, $Zr_4$, $Cb_5$, and $Mo_2$ are plotted according to the requirements of equation (5b). In the original communication dealing with this equation, a line was drawn through all the points except that for strontium, and the high value for this element was attributed to inaccurate melting point information. But a more careful study shows that this conjecture is highly improbable, and moreover, that if true it would completely disrupt the scheme of the graph, throwing the barium value out by too great an amount. There is an alternative method of plotting which deserves careful consideration. It is indicated by line A. The agreement, although only fair, is not unsatisfactory.

The possible interpretations of the break in this line, A, will become more definite after we have examined some further features of this graph. Heretofore we have found that the slope of the line representing equation (5b) was determined by the points for the first two elements in any period. Therefore let us draw a line through the points Rb and $Sr_2$, which we shall designate as line B, and which we shall refer to hereafter as the line of normal variation. Now, if we assume the number of valence electrons in zirconium to be 3 instead of 4, we get the point $Zr_3$ which, as is seen, falls precisely on line B. We might infer therefore that the constraint of zirconium is under the influence of only three valence electrons. But no such device will cause the actual constraint values of the other divergent elements to fall on line B, although certain regularities between the plotted points are apparent. On the other hand, if we ascribe to all the elements 3 valence electrons, we obtain the line C, in which the only marked defect is the questionable point for

strontium. This result can scarcely be fortuitous. And yet, if it is not accidental, it means that in the term ln (Z+e), e is characteristic of this series of ions and that the constraint is subject only to the effect produced by changes in the atomic number. Without going into the matter more deeply, we may observe that in the line C the only point that is common to the original line, A, is the point $Y_3$, a fact that may be of real significance.

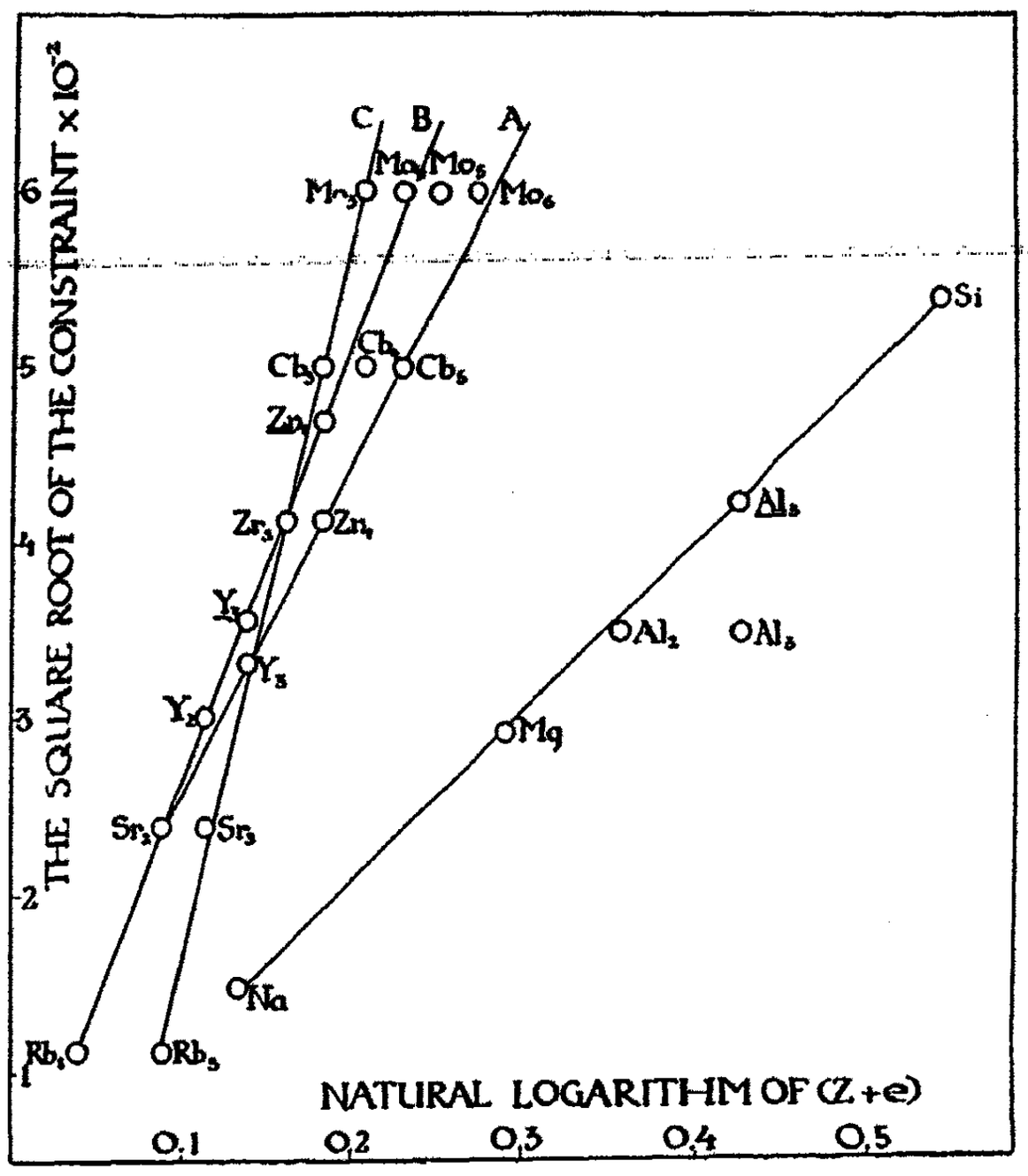



FIG. 5

Variation of $k_j$ with Function of Atomic Number and Number of Valence Electrons.

There is still another feature of this graph that should perhaps be pointed out. We may obtain the ideal hypothetical point $\underline{Zr}_4$ on the line B, and in view of the above conditions it is not surprising to find that this constraint figure corresponds exactly to that of point $\underline{Zr}_4$ shown in Fig. 4. And the same is true of the ideal point $\underline{Y}_3$. What is singular, however, is the fact that if we should obtain in the same way the hypothetical constraint values for columbium and molybdenum when e = 4; and if the points for these elements in Fig. 4 are plotted from these values, the points lie on the line through

the points Rb, Sr, and $\underline{Zr}_4$. This is only another way of saying that the lattice distances of columbium and molybdenum behave as though they were controlled by four valence electrons while the constraints are subject to entirely different factors.

Similar and less qualified evidence of the same nature is afforded in the case of aluminium. In Fig. 5 the points for sodium, magnesium, aluminium, and silicon are plotted on the same scale as the other lines although there is no relation between them. Here the point marked $Al_3$ is based on the constraint figure calculated from the frequency value obtained from rather accurate heat capacity measurements. In the author's previous communication it was shown that this frequency value was much too low to comply with the type of variation exhibited by the other elements. Consequently a normal hypothetical quantity was determined by interpolation. Subsequently it was noted that the constraint calculated by means of this hypothetical frequency fell precisely on the line as indicated by the point $\underline{Al}_3$ in Fig. 5; but itwas also on the extension of the line through the points for scandium, yttrium, and lanthanum. Now it is clear that the point $\underline{Al}_3$ is analogous to the point $\underline{Zr}_4$ and is the hypothetical ideal point. To bring the actual constraint quantity on the line of normal variation it is only necessary to set $e = 2$; and the result is shown in Fig. 5 by the point $Al_2$. Here again we have a case where the lattice distance seems to be determined by the maximum number of valence electrons whereas the constraint is subject to the influence of a lesser number. What is most significant, however, is the fact that the divergence from the normal may be attributed to the effect of an integral number of electrons.

If the cases just cited are accepted as establishing a criterion for the number of valence electrons affecting the constraint, a number which is smaller than that controlling the lattice distance, we are at once faced with the difficulty of accounting for the "lost" electron or electrons as the case may be. But this difficulty is due to the lack of a suitable theory of the metallic state, a problem which is still unsolved. The following suggestions, however, may have some bearing on the difficulty in question.

Since we have already tentatively proposed to consider the behavior of the valence electrons in the metallic state to be somewhat analogous to their behavior in the atom, that is, to be subject to the same fundamental forces, it is only natural to turn first to atomic theory for information. Now, according to the Bohr theory, the Z-th electron in potassium, rubidium, and cesium skips the most probable quantum orbit and takes up a position in an orbit possessing less energy. This abnormality in filling up the orbits is ascribed to the effect of the ionic shell of electrons made up of $(Z-1)$ electrons about the nucleus. But this effect persists only for the next few additional electrons in each period when the concomitant increase in the nuclear charge offsets the disturbing influence of the ionic shell and compels the additional electrons to follow the normal rule. This break in the sequence is supposed to occur at scandium, yttrium, and lanthanum in the respective periods. In fact such a break has already been observed in Fig. 1. Hence, since in that figure we

were dealing only with ions, we must attribute the break to a change in the forces which control the electrons in the outer group and which are inherent in the atom. Consequently, if the relation of the valence electrons to the ionic electrons is as intimate as we have supposed it to be, we may reasonably believe the abnormality encountered in zirconium to be the natural result of these changes in the atomic forces. An alternative view of the matter would be to assume certain fixed states for the valence electrons in the metallic state analogous to the orbits in the atom. Then the "effective" valence electrons may be assumed to be those in the outermost positions. But this conception of the situation also has many obstacles to overcome. Obviously it is too early to make a guess at the correct solution because we have no convincing hypothesis of the metallic state; yet these considerations will be of assistance in deciding the line of further analysis and in understanding the results.

Returning to the examination of Fig. 4, it is clear that if the above ideas have any bearing on the deviation of the point for zirconium, we must look for divergences in other cases. In fact the break in any sequence should make its first appearance, at least according to the first alternative, at scandium, yttrium, and lanthanum. In a word, a mistake was presumably made in establishing the conditions for the construction of Fig. 4. The revised conditions to be substituted for the similarly numbered conditions already given are:

3a. K — (Ca) — Sc — Ti
4a. Rb — (Sr) — Y — Zr
5a. Cs — (Ba) — La

The elements where a discontinuity is to be expected are enclosed in brackets. The problem now is to investigate this set of new conditions. Regarding Series 3a nothing definite can be stated because all the information about the critical element, scandium, is hypothetical. It may be observed, however, that the constraint value for the point $Sc_3$ is the one employed in making Fig. 3; but if we were to consider scandium to be analogous to aluminium, we should have the point $Sc_2$. Two singular relationships of this last point may be indicated: first, it lies on the line through the points $Zr_3$, Cb, and Mo; and second, a line through it and the point Ti most probably passes through the point for boron. More confidence may be had in discussing the other two series, for we have some actual measurements to go by. The conditions of Series 4a are fulfilled completely; moreover, a continuation of the line through the points of the last three elements passes clearly through the point for silicon. This relationship is doubtless associated with the fact that the point for thorium (obtained by plotting the value of $d_o$ on the line through the points Ra and U) lies also on the line through the points $Zr_3$ and Si. In connection with the data for Series 5a, a statement should perhaps be made concerning the point for lanthanum. Apparently there is a similarity between the properties of this element and those of zirconium because the constraint value, if determined in a manner analogous to that used in Fig. 5, is identical for lines A and B when $e=3$ and 2 respectively. Finally, as can be seen in Fig. 4, the points $Sc_3$, $Y_3$, and $La_2$ satisfy the conditions set down for Series 8.

While these results are consistent with our theoretical expectations, they are not decisive enough to permit a definite explanation of the cause of the break in the mode of variation of $d_o$ with $k^{1/4}$. An examination of the conditions in the ions would be of great assistance towards an understanding of this difficulty. For it has already been suggested that a relationship analogous to equation (4) should hold for the radius of domain of the ion, $r$, and the constraint $f$. Such an expression would be:

$$r = c\, f^{1/6} + d \qquad (6)$$

In this equation c and d are constants analogous to m and n in equation (4). For the object in question the necessary data are wanting. But a representation of the data in Table I shows that equation (6) holds well within the limits of the accuracy of the data. The graph is not given, however, because it would not contribute especially to the discussion. The fact that equation (6) does hold approximately shows two things: first, why the square-root of the constraint was used in Figs. 1 and 2; and second, that the premise regarding the subjection of valence electrons to the same law of force as the ionic electrons is not entirely impossible.

Our results so far may now be viewed from the standpoint of our original problem, which concerned the relationship between the so-called chemical forces and the atomic volumes of the elements. If we consider the lattice distance so as to avoid the complications involved in the different types of lattice structure, and if we remember that $k^{1/4}$ is taken as a measure of the chemical "affinity", we may conclude that there are definite limitations to the correlation of these two factors. These limitations appear presumably because of certain divergences in the variation of the lattice distances and constraint forces in respect to the atomic forces. The normal rule which we assumed to describe the variation in the above cases is evidently modified in the latter case by some factor closely allied to the atomic forces. It is noteworthy, furthermore, that this modifying factor may be traced to the effect of valence electrons. Finally, it will be observed, the limitations just mentioned do not seriously vitiate the validity of the generalization that there is a relative correspondence between changes in spatial dimensions and chemical forces in the cases of those elements whose ions have structures similar to the inert gases.

While for this simple class of metals the variation of the lattice distance with the square-root of the constraint is rather clear, the case of the other metals is quite different. Such a result is now intelligible because of the greater variability in valence which these elements exhibit. The situation for many of the remaining elements is portrayed in Fig. 4. A word should perhaps be said concerning the point for tin. Since the lattice distance is unknown exactly, a line was drawn through the points for germanium and lead, and the proper constraint value was plotted on this line. The result seems to be peculiarly satisfactory. The line through the points for magnesium, zinc, and cadmium should be remarked especially because of the deductions of Bohr based on his interpretation of their spectra. In general, however, the behavior of different groups and periods of this class of metals is altogether

different from that of the other type. Not only is this due to the greater possibilities of valence variation but also to the entirely different electronic structure of the ions. A feature that is somewhat puzzling, nevertheless, is the frequent interrelations shown by the points of these two groups of metals. A discussion of the characteristics of the second group must be postponed, however, until a subsequent communication in which the author hopes to show the underlying principle which is common to these two groups of metals and the non-metallic elements.

All the difficulties thus far encountered may conceivably be focussed in one general problem which concerns itself with the rôle played by the electrons in determining the constraint and the lattice distance in a metallic crystal. Whereas for a series of iso-electronic ions each valence electron has a definite and uniform effect upon the lattice distance, the effect produced on the constraint is not the same, even though it apparently follows a simple rule. If this divergence, however, were the only difficulty, it might possibly be overcome by making certain postulates: either that the effect of a valence electron on the lattice distance is invariable while the constraint is determined by the outermost electrons; or that the non-uniformity in the constraint variations is inherent in the structure of the atoms themselves. But actually this is not the sole difficulty. There is also the difficulty of accounting for the uniform effect these valence electrons have, no matter what the structure of the parent ion may be; witness the parallelism of the lines through the points of the elements of the first, second, and fourth groups. This effect becomes even more pronounced if we make one further hypothetical assumption. Let us assume that yttrium and lanthanum have two valence electrons such as we have concluded aluminium to have. To get the constraint values under this condition we have merely to interpolate on the normal line, B, in Fig. 5. The desired point is $Y_2$. The values for scandium and lanthanum can be obtained in the same way. These latter values are designated by the points $Sc_2$ and $La_2$ in Fig. 4. Now, when they are plotted in Fig. 4, it is seen that a line passes through them as well as through the corresponding point for aluminium, $Al_2$, and that the line is parallel to the other group lines.

There remains still unanswered the question why the lines for the different groups are straight lines like the lines for the different periods. But since they are straight lines and practically parallel, a situation which seems to be true also of the lines for the second, third, and fourth periods of elements, it is only natural to expect to find other interrelations of the points for the elements. But because no significance can be attached to these further relationships, a summary of them is omitted.

In the light of the evidence here presented it is at once apparent that the metallic state is exceedingly complex. To account for some of the results we could jump to the conclusion that there is a sort of equivalence in the effect of valence electrons and the effect of the various ionic groupings of electrons; but this would explain nothing. Or, we could outline the chain of evidence pointing unmistakably to the conclusion that the properties of the metallic

state which we have discussed are definitely linked to the atomic forces. But this statement too would add little to the belief which is practically universal. These two ideas may be united by assuming that the valence electrons are not solely responsible for the similarity in properties of the different groups of elements. To restate this in another way, the inherent atomic forces which arrange the Z electrons of an atom in such a way that there are *e* valence electrons manifest themselves also in the similar nature of the ionic forces of all atoms with the same *e* electrons. In short, therefore, we may look for a similarity in ionic forces as well as for a similarity attributable to the presence of an equal number of valence electrons. In fact the frequently emphasized similarity in properties between elements of different valences such as beryllium and aluminium, and boron and silicon, shows that the valences are not the sole determining factors. Moreover, one could argue from the unique similarity in the ionic forces of the inert gases that this similarity does not vanish completely with uniform increases in the nuclear charge. Indeed, Figs. 1 and 2 are based on an assumption somewhat like this.

Despite the rather obscure character of the principle underlying the above considerations, it may be possible to see some confirmation of it in the following data. In Table IV are given the atomic volumes of a number of elements obtained by dividing the volume of one gram atom by Avogadro's number. We thus have a quantity which represents roughly the volume ascribable to a unit atom. The data employed to compute these volumes are taken from Landolt-Börnstein's Tabellen. Now, to determine the "electronic" volume, that is, the volume ascribable to each electron in an atom, assuming them all

TABLE IV

Atomic Volumes and "Electronic" Volumes

| Element | Atomic Vol. $\times 10^{23}$ cc. | "Electronic" Vol. $\times 10^{24}$ cc. | Element | Atomic Vol. $\times 10^{23}$ cc. | "Electronic" Vol. $\times 10^{24}$ cc. |
|---|---|---|---|---|---|
| Lithium | 2.16 | 5.39 | Rubidium | 9.26 | 2.44 |
| Beryllium | 0.81 | 1.63 | Strontium | 5.73 | 1.47 |
| Boron* | 0.73 | 1.22 | Yttrium* | 3.44 | 0.86 |
| Carbon | 0.57 | 0.81 | Zirconium | 2.36 | 0.58 |
| Sodium | 4.01 | 3.34 | Columbium | 1.98 | 0.47 |
| Magnesium | 2.32 | 1.78 | Molybdenum | 1.56 | 0.36 |
| Aluminium | 1.67 | 1.19 | Caesium | 11.80 | 2.11 |
| Silicon | 1.99 | 1.33 | Barium | 6.51 | 1.14 |
| Potassium | 7.53 | 3.77 | Lanthanum | 3.75 | 0.65 |
| Calcium | 4.29 | 2.04 | Cerium | 3.31 | 0.56 |
| Scandium* | 2.77 | 1.26 | Lead | 3.02 | 0.36 |
| Titanium | 1.78 | 0.77 | Tantalum | 2.08 | 0.28 |
| Vanadium | 1.87 | 0.78 | Radium | 7.83 | 0.88 |
| Germanium | 2.21 | 0.67 | Thorium | 3.50 | 0.31 |

*From a compilation by Sommerfeld: "Atomic Structure and Spectral Lines," page 99.

to be equally dispersed, use is made of a device of Bridgman.[1] Assume the nuclear charge to be of the same dimensions as the electrons. Then the "electronic" volume of an electron in an atom of atomic number Z is equal to the aforesaid atomic volume divided by the quantity (Z+1). These figures are also included in Table IV. Although there is no physical significance to be attached to the "electronic" volumes, we may consider them to be a measure of the degree of packing of the electronic orbits in the atom when in the solid state.

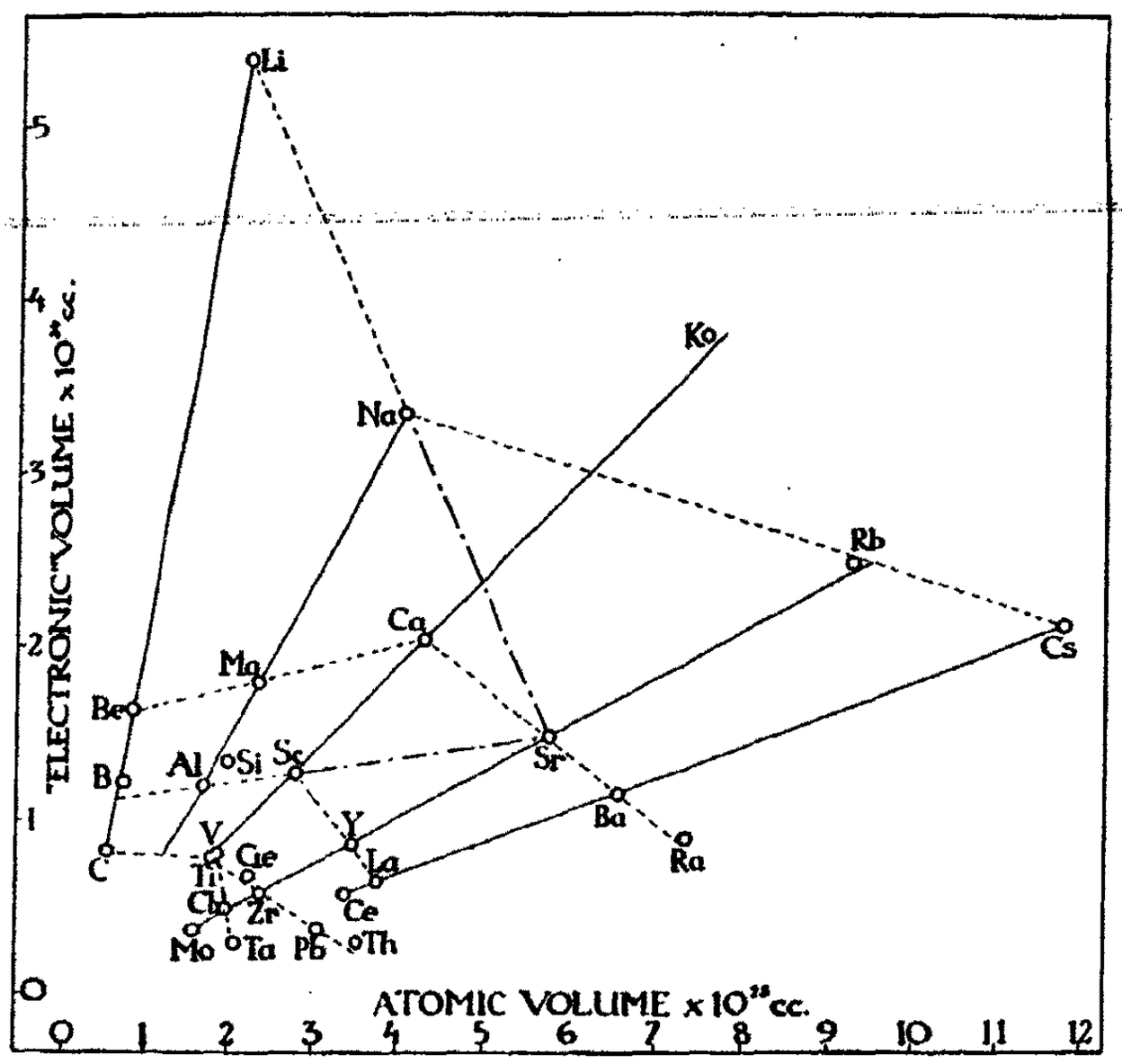



FIG. 6

"Electronic" Volumes of Elements plotted against Atomic Volumes.

In Fig. 6 we have the "electronic" volumes plotted against the atomic volumes. That the points for a series of iso-electronic ions should fall on an approximately straight line, is inherent in the scheme of the plotting, provided of course that the atomic volumes decrease regularly with increasing nuclear charge. For this reason discrepancies such as make their appearance with silicon and boron are no doubt to be attributed to uncertainties in the data rather than to some divergence from the normal behavior. The novel feature of this type of graph, however, is to be found in the lines representing the various groups. Regarding the grossly irregular position of the point for

[1] Bridgman: Phys. Rev., 27, 68 (1926).

potassium, it may be observed that there is abundant evidence of the fact that this element has a particularly loose electronic structure and furthermore that in the solid state it lacks a definite crystalline state except possibly at very low temperatures. No further comment on this diagram will be made, first, because the precise significance of the terms employed is unknown at present; and second, because a possible qualitative interpretation has already been discussed.

## Summary

The present paper is to be regarded as a preliminary study of the relationship between the distance between ions in a crystal lattice of a metal and the chemical forces of that element. It is an attempt to find a more precise expression for the qualitative relationships which are known to exist between the chemical and physical properties of elements. The results may be summarized as follows: (a) The variation in $d_o$ with $k^{\frac{1}{5}}$, which term is taken to represent the forces of chemical "affinity", may be expressed by a linear equation for certain series of ions; (b) the relationship between $k$ and $f$ for any series of iso-electronic ions is likewise linear and possibly represents a necessary condition for the existence of a crystal lattice; (c) the effect of changes in the nuclear charge upon $f$ is found to be uniform for different series of iso-electronic ions. Deviations from (a) appear, however, in certain cases, and they are shown to correspond in some manner to the influence contributed by the valence electrons. In the data presented evidence has also been seen for the view that the valence electrons in a crystal are not "free" in the classical sense, but are still integral components of individual atoms. This concept constitutes, in fact, the guiding principle of this study. Moreover, considerations are advanced to show that the determining factors in group properties are to be sought in the characteristics of ions as well as in the number of valence electrons. And finally, a figure is presented portraying the surprising relationship which obtains between $e$ "electronic" volumes and atomic volumes in metals.

In a subsequent paper the author hopes to extend these ideas and to discuss the application of these principles to the cases of non-polar elements and simple salts.

# ADSORPTION FROM SOLUTION BY ASH-FREE ADSORBENT CHARCOALS I. A METHOD FOR THE PURIFICATION OF ADSORBENT CHARCOALS[1]

BY ELROY J. MILLER

Adsorbent charcoals because of their relatively great activity have been used perhaps more frequently than any other adsorbent in studies on adsorption from solution. Sometimes the assumption has been tacitly made that the material was essentially pure carbon and the role of the other constituents was ignored. It has been more generally recognized, however, that these adsorbents are extremely poorly defined substances and it is, therefore, not surprising that the results of these researches reported in the literature are largely discordant.

Many attempts have been made to purify these materials but they have been uniformly unsuccessful as far as any appreciable reduction of the inorganic content was concerned. The usual procedure was to extract the charcoals with concentrated acids, although occasionally fusion with alkali was attempted. Merck's blood charcoal seems to have been the favorite material for adsorption studies. While it is labelled, "Purified by Acids" it nevertheless contains in the neighborhood of 8 per cent of inorganic matter. Numerous investigators have sought to reduce the ash content further before use in their adsorption studies. Thus, for example, Freundlich and Losev[2] showed that the ash content of this material is not appreciably lowered by treatment with concentrated hydrochloric acid. They boiled the charcoal repeatedly with concentrated hydrochloric acid and then washed with hot distilled water and finally with conductivity water. The charcoal before treatment had an ash content of 7-8 per cent. After treatment the ash content was still 5-8 per cent.

Odén and Andersson[3] used essentially the same method and in addition subjected the charcoal to a final extraction with organic solvents.

Recently Firth and Watson[4] in a study of the catalytic decomposition of hydrogen peroxide solution by blood charcoal have carried out extensive studies on the removal of ash from blood charcoal by extraction with aqua regia. The charcoal before treatment gave on ignition 8.82 per cent of ash. Digestion with hot aqua regia for several days reduced the ash content to 7.30 per cent. After prolonged treatment for about a month with aqua regia the ash content was but little lowered. It still contained 6.32 per cent ash. Only by very prolonged treatment could the ash content be appreciably reduced

[1] Published as Journal Article No. 36 from the chemical laboratory of the Michigan Agricultural Experiment Station. Published by permission of the Director.

[2] Z. physik. Chem., 59, 284 (1907).

[3] J. Phys. Chem., 25, 311 (1921).

[4] Trans. Faraday Soc. 19, 601 (1924).

below this figure. This drastic treatment resulted in the loss of a considerable portion of the charcoal and in some cases the whole of the charcoal passed into solution.

In a previous paper[1] it was shown that boiling commercial sugar charcoal with concentrated hydrochloric acid reduced the ash content from 0.57 to 0.55 per cent a practically negligible amount, and this in spite of the fact that the ash remaining after burning off the carbon was largely iron and almost completely soluble in hydrochloric acid.

These illustrations from the literature on the subject are typical of the results obtained in efforts to purify adsorbent charcoals. Obviously, any method that could be used to purify these adsorbents should aid materially in furthering our knowledge of adsorption by eliminating the complications due to the uncertain action of the ash and should make the results of all investigators more easily reproducible and comparable. In previous publications[2] it has been shown that concordant and reproducible results can be obtained by the use of activated ash-free sugar charcoal.

It is the purpose of this paper to describe a method by which adsorbent charcoals of both animal and vegetable origin may readily be purified so that their ash content is reduced to a few hundredths or less of one per cent. The method has for its basis the use of hydrofluoric acid either alone or in mixtures with other suitable acids such as hydrochloric or sulfuric acids.

## Method of Purification

The purification may be carried out in a number of ways but the following procedure has been found to be as satisfactory as any. The charcoal after thorough drying is ground to pass a 300-mesh sieve. It is then mixed in a platinum vessel with sufficient concentrated hydrofluoric acid to make a thin paste and warmed gently over a low flame (pilot light of a Bunsen burner is quite satisfactory) until most of the hydrofluoric acid has been driven off. When most of the hydrofluoric acid has been expelled the heating is increased to insure complete removal of hydrofluoric acid. The charcoal is next boiled with concentrated hydrochloric acid, diluted, and filtered through hardened filter paper in a Büchner funnel. This extraction with concentrated hydrochloric acid is repeated a second time after which the charcoal is washed by repeated boiling with distilled water until most of the hydrochloric acid has been removed. At this point the ash content of the charcoal has been reduced to a few tenths of a per cent, depending upon the kind and fineness of the charcoal and other factors. In order to reduce the ash content still further the charcoal is dried in an oven at 115° or higher and then ignited at a temperature of 900°-1200° in silica vessels from which air is excluded to prevent oxidation and loss of carbon. The above treatment with hydrofluoric acid and extractions with hydrochloric acid are repeated until the desired purity has been obtained. When the ash has been removed, the charcoal is ignited to

[1] Bartell and Miller: J. Am. Chem. Soc., 44, 1866 (1922).
[2] J. Am. Chem. Soc., 45, 1106 (1923); 46, 1150 (1924); 47, 1270 (1925).

drive off adsorbed acids and finally washed by boiling several times with a good grade of distilled water or preferably conductivity water and then dried. Ignition drives off practically all the adsorbed acids. A minute quantity of acid, however, remains even after the ignition. The amount is negligible for most purposes. It may be removed readily by boiling a suspension of the charcoal in conductivity water to which has been added approximately 1 cc. of 0.02 N sodium or potassium hydroxide per gram of charcoal. The excess alkali and the inorganic salt formed are quantitatively removed by boiling and filtering three or four times.[1]

## Results obtained in the Purification of Different Types of Charcoals

The method of purification described above seems to work equally well on all types of adsorbent charcoals. As examples of typical results obtained during the past several years in this laboratory in the purification of charcoals of animal, vegetable, and carbohydrate origin results for the following are presented: blood charcoal, Norit,[2] and activated sugar charcoal as representative of charcoals of animal, vegetable, and carbohydrate origin respectively. In Table I are given the results of ash determinations made on samples of charcoals taken after each of a series of treatments with hydrofluoric acid. Samples of charcoal weighing one to two grams each were ashed in platinum dishes over Meker burners or in an electric muffle.[3]

TABLE I

Ash Content of Charcoals after Successive Treatments with Concentrated Hydrofluoric Acid.

| Kind of Charcoal | Number of Times treated with Hydrofluoric Acid | Per cent of Ash (Average of duplicate determinations) |
|---|---|---|
| Blood Charcoal (Lot A) | Before Treatment | 8.39 |
| | 1 | 0.68 |
| | 2 | 0.13 |
| | 3 | 0.06 |
| | 4 | 0.06 |
| | 5 | 0.06 |
| Norit | Before Treatment | 6.47 |
| | 1 | 0.09 |
| | 2 | 0.04 |
| | 5 | 0.04 |
| Activated Sugar Charcoal | Before Treatment | 0.10 |
| | 1 | 0.00 |

[1] Miller: J. Am. Chem. Soc. 47, 1270 (1925).

[2] Tanner: Ind. & Eng. Chem. 17, 1191 (1925).

[3] *Note.* The ash remaining in the platinum dishes after burning off the carbon is usually largely insoluble in hot concentrated hydrochloric acid. The addition of a few drops of hydrofluoric acid dissolves the ash without injury to the dish or loss of platinum.

Inspection of the data in Table I reveals the fact that two or three extractions remove practically all of the inorganic matter from blood charcoal and that subsequent extractions do not reduce it further. Norit is somewhat more readily purified than blood charcoal but a minimum value is also reached, beyond which continued treatment is futile. The sample of sugar charcoal was prepared from recrystallized sugar and the introduction of the inorganic matter occurred after activation. This undoubtedly accounts for the fact that the ash content is reduced below one one hundredth of a per cent by the first extraction. In the case of animal and vegetable charcoals the small amounts of ash which cannot be removed are undoubtedly held within charcoal particles and they are, therefore, protected from the action of the acid. Further evidence substantiating this view will be found in Table II.

Experiments were conducted with the view of determining whether a mixture of hydrochloric and hydrofluoric acids might be substituted for the hydrofluoric acid alone, thereby eliminating the use of large quantities of the relatively expensive hydrofluoric acid. At the same time tests were made to see how much of a factor the fineness of division of the charcoal might be. Accordingly, samples of blood charcoal, one ground to pass a 300-mesh sieve, the other just as received, were treated as described in the above method with the exception that the charcoal was made up to a paste and heated with a mixture of approximately three parts of concentrated hydrochloric acid to one part of hydrofluoric acid. The data are presented in Table II. It is apparent that the purification of the charcoal can be effected by using a mixture of hydrochloric and hydrofluoric acids in which the proportion of

TABLE II

Ash Content of Charcoals after Successive Treatments with a Mixture of Concentrated Hydrochloric and Hydrofluoric Acids.

| Kind of Charcoal | Number of Times treated | Per cent of Ash (Average of duplicate determinations) |
|---|---|---|
| Blood Charcoal (Lot B) Ground to pass 300-mesh sieve. | Before Treatment | 7.85 |
| | 1 | 0.44 |
| | 2 | 0.12 |
| | 3 | 0.08 |
| | 4 | 0.06 |
| | 5 | 0.04 |
| Blood Charcoal (Lot B) (Not ground) | Before Treatment | 7.85 |
| | 1 | 0.71 |
| | 2 | 0.19 |
| | 3 | 0.15 |
| | 4 | 0.12 |
| | 5 | 0.13 |

hydrofluoric acid is relatively small. The purification is accomplished with practically the same number of treatments that are required with hydrofluoric acid alone.

It is also apparent that the fineness of division of the charcoal determines the amount of ash that cannot be removed on continued extraction. The coarser sample had a final ash content three times that of the one which had been ground to pass the 300 mesh sieve.

### Use of Other Acids with Hydrofluoric

Mixtures of hydrofluoric and sulfuric acids were also tried and found to work fairly satisfactorily. They seemed to have no distinct advantage over the hydrofluoric-hydrochloric mixtures and, moreover, oxidation by the sulfuric acid with attendant loss of carbon was an undesirable possibility.

### Removal of Nitrogen

Determination of the nitrogen in blood charcoal before and after purification showed that a marked reduction accompanied the removal of the ash. Prior to purification one sample of blood charocal contained 0.59% nitrogen by the Kjeldahl method. After purification the nitrogen content was 0.26%. It was found, however, that prolonged heating alone would remove nearly all of the nitrogen from the charcoal. One sample when heated in a closed silica crucible for 7 hours at approximately 1000° lost all but 0.06% of its nitrogen. Another sample heated for 3½ hours under the same conditions lost all but 0.15%. Since the nitrogen could be removed without reducing the ash content it seems that heating during the purification process rather than any action by the acid was responsible for the removal of the nitrogen from the charcoal.

### Discussion

The method of purifying charcoals herein described effectively reduces the ash content to an insignificant amount. Previous attempts to purify adsorbent charcoals before use in adsorption studies by treatment with reagents such as concentrated hydrochloric and nitric acids, aqua regia, bromine, and chlorine have not met with success. Treatment with these reagents does not appreciably lower the ash content of the charcoal and in some cases in addition, results in the loss of a large proportion of the charcoal. The present method is free from these disadvantages and in addition does not appreciably affect the adsorbent power of the charcoal.

By means of this method adsorbent charcoals may be readily purified so that their ash content is practically the same as that of pure sugar charcoal. Data which have been obtained in adsorption studies with these purified charcoals are concordant and free from the contradictory results obtained with the unpurified materials. In every respect their adsorptive properties are identical with those previously reported for pure activated sugar charcoal. These results will shortly be submitted for publication.

## Summary

(1) A method has been described for the purification of adsorbent charcoals.

(2) Data on the purification of animal, vegetable, and carbohydrate charcoals have been presented.

(3) By the use of this method it is possible to reduce the ash content of charcoals to a few hundredths or less of one per cent.


*East Lansing,*
*Michigan.*

# ADSORPTION AND REACTION. I

## The Setting of Plaster of Paris*

BY HARVEY A. NEVILLE

The setting of plaster of Paris is accelerated or retarded by various inorganic and organic substances which apparently act as catalysts in the reaction. The effect of this catalysis is such that a plaster which ordinarily sets in thirty-five minutes may be caused to set in five minutes by the addition of an accelerator, or delayed for an hour or more by a retarder. In attempting to account for this effect, Rohland[1] stated that any substance which increases

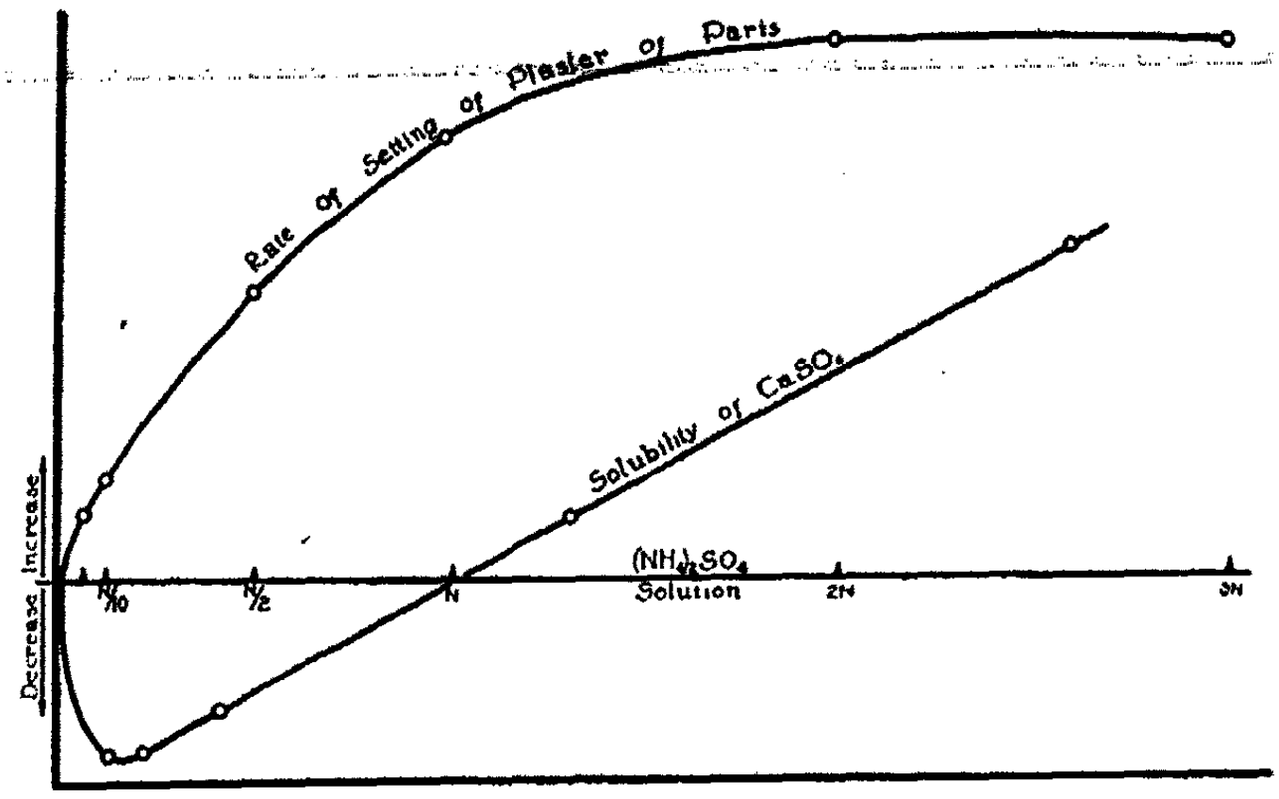



FIG. 1

The Rate of Setting of Plaster of Paris, and the Solubility of Calcium Sulfate as influenced by Ammonium Sulfate.

the solubility of calcium sulfate will accelerate the setting of plaster of Paris, and that substances which decrease the solubility of calcium sulfate must retard the setting.

That this explanation is unsatisfactory is shown in Fig. 1, in which the effect of increasing concentration of ammonium sulfate on the rate of setting of plaster of Paris is compared with the effect of ammonium sulfate upon the solubility of calcium sulfate[2]. A complete absence of any relation is demonstrated. Furthermore, the solubility of calcium sulfate is *decreased* by small amounts of practically all soluble sulfates, yet these exert a marked accelerating effect upon the setting of plaster of Paris.

* Contribution from the Department of Chemistry of the University of Illinois.

[1] P. Rohland: Z. Elektrochem., 14, 421 (1908).

[2] The solubility data are from Seidell's Tables of Solubilities; the data for rate of setting of plaster of Paris are from experiments described in this paper.

The explanation offered by Rohland was based upon the assumption that the mechanism of the setting of plaster of Paris is:

(a) The hemihydrate, $CaSO_4 . \frac{1}{2}H_2O$, dissolves in water to form a saturated solution.

(b) Hydration of the hemihydrate to the dihydrate, $CaSO_4 . 2H_2O$, occurs.

(c) Since the dihydrate is less soluble than the hemihydrate, the solution is now supersaturated and gypsum crystallizes, forming a compact mass of interlacing needle-shaped crystals.

If this were the true mechanism of the process, the effect of added substance would, no doubt, be as Rohland anticipated. More recent results, however, indicate that colloidal phenomena are concerned in the setting of plaster of Paris, as in the setting of lime-silica cements.

Cavazzi[1] and Traube[2], for independent reasons, suggested that the setting of plaster of Paris consisted in the formation of a gel which gradually changed into the needle-shaped crystals of gypsum. Traube studied the effect of accelerators upon the time of setting, measuring the time required for the plaster to attain that state of hardness where it was not displaced by a considerable pressure of his finger. He showed that the cations are the important factors in the acceleration, and concluded that their activity here agrees with the order in which they precipitate colloids from solution.

A kinetic method of studying the problem was developed by Wo. Ostwald and Wolski.[3] Their procedure was to measure, at intervals, the viscosity of dilute suspensions of plaster of Paris (2 to 5 per cent) and to consider the increase in viscosity an index of the progress of the action. The viscosity-time curves are found to be S-shaped; the viscosity rises slowly at first and then rapidly to a constant at its maximum value. By this method they were able to study the effect of varying the temperature, the concentration of the suspension, the age and fineness of the material, and the effect of added solutes. As a result of these experiments they conclude that the setting of plaster of Paris is a colloidal process, and they point out the similarity of its viscosity curves to those of gelatin.

## Experimental Part

*Method and Materials.*—Since the hydration of plaster of Paris is an exothermal reaction, completely expressed,

$$CaSO_4 . \tfrac{1}{2}H_2O + 1\tfrac{1}{2}H_2O = CaSO_4 . 2H_2O + 3{,}900 \text{ calories},$$

it was thought that the reaction could best be followed thermometrically. By relating rise in temperature to time, a curve may be drawn which indicates the course of the reaction. By this method it is possible to use mixtures containing a much larger proportion of the solid than could be studied by the viscosity measurements, since the viscosity of mixtures which actually set quickly becomes infinite.

[1] Cavazzi: Gazz. chim. ital., **42** II, 626 (1912).
[2] Traube: Kolloid-Z., **25**, 62 (1919).
[3] Ostwald and Wolski: Kolloid-Z., **27**, 78 (1920).

A high-grade commercial plaster of Paris was used. In each experiment 40 g. of the plaster were used with 20 to 120 cc. of water or a solution. These materials were stirred for a definite length of time in a paraffined paper cup, the cup was then placed within another cup in a well insulated receptacle; a thermometer was placed in the mixture through a hole in the asbestos plate which covered the cup. The rise in temperature was noted at short intervals as the process of setting took place. The time-temperature curves showed a definite maximum which was reproducible within 30 seconds. The time corresponding to this peak was considered the setting time for the particular mixture, and comparative values for different mixtures were thus obtained.

TABLE I

40 g. of plaster of Paris stirred ¼ minute with 30 cc. of water or a solution. Time corresponding to maximum rise in temperature is given.

| Reagent | Time in Minutes |
|---|---|
| Pure water | 44 |
| N. HCl | 18 |
| " LiCl | 19 |
| " NaCl | 12 |
| " $NH_4Cl$ | 10.5 |
| " KCl | 6 |
| " KBr | 6.5 |
| " KI | 8.5 |
| " $KNO_3$ | 7 |
| " $K_2SO_4$ | 7.5 |
| " $Na_2SO_4$ | 12.5 |
| " $(NH_4)_2SO_4$ | 6 |
| " $CuSO_4$ | 12 |
| " $MgSO_4$ | 20 |
| " $ZnSO_4$ | 12 |
| " $Al_2(SO_4)_3$ | 25 |
| Saturated $CaSO_4$ | 44 |
| " $H_3BO_3$ | 63 |
| " NaCl | 180 |
| " $Na_2B_4O_7$ | 3 days. |

*Results.*—In Fig. 2 are illustrated the reaction curves for a mixture of 40 g. of plaster of Paris with 30 cc. of water, for a similar mixture accelerated by potassium sulfate, and for one retarded by glycerine. When plaster of Paris and water, in the proportions noted, are thoroughly stirred for a short time, a thin paste or cream is formed which can easily be poured into molds. There is a slight rise in temperature at this point—usually less than one degree—due to the heat of wetting or adsorption, sometimes referred to as the Pouillet effect. After standing about six minutes, however, the mixture can no longer be poured. When 40 g. of the plaster are mixed with 30 cc. of normal $K_2SO_4$ solution the materials cannot be stirred for longer than one-

half minute, for the mixture is stiff at the end of that period. Prolonged stirring shortens the time required for setting, hence a half-minute uniform stirring was adopted for the experiments. The point -S- on the curves corresponds to the initial set stage. At this point the plaster is perfectly rigid, resists indentation, and has a dry appearance. The broken-line curve represents the volume change, with time, of a mixture of 40 g. of plaster of Paris and 30 cc. of water, corresponding to the temperature-time curve labelled "Water".

The effect of various substances in modifying the rate of setting of plaster of Paris is shown in Table I. The time noted corresponds to the maximum

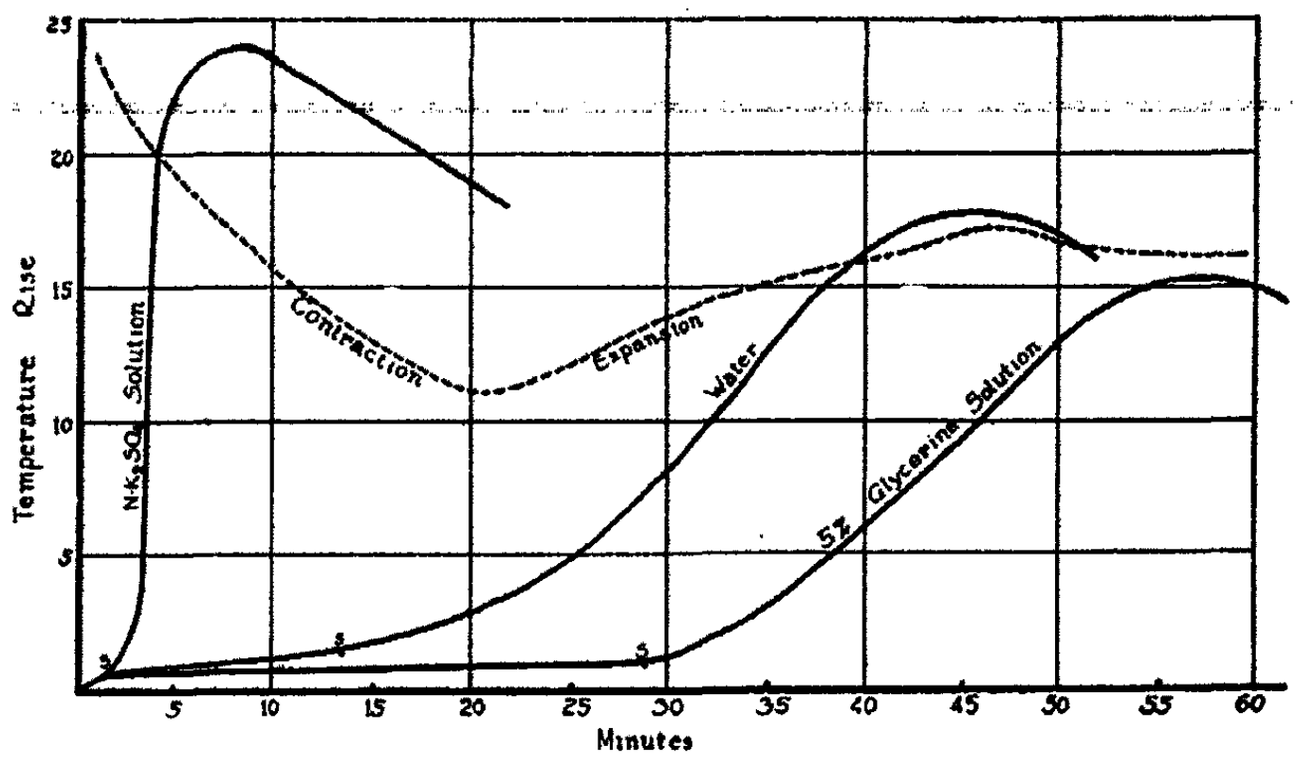



FIG. 2

Time—Temperature Curves for the Setting of Plaster of Paris. Broken Line = Volume Change for Water – Plaster.

temperature reached, or final set. The initial set, indicated by the point -S- on the curves in Fig. 2, was affected proportionately in each case. In addition, it was observed that the setting was faster when the original temperature of the water was higher; and that it was slower when larger proportions of water were used.

## Discussion

From a consideration of the curves in Fig. 2, it is apparent that there are two stages in the setting process. Since the point -S- is on the flat part of the curve, before the evolution of heat has begun, the hydration of plaster of Paris to form gypsum cannot have occurred to any appreciable extent. It follows, therefore, that the initial hardening of the mixture is not due to chemical combination with water. The facts point rather to the formation of a gel or adsorption complex in which only physical or secondary chemical forces are concerned. The volume-time curve in Fig. 2 confirms this conclusion. It indicates clearly that two processes are involved: adsorption of

water, accompanied by a contraction in volume; formation of gypsum crystals from the adsorption complex, accompanied by an expansion. The final volume is less than the sum of the original volumes of the materials by about seven per cent, as can be calculated from the respective densities of the substances concerned.

Ordinary plaster of Paris, made by the partial dehydration of gypsum, must have a very incomplete crystal structure with residual crystal forces and an enormous surface. It is to be expected that this type of material would have very strong adsorptive forces. It is reported that a crystalline form of $CaSO_4 . \frac{1}{2}H_2O$, obtained by prolonged boiling of gypsum with water, does not set as does plaster of Paris.[1] It is likewise to be expected that lime, made by the calcination of calcium carbonate, would have a porous structure like that of plaster of Paris. Hence it is of interest to note that Kohlschütter and Walther[2] concluded that an intermediate colloidal state first occurs when lime is mixed with water to form a true solution of calcium hydroxide.

The forces of adsorption having brought the plaster of Paris and water into the sphere of chemical action, chemical forces effect a reaction between the two substances to form gypsum, crystals of which grow throughout the material. An approximate determination of the heat evolved indicates that practically all of the hemihydrate has reacted at the time corresponding to the maximum temperature reached.

It is apparent that the reaction is very susceptible to catalysis. A measure of this, as given in Table I, brings out certain interesting relations. As pointed out by Traube, the accelerating effect of a salt is due to the cation, controlled to some extent by the anion which is present. It is seen that, in general, the activity of the cation increases with its weight. Thus, with the monovalent ions, $K > NH_4 > Na > Li$. Here the ammonium ion has a greater activity than the sodium ion although its weight is less. Among the divalent cations the same relationship holds: $Cu > Mg$, and $Zn = Cu$, since the latter pair are practically equivalent in weight.

The anions exert a minor influence, apparently limiting to some extent the activity of the cation. Considered as retarders, the order of the monovalent anions is: $I > NO_3 > Br > Cl$. Here the nitrate ion shows a greater retarding effect than the bromide ion, although the latter is heavier. Perhaps the size of the nitrate and ammonium ions may compensate for their lighter weight.

The relations outlined are certainly suggestive of colloidal phenomena. The order of the alkali metals in accelerating the setting of plaster of Paris is the same as that observed in the coagulation of a negative colloid of the suspensoid type. The order of the anions is likewise normal in that sense. An exception is shown in the order $K > Mg > Al$, since the polyvalent ions are usually the more active in colloidal processes. The exact role of the accelerating ions is not clear, although it is evidently twofold. That is, the adsorption

[1] W. A. Davis: J. Soc. Chem. Ind., 26, 727 (1907).
[2] Kohlschütter and Walther: Z. Elektrochem., 25, 159 (1919).

of water to form the gel is accelerated by these ions; then the chemical reaction between the hemihydrate and water is catalyzed. The substances which retard the setting of plaster of Paris—for example, borax and saturated sodium chloride solution—do so because they prevent the formation of the gel. Here the setting process is probably one of solution, hydration and crystallization; and the set mass which results after this slow process is composed of large crystals, is crumbly and without strength.

The results of Ostwald and Wolski[1] from viscosity measurements of dilute suspensions of plaster of Paris indicate the colloidal nature of the mixture by analogy to properties of known colloids. We are not able, however, to discover from their data the point at which the dihydrate is formed or if it is formed at all. The thermometric method shows definitely the two stages in the setting. Ostwald and Wolski emphasize the importance of the maximum viscosity attained in each case and the effect of varying conditions upon this maximum. It would seem, rather, that the rate of increase in viscosity is of more importance, since it probably indicates the rate of setting. If the slope of each viscosity-time curve constructed by those authors is considered the *rate of viscosity increase*, then varying conditions affect this factor just as they do the *rate of setting* of plaster of Paris, studied by the method described here. It is of interest to note that it was found in both of the investigations that it made no difference if a saturated solution of gypsum was used in place of pure water.

Part of the experimental work for this paper was performed by Victor L. Soderberg, to whom acknowledgement is hereby made.

## Summary

1. The setting of plaster of Paris occurs in two stages. This is shown by relating rise in temperature to time and also by measuring the change in volume with time.

2. The two stages of the process are: (a) adsorption, accompanied by a contraction in volume and a slight heat effect, whereby the two reactants are brought into chemical contact; (b) a resulting exothermic chemical reaction between the adsorbed liquid and the adsorbent, with an increase in volume.

3. The relative effectiveness of various substances in accelerating the setting is shown. This effect is not due to increased solubility of calcium sulfate, but results from the colloidal nature of the mixture of plaster of Paris and water.

*Urbana,*
*Illinois*

[1] Ostwald and Wolski: loc. cit.

# GERMANIUM XIII.* MODIFIED FORM OF VACUUM APPARATUS FOR THE PURIFICATION AND STUDY OF VOLATILE COMPOUNDS OF GERMANIUM[1]

BY A. W. LAUBENGAYER AND R. B. COREY

## Introduction

In the study of the hydrides of germanium, Dennis, Corey and Moore[2] used an apparatus which was a modified form of that employed by Stock[3] in his work on the hydrides of boron and silicon. This apparatus has been employed in subsequent investigations in this laboratory in the course of which it has undergone considerable modification. To simplify the discussion of experimental details in the several articles later to be published, the most recent form of this apparatus is here described and the new features of manipulation are discussed.

The main chain of apparatus as shown in Fig. 1 differs from that described by Dennis, Corey and Moore in the following essential features.

Stock's modification[4] of his mercury float valve is employed and has been found to be very satisfactory.

The fractionation bulbs, $B_1$, $B_2$, and $B_3$, are attached to the main line through mercury floating valves $V_2$, $V_3$, and $V_4$. In the apparatus as previously used, the fractionation bulbs and the connecting valves were in series as integral parts of the main line of the apparatus. This earlier arrangement was found to possess many disadvantages. If the third bulb contained a fraction of material it was impossible to bring fractions from either of the first two bulbs into the remainder of the apparatus for vapor tension measurements or other operations. It was, furthermore, impossible to remove and replace one of the fractionating bulbs or the connecting valves without disturbing fractions in adjacent portions of the apparatus. Also the replacement of a valve required two glass seals in series in a rigid system. In the apparatus as modified with the bulbs attached as side chains, each bulb is independent of the others and the above difficulties are not encountered. This arrangement also lends itself to any desired additions to the apparatus.

A side-arm has been added between Stopcock $S_3$ and ground joint E. This side-arm is connected through stopcock $S_4$ to the evacuating pumps. When the weighing tube F is removed and replaced, air is trapped in the space between stopcocks $S_3$ and $S_5$. This air must be removed before F is opened to the rest of the chain. In the earlier form of the apparatus this could be accomplished only by pumping through the main chain, thus introducing the

---

*Contribution from the Department of Chemistry, Cornell University.

[1] The work upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Dennis, Corey and Moore: J. Am. Chem. Soc., **46**, 657 (1924).

[3] Stock and Somieski: Ber., **49**, 111 (1916); Stock: Ber., **50**, 989 (1917); **54A**, 142 (1921).

[4] Stock: Z. Elektrochem., **23**, 33 (1917).

possibility of fouling the apparatus, and necessitating a comparatively lengthy period of evacuation. The addition of the side tube permits rapid removal of the air without involving the rest of the apparatus.

A Hempel gas burette H has been attached for use in the calibration of the volume of various portions of the chain. In the earlier type of apparatus calibration was effected by introducing carbon dioxide into the portion to be calibrated, recording the pressure and the temperature, condensing the gas in the weighing tube, removing the weighing tube from the chain, and measuring the gas volume in a Hempel burette. With the burette attached as shown in Fig. 1, calibration can be effected by the following simple manipulation. The apparatus is completely evacuated and valves $V_2$, $V_3$, $V_4$, $V_5$ and $V_7$ are closed. The mercury in $V_6$ is brought to a mark on the stem. Dry air is admitted through Stopcock $S_1$ and $V_1$ is closed. The mercury in manometer D is brought to an arbitrary mark. The pressure of the gas in the system is noted. Stopcock $S_6$ is then opened and the volume of the system is increased about 50 cc. by lowering the mercury in burette H. The mercury in the manometer D is again brought to the mark and the exact increase in volume of the system and the corresponding pressure are recorded. From these data the volume of the system is calculated. Checks may be run by simply varying the level of the mercury in the gas burette and noting the corresponding pressures. This modification very considerably reduces the time and manipulation required for the calibration of the apparatus. Burette H may also be used for the introduction of definite volumes of gases into the apparatus. Other gases instead of air may be employed in the calibration if desired.

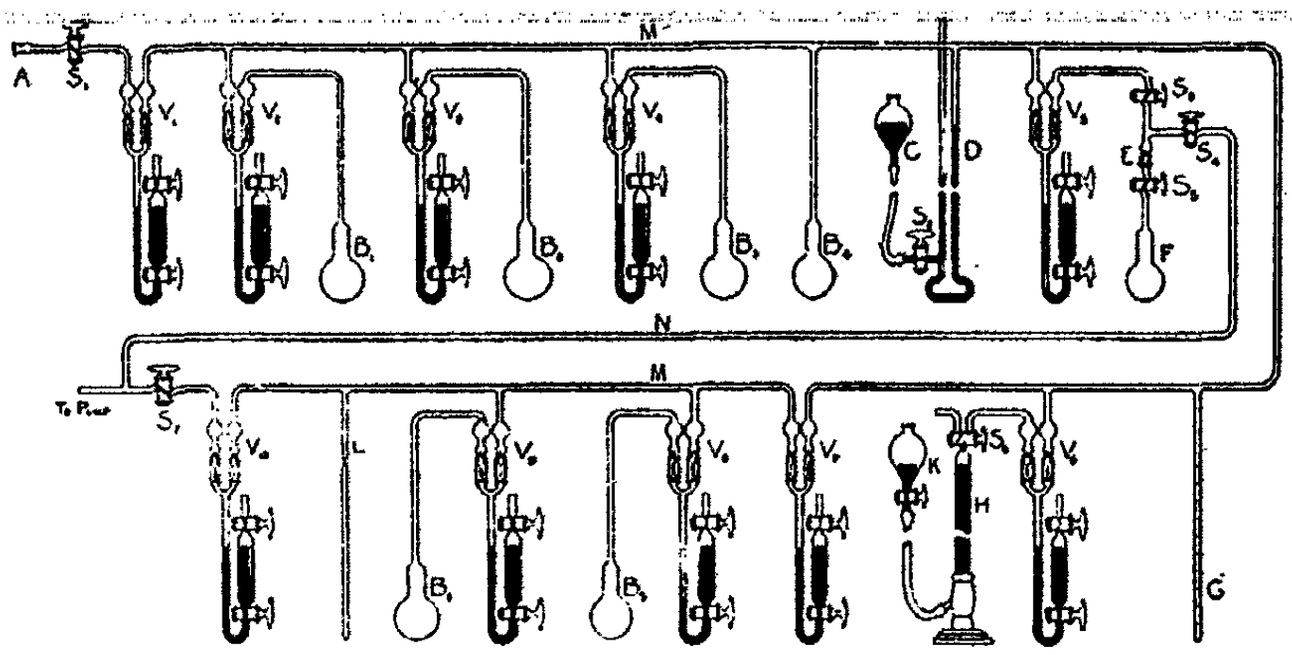



FIG. 1

Valve $V_7$ has been placed in the main line. When closed, it reduces the volume of the apparatus involved in fractionation and in vapor-pressure measurements. It also is used to shut off a definite part of the apparatus for calibration, and permits changes or additions to be made in the rest of the chain without altering the calibrated volume.

It has been found advantageous to increase the number of storage bulbs $B_5$ and $B_6$. The number of sampling tubes L may be suited to the particular investigation.

Fig. 2 shows the modified form of apparatus for the determination of vapor tensions of substances whose boiling points lie above room temperature. This system differs considerably from that described by Dennis, Corey and Moore. The bulb O permits fractionation during the process of transfer, and a modified form of vapor pressure tube, PQR, eliminates the necessity of sealing the tube in the presence of the sample, and facilitates the manipulation. Furthermore, since the mercury float valves in the former apparatus served no useful purpose, they have here been replaced by stopcocks.

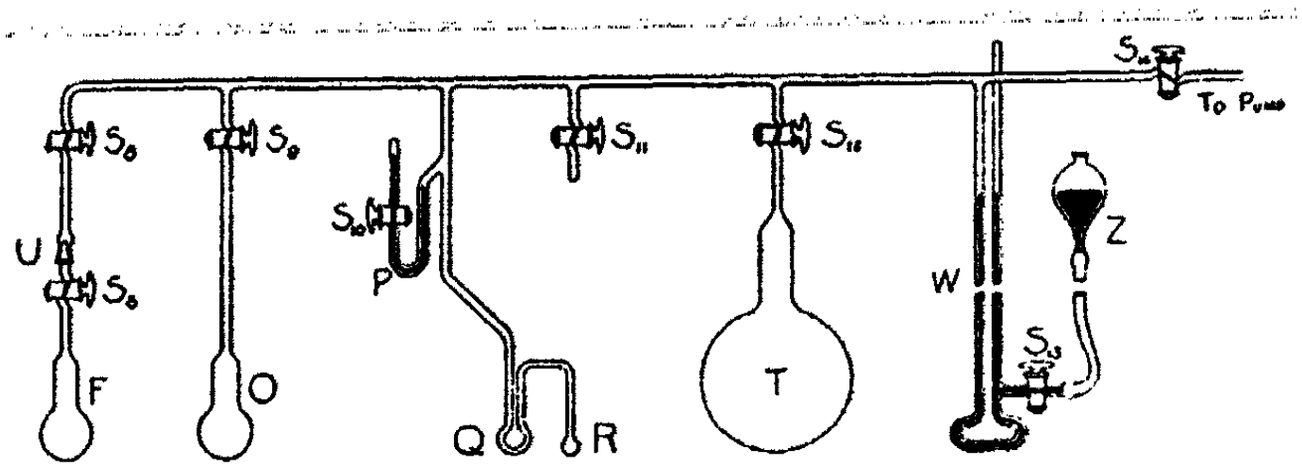



FIG. 2

The sample is brought into the weighing tube F, Fig. 1. The tube is then detached, and is connected to the apparatus Fig. 2 by the ground joint U. The arm P is filled, as shown, with carefully purified mercury. The entire apparatus above stopcock $S_5$ is then evacuated. Stopcocks $S_{12}$ and $S_{14}$ are closed. $S_5$ is opened and a small fraction of the sample is distilled into O. $S_9$ is closed and a middle fraction is distilled into bulb R. Stopcocks $S_8$ and $S_5$ are closed and R is immersed in liquid air. Stopcock $S_{10}$ is very cautiously opened and the mercury in the arm P is allowed to trickle slowly into Q until a small differential manometer is formed.

In order to make sure that no decomposition or contamination of the sample in R has occurred during its transfer or the formation of the manometer, the vapor tension at 0° of the fraction is determined and compared with the value previously obtained for the substance in the fractionation apparatus. If concordant results are not obtained, the liquid in bulb R is allowed to warm slowly and some of its vapor is bubbled through the mercury in Q carrying out with it any contaminating volatile matter. Q is made of 5 mm. tubing sealed on to the regular 7 mm. tubing bent in the form shown. This design insures the breaking up of the mercury column as the vapor pushes through. By this process it is usually possible to obtain a fraction in R whose tension at 0° is identical with that of the pure material as obtained in the fractionation chain.

The bulb T serves to give sufficient capacity to the system to permit of accurate adjustment of the manometer. The volume of this bulb is added to the apparatus by opening stopcock $S_{12}$. QR is immersed in a bath whose temperature is gradually raised. The vapor tension developed in R is balanced by admitting air through stopcock $S_{11}$ and the pressure is read on manometer W when the differential manometer Q indicates identical pressures on both arms.

*Ithaca,*
*New York*

# GERMANIUM XIV* GERMANIUM TETRACHLORIDE[1]

BY A. W. LAUBENGAYER AND D. L. TABERN

In the preparation of germanium tetrachloride in this laboratory, the method first used by Dennis and Hance[2] was the action of chlorine on heated metallic germanium. They at first freed the resulting tetrachloride from the excess of chlorine by shaking the liquid with mercury, but this procedure proving to be unsatisfactory it was abandoned and the chlorine later was removed by passing dry air through the germanium tetrachloride.

This procedure has now been improved by utilizing the fact that mercurous chloride readily unites with chlorine.[3] Upon adding mercurous chloride to the germanium tetrachloride containing free chlorine, and boiling the liquid for one hour with reflux condenser, all free chlorine was removed and the tetrachloride, when distilled, was found to be spectroscopically free from mercury.

Still another method of preparing germanium tetrachloride is that directly from germanium dioxide, which was recently developed[4] in this laboratory.

The boiling point of germanium tetrachloride prepared by these later methods was found to differ from that given by Dennis and Hance, and for this reason it seemed desirable to redetermine some of the physical constants of the substance, using the new preparations.

The vapor tension at 0° of the middle fraction of samples made by both of these later methods was found to be 24.3 mm.

*Vapor Tension.* The vapor tension from −40 to 84° of several samples of germanium tetrachloride prepared by both methods was determined with the aid of the apparatus described by Laubengayer and Corey.[5] A typical set of measurements follows:—

Vapor Tension of Germanium Tetrachloride

| Temp. C | Pressure mm. | Temp. C | Pressure mm |
|---|---|---|---|
| −40 | 1.1 | 62.2 | 381.0 |
| −18 | 3.3 | 64.9 | 422.1 |
| −12 | 10.9 | 69.2 | 488.2 |
| − 5 | 17.9 | 70.7 | 513.2 |
| 0.0 | 24.3 | 74.7 | 584.5 |
| 9.7 | 43.4 | 78.6 | 663.2 |
| 20.6 | 69.2 | 81.0 | 708.5 |
| 27.2 | 93.6 | 82.6 | 746.7 |
| 32.9 | 122.3 | 83.4 | 767.2 |
| 39.4 | 161.0 | 84.2 | 786.7 |
| 49.8 | 241.0 | | |

*Contribution from the Department of Chemistry, Cornell University.

[1] The work upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Dennis and Hance: J. Am. Chem. Soc., 44, 304 (1922).

[3] Naik and Avasare: J. Indian Chem. Soc., 1, 75 (1924).

[4] Tabern, Orndorff and Dennis: J. Am. Chem. Soc., 47, 2040 (1925).

[5] Laubengayer and Corey: J. Phys. Chem., 30, 1043 (1926).

*Boiling Point.* The boiling point of germanium tetrachloride, as taken from the vapor tension curve, is 83.1°. The boiling point obtained during fractionations of the samples in their preparation was 83.2°. The boiling point of the compound may therefore be placed at 83°.

*Melting Point.* The germanium tetrachloride was found to melt at −50° by the dropping-ring method.[1]

*Density as Liquid.* The density as liquid was determined by means of a pycnometer. $d\ {}^{20°}_{20°} = 1.879$.

*Refractivity.* The refractivity of germanium tetrachloride was determined with an Abbé refractometer.

| Temperature | Index of Refraction |
|---|---|
| 12.5° | 1.4683 |
| 20.0° | 1.4638 |
| 25.0° | 1.4614 |
| 27.0° | 1.4602 |

Applying the formula of Lorentz and Lorenz[2] the molecular refractivity of germanium tetrachloride was calculated to be 31.465. If the atomic refractivity of chlorine be taken as 5.967, then the atomic refractivity of germanium is 7.597.

## Thermal Stability of Germanium Tetrachloride

Germanium tetrachloride was distilled back and forth through a heated quartz tube by means of liquid air. The temperature was slowly raised to 950° but no decomposition could be detected.

## Summary

Redeterminations of some of the physical constants of germanium tetrachloride which was purified or prepared by two new methods are given.

*Ithaca,*
*New York.*

[1] Dennis, Corey and Moore: J. Am. Chem. Soc., **46**, 665 (1924).
[2] Landolt and Börnstein: "Physikalisch-chemische Tabellen," 985 (1923).

# GERMANIUM XV.* GERMANIUM CHLOROFORM[1]

BY L. M. DENNIS, W. R. ORNDORFF AND D. L. TABERN

## Introduction

Winkler passed hydrogen chloride over heated germanium or its sulphide, and obtained a clear, mobile liquid which he first thought was germanium dichloride.[2] In his second article,[3] he corrects his previous announcement and states that the substance formed by the action of hydrogen chloride on germanium is germanium chloroform. He adds that germanium dichloride *may* be formed when germanous sulphide is heated in hydrogen chloride, but says that this still lacks experimental confirmation ("was jedoch noch des bestimmten Nachweises bedarf"). Notwithstanding this definite statement, several modern Handbooks and Textbooks, apparently overlooking Winkler's correction in his second article, credit him with the preparation of germanium dichloride, and ascribe to the substance properties which are those of the chloroform.

Furthermore, consideration of the boiling points and melting points of the chlorides of tin and lead, analogous elements in Group IV, renders it evident that germanium dichloride might be expected to be a solid at room temperature and not a liquid of comparatively low boiling-point.

| | $SnCl_2$ | $SnCl_4$ | $PbCl^\circ$ | $PbCl_4$ |
|---|---|---|---|---|
| B. Pt. | 606° | 114.1° | 956° | Decomposes |
| M. Pt. | 250° | −33° | 500° | −15° |

The fact that Winkler obtained germanous hydroxide by adding an alkali to what he first thought was germanium dichloride furnishes no evidence that he prepared the last-named compound, because, as will later appear in this article, germanous hydroxide is formed when an alkali, such as potassium hydroxide, acts upon germanium chloroform.

## Experimental

The study of germanium chloroform was first taken up in the Cornell Laboratory in 1922 by E. B. Johnson, who used for its preparation the same reaction that Winkler had employed. He confirmed Winkler's statements that a volatile liquid is formed, and that this becomes cloudy with the separation of a second liquid phase when the oxygen of the air acts upon it. Using a closed apparatus filled with pure nitrogen, Johnson obtained a clear liquid which was stable under a nitrogen atmosphere, and which yielded on distillation a large fraction of a constant boiling point. His analyses, however, showed that the substance was not pure germanium chloroform, and he con-

*Contribution from the Department of Chemistry, Cornell University.

[1] The work upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Winkler: J. prakt. Chem., **142**, (N. S. **34**) 222 (1886).

[3] Winkler: J. prakt. Chem., **144**, (N. S. **36**) 188 (1887).

cluded that the agreement of Winkler's result for chlorine in the compound[1] with the calculated percentage was accidental.

It seemed probable, therefore, that when hydrogen chloride acts upon metallic germanium, more than one volatile substance, liquid at ordinary temperatures, is formed.

Continuation of the investigation of the chloroform was deferred awaiting the construction of a vacuum-fractionation apparatus.[2] When this became available, A. W. Laubengayer took up the further study of the chloroform. He also employed the Winkler method for the preparation of the substance, and found that hydrogen chloride acts rapidly at 480°-500° upon germanium that had been prepared by reducing the oxide in hydrogen. The resulting liquid was transferred to the fractionation apparatus referred to above, great care being taken to avoid contact with atmospheric oxygen or moisture. Prolonged fractionation did not yield pure germanium chloroform. In one typical series, ten successive fractions of practically identical 0° vapor tension were obtained, and yet the vapor densities were higher than that calculated for the chloroform. Analyses of this material disclosed that the germanium was about one per cent. below, and the chlorine about 2 per cent. above the percentages calculated for $GeHCl_3$. These results appeared to show that the Winkler method of preparing germanium chloroform yields a mixture of the chloroform and germanium tetrachloride, and that these two substances are not separable by long continued fractionation in the vacuum apparatus. Assuming that only these two compounds were present, the analysis indicated that the mixture contained 70.3 per cent. $GeHCl_3$ and 29.7 per cent. $GeCl_4$. This was confirmed by titrating samples of the liquid with iodine[3] which acts upon the chloroform only.

$$GeHCl_3 + 2I = GeICl_3 + HI.$$

The titration indicated 71 per cent. $GeHCl_3$.

It thus clearly became evident that to avoid the simultaneous formation of germanium tetrachloride, a different method of synthesis of the chloroform was necessary. This was found in the action of hydrogen chloride upon germanium dichloride.[4]

## Preparation of Germanium Chloroform by the Action of Hydrogen Chloride on Germanium Dichloride

*Experimental Work by D. L. Tabern*

Germanium dichloride was prepared by passing the vapor of germanium tetrachloride over heated germanium. Dry hydrogen chloride was passed into the vacuum fractionation apparatus[5] at A and was solidified in bulb B[1] by means of liquid air. A tube containing freshly prepared germanium

[1] Winkler did not determine germanium in the substance.
[2] Dennis, Corey and Moore: J. Am. Chem. Soc., 46, 660 (1924).
[3] See p. 1052.
[4] The preparation and properties of this compound will be described in a later article.
[5] Laubengayer and Corey: J. Phys. Chem., 30, 1043 (1926).

dichloride was connected to A by a ground slipjoint. To the other end of the tube there was fused a bulb similar to $B^1$. The liquid air around $B_1$ was then removed, and there was brought up around $B_1$ a bath of alcohol-ether cooled to $-100°$. Liquid air was brought around the bulb at the other end of the tube and hydrogen chloride was in this manner slowly drawn over the germanium dichloride. The speed of flow of the hydrogen chloride was easily controlled by raising or lowering the liquid air and in this manner it was possible so to regulate the reaction, which is highly exothermic, as to avoid the decomposition of the germanium dichloride. When all of the hydrogen chloride in $B_1$ had passed over, the process was reversed, $B_1$ being cooled by liquid air and the further bulb by the alcohol-ether at $-100°$.

$$GeCl_2 + HCl = GeHCl_3.$$

The temperature in the reaction tube was held below 50°, usually about 30°. With a sample of about 20 g. of germanium dichloride, the conversion to the chloroform was practically completed by three passages of the hydrogen chloride, which took about thirty minutes. In this manner there was collected in $B_1$ a mixture of germanium chloroform and hydrogen chloride.

Most of the hydrogen chloride in the mixture was distilled off at $-80°$ and was discarded. The residue was then distilled into $B_2$ and was there held at $-45°$ and pumped for over an hour to remove the remainder of the hydrogen chloride. The liquid remaining in $B_2$ was next separated into six fractions by distillation, and the vapor tension at 0° of each fraction was determined. The results were 26.1, 26.2, 26.2, 27.1, 26.7 and 26.1 mm. The corresponding six fractions of a second sample of the product, prepared anew, gave identical vapor tensions at 0°, 26.3 mm. The vapor tension of the whole of a third sample was 26.0 mm. These results demonstrated the uniformity of the product.

### Analysis

The colorless, mobile liquid was then analyzed. Chlorine was determined in samples 1 and 2 by placing a small bulb, containing a known weight of the liquid, in a bottle partly filled with dilute nitric acid, breaking the bulb by shaking, adding a few drops of perhydrol, and precipitating the halogen as silver chloride.

Germanium was determined in samples 3, 4, and 5, by breaking the tube carrying the sample in a stoppered flask containing 6 N. sulphuric acid to which a few drops of perhydrol had been added, and then following the method of Johnson and Dennis.[1]

Anal. Determination of Cl. Subs., (1) 0.5415, (2) 0.3296; AgCl, 1.2930, 0.7866. Calcd. for $GeHCl_3$: Cl, 59.10. Found: 59.07, 59.04.

Subs. Determination of Ge. (3) 0.4692, (4) 0.5710, (5) 0.3531: $GeO_2$, 0.2703, 0.3310, 0.2039. Calcd. for $GeHCl_3$: 40.33. Found: 39.99, 40.23, 40.08.

Two determinations of germanium by Müller's method[2] gave 40.64 and 40.07 per cent.

[1] Johnson and Dennis: J. Am. Chem. Soc., **47**, 791 (1925).
[2] Müller: J. Am. Chem. Soc., **44**, 2493 (1922).

The analyses do not show close agreement with the calculated amounts of germanium and chlorine, which is probably due, in part at least, to the difficulty of sealing the small sample bulbs and tubes without some decomposition of the substance. They suffice, however, to show that the product is germanium chloroform of a fairly high purity.

Titration of the chloroform with iodine, while yielding results somewhat below the theoretical, was found to be a useful and rapid method for approximately determining the purity of various preparations of the chloroform. It was carried out by breaking a sealed bulb, containing the sample, under a solution containing an excess of iodine and some hydrochloric acid, and titrating the excess with sodium thiosulphate.

*Melting Point.* Two determinations of the melting point gave $-71°$.

*Density as Liquid.* The density of the liquid sample was determined at 0°, the result being 1.93 g. per cc.

*Density of Germanium Chloroform as Gas.* The method devised by Dennis, Corey and Moore[1] was used, the apparatus being the modified form devised by Laubengayer and Corey.[2]

Weight of one liter of the gas: Calcd. 8.034 g. Found: 8.005 g. and 7.955 g. Av. 7.980 g.

*Vapor Tension.* Two closely agreeing determinations were made using the apparatus described by Laubengayer and Corey. The results of one run were as follows:—

| Temperature | Pressure mm. | Temperature | Pressure mm |
|---|---|---|---|
| −25.0 | 0.8 | 60.9 | 456.7 |
| −20.0 | 2.7 | 62.4 | 482.2 |
| −15.0 | 5.2 | 64.3 | 518.7 |
| −10.0 | 9.2 | 66.0 | 553.2 |
| − 5.0 | 13.2 | 67.2 | 574.7 |
| 0.7 | 26.5 | 68.4 | 602.1 |
| 10.3 | 45.3 | 69.3 | 620.5 |
| 15.5 | 61.6 | 70.3 | 640.9 |
| 19.5 | 75.2 | 71.3 | 655.5 |
| 24.9 | 98.6 | 72.3 | 688.9 |
| 30.5 | 129.2 | 73.8 | 723.2 |
| 34.8 | 156.3 | 74.6 | 745.2 |
| 39.7 | 192.7 | 75.2 | 759.2 |
| 44.7 | 241.0 | 76.3 | 791.8 |
| 49.0 | 287.8 | 78.3 | 838.9 |
| 54.2 | 354.0 | | |

[1] J. Am. Chem. Soc., 46, 663 (1924).
[2] J. Phys. Chem., 30, 1043 (1926).

*Boiling Point.* The boiling point of germanium chloroform as taken from the vapor-tension curve is 75.2°.

*Thermal Decomposition.* Germanium chloroform was distilled back and forth between two bulbs that were joined to the opposite ends of a tube which was electrically heated. Decomposition of the chloroform began at 140° and was rapid at 175°, germanium dichloride and hydrogen chloride being apparently first formed, the dichloride then slowly dissociating, as the temperature rose, yielding metallic germanium and germanium tetrachloride.

*Chemical Properties. Reaction of Germanium Chloroform with Dry Oxygen.* Winkler observed[1] that the substance which he supposed to be pure germanium chloroform became turbid in the presence of air. He thought this was due to the formation of an oxychloride.

$$2\ GeHCl_3 + O_2 = 2\ GeOCl_2 + 2\ HCl.$$

If his assumption were correct, then for each atom of oxygen absorbed, one molecule of hydrogen chloride would be liberated.

To gain light upon this point, a weighed sample of germanium chloroform was brought into bulb O, Fig. 2, of the vacuum apparatus[2] and was there held at −45° by means of a cooled alcohol bath. Carefully dried oxygen was admitted to the chain through $S_{11}$, until it had reached the pressure of the atmosphere. This stopcock was then closed and the alcohol bath around O was removed. Reaction between the oxygen and the chloroform began at about 0°, the union of the two soon raising the liquid to the boiling point. A heavy oil separated out; the supernatant liquid was clear. The bulb was then again surrounded by the bath at −45°, and a known amount of oxygen was forced into the apparatus by means of a gas burette attached to $S_{11}$ until the atmospheric pressure had been restored. Using the burette as a pump, the gas in the system was drawn into the burette and was then forced through a spiral gas-washing bottle containing silver nitrate. Five oxidations were carried out, employing various temperatures of oxidation and various speeds of oxidation; in no case was there any evidence of the formation of even traces of hydrogen chloride.

The supernatant liquid in the bulb was identified as germanium tetrachloride by its refractive index and vapor tension. The viscous, light-colored oil in the reaction bulb which remained after the supernatant germanium tetrachloride had been carefully distilled off at −15°, decomposed when warmed and left a residue that appeared to be germanium dichloride.

The amount of germanium tetrachloride that was formed in the reaction is quite close to one molecule for each two molecules of germanium chloroform. While this fact indicates that the reaction might be expressed by the equation

$$4\ GeHCl_3 + O_2 = 2\ GeCl_4 + 2\ GeCl_2 + 2\ H_2O,$$

the fact that the oxygen absorbed considerably exceeds the amount called for in the equation makes it evident that secondary reactions, which need further study, occur.

[1] J. prakt. Chem., **144**, 190 (1887).
[2] Laubengayer and Corey: J. Phys. Chem., **30**, 1043 (1926).

*Reaction of Germanium Chloroform with Water.* When the chloroform is brought together with about three times its volume of water that has been freed from dissolved oxygen, a white solid is formed. If a considerably larger amount of water is added to the chloroform, there is produced an orange-colored precipitate, germanous hydroxide.

The white substance that is formed when only a small amount of water is added is soluble in dilute hydrochloric acid, but on the addition of water to this solution or neutralization of the acid by ammonium hydroxide, germanous hydroxide is precipitated.

## Summary

The method of preparing germanium chloroform that was used by Winkler is shown to yield a mixture of germanium chloroform and germanium tetrachloride.

A new method for preparing germanium chloroform by the action of hydrogen chloride on germanium dichloride has been devised and some of the physical and chemical properties of the chloroform are given.

*Ithaca,*
*New York.*

# GERMANIUM. XVI.* GERMANIUM TETRAMETHYL.[1] ANALYSIS BY COMBUSTION OF A LIQUID CONTAINING CARBON AND HYDROGEN

BY L. M. DENNIS AND F. E. HANCE

Germanium tetramethyl was prepared by the Grignard reaction. In preliminary experiments it was found to be practically impossible to separate the germanium alkyl from ether in the vacuum fractionation apparatus.[2] This made it necessary to depart from the usual procedure so that the amount of

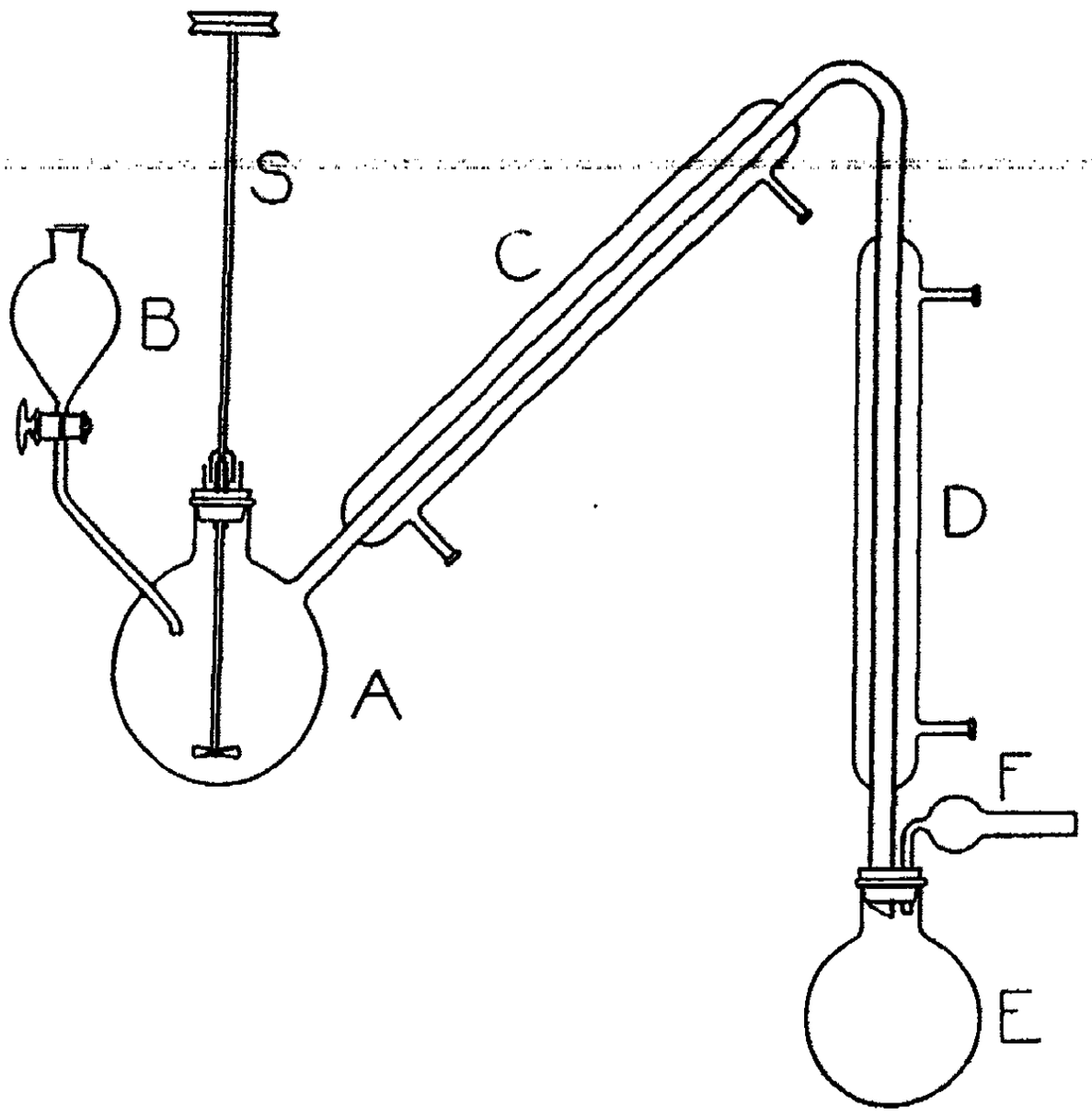



FIG. 1

ether in the product might materially be lessened. The apparatus that was designed for the purpose is shown in Fig. 1. The round bottom flask[3] A of one liter capacity carried a separatory funnel B fused through the side as shown,

*Contribution from the Department of Chemistry, Cornell University.

[1] The work upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Laubengayer and Corey: J. Phys. Chem., 30, 1043 (1926).

[3] A pyrex flask was first used. Spectroscopic examination of the product by Professor Papish showed the presence of boron. Flasks of R glass (Greiner and Friedrichs) were therefore employed in later runs.

and a condenser C. The stirrer S passed through a mercury seal. An upright condenser D was fused to C, and the receiver E, attached to the lower end of D by a cork, carried a calcium chloride tube F.

Twenty grams of magnesium turnings and 200 cc. of dry ether were placed in A, and the mixture was cooled with ice and salt. Water was started flowing through condenser C. Eighty grams of methyl bromide was dissolved in about 100 g. of dry ether at $-20°$. This solution was slowly introduced into A through B, the contents of the flask being vigorously stirred during the addition. When the reaction became quiet, the contents of A was heated and the ether was refluxed for about 30 minutes. C was emptied of water, water was turned on through D, and the bulk of the ether was distilled over into E, and was removed. The stirrer was then removed, flask A was closed with a cork, the Grignard reagent in A was heated to 100°, and suction was applied at F to remove as much as possible of the uncombined ether. The stirrer was then replaced in the neck of A, and 200 cc. of xylene, dried over sodium, was added through B. Water was turned on through C, and the contents of the flask was stirred and was heated until the xylene quietly refluxed.

Germanium tetrachloride, one mol to eight moles $MgCH_3Br$, was then slowly introduced through the separatory funnel B, the contents of the flask being kept warm. When the reaction was complete, the water was withdrawn from C and the mixture of germanium tetramethyl and the ether which is set free from the Grignard reagent in the reaction was distilled over into E. The xylene was held back by the empty receiver C.

The liquid in E was then fractionally distilled through a nine-ball column. The greater part of the liquid passed over at 34°. Careful and prolonged fractionation with the vacuum apparatus of Laubengayer and Corey failed to separate the ether from the alkyl. In the study of germanium tetraethyl, the authors had found that that compound was not affected by cold, concentrated sulphuric acid. Consequently the mixture of the tetramethyl and ether was treated with about twice its volume of cold, concentrated sulphuric acid. The ethyl sulphuric acid separated as a heavy, syrupy layer which was easily drawn off in a separatory funnel from the lighter germanium tetramethyl above it. The latter substance was washed with water several times in the funnel and was then dried over calcium chloride. An arc spectrum photograph by Professor Papish showed the product to be practically free from all impurities. A second preparation of about the same amount (65 cc) was found to be equally pure.

The two samples were separately distilled with a ball column, the bulk of the material passing over in each case at 43.2°.

The constant boiling fraction of the first preparation was brought into bulb $B_1$, Fig. 1[1], of the vacuum fractionation apparatus, and that from the second sample into bulb $B_6$. The physical constants of the two samples were determined separately. Each was subjected to careful fractionation in the

[1] Laubengayer and Corey: J. Phys. Chem., **30**, 1043 (1926).

apparatus, and those portions showing practically the same vapor tension at 0° were retained, while the other small fractions of different vapor tension were removed from the apparatus.

*Vapor Tension at* 0°. The values observed in ten determinations with each sample showed a maximum variation of 0.5 mm. Av. 139.3 *mm.*

*Analysis.* Carbon and hydrogen were determined by combustion with copper oxide in a current of air. The apparatus which was used, and which we regard as a distinct improvement over that employed for the analysis of germanium tetraethyl,[1] is shown in Fig. 2.

The bulb A, into which the sample is brought, is provided with two stopcocks as shown, and the end of the neck is ground to fit the slipjoint E, a slipjoint of the apparatus used for determining the germanium (see later),

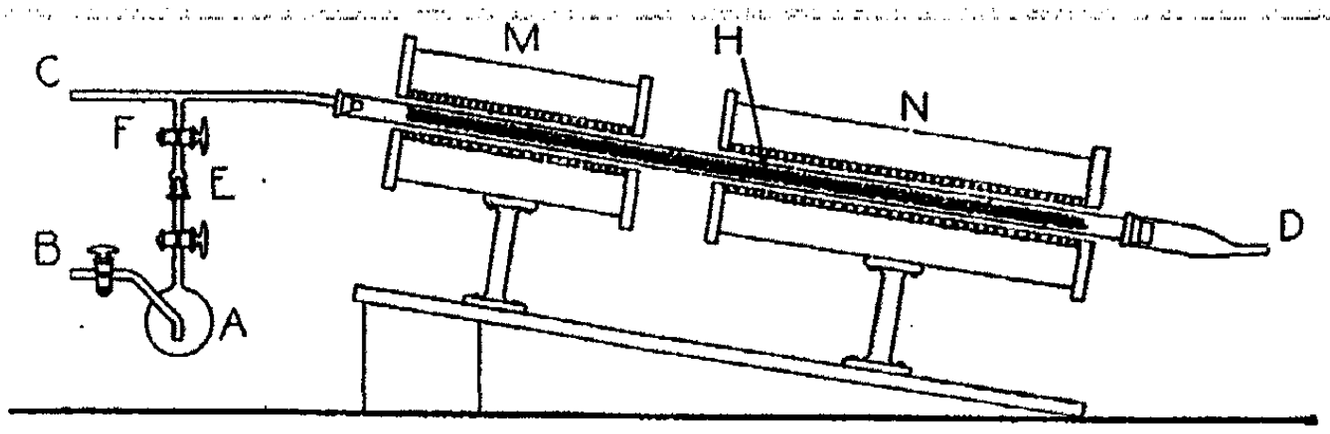



FIG. 2

and a slipjoint (not shown in the drawing) of the vacuum fractionation apparatus. A sample of the germanium tetramethyl was first distilled into bulb F of the vacuum apparatus. $S_5$ was closed and the bulb was detached and weighed. It was then again attached to the chain at E and a suitable portion of it was distilled over in the usual manner into the bulb A of the apparatus for analysis. The two stopcocks on A were closed and it was weighed. The bulb F of the vacuum apparatus was weighed again. This method gave double weighing on each sample.

Bulb A was then attached to the apparatus as shown in Fig. 2. M and N are two heating units of an electric combustion furnace. A single quartz tube, filled with copper oxide, passed through both units. The usual absorption apparatus was attached to the tube at D. The furnaces were brought to a temperature of about 150° and air was drawn through the apparatus through a purifying chain attached to C. The current through unit M was then turned off and the portion of the combustion tube lying in N was brought to a bright red heat beyond the point H. The stopcock beyond C was then closed, and that of the purifying chain attached to B, together with the two stopcocks of A, and stopcock F were opened. Air was slowly drawn through A carrying with it the vapor of the sample. This burned when it entered the furnace N, but backfire of the explosive mixture of alkyl and air was pre-

[1] Dennis and Hance: J. Am. Chem. Soc., 47, 370 (1925).

vented by the layer of cold, closely-packed copper oxide in M. When all of the sample had been carried out of A, unit M of the furnace was heated, and the combustion was completed in the usual manner.

Germanium was determined by bringing a weighed amount of the sample into bulb A and attaching that by means of the slipjoint to a 100 cc. flask containing a mixture of equal volumes of concentrated sulphuric acid and fuming nitric acid. An upright condenser was fused to the upper end of the flask. The acid mixture was cooled to about $-20°$ and the sample was slowly driven over by air pressure into the acid. A water-bath was then brought up around the flask, and the contents was heated until oxidation was complete. The solution and rinsings were evaporated to dryness in platinum, the excess of sulphuric acid was fumed off, the residue was dissolved in a ten per cent. solution of potassium hydroxide, and concentrated sulphuric acid was added until the acid concentration was 6 N. Germanium was precipitated from this solution as $GeS_2$, the remaining steps of the determination being as given by Dennis and Johnson.[1]

Anal. Subs., 0.1345, 0.3145. Calcd. for $Ge(CH_3)_4$: C, 0.0486, 0.1137 = 36.17 per cent. H, 0.0122, 0.0286 = 9.11 per cent. Found: C, 0.0486, 0.1137; Av., 36.17 per cent; H, 0.0123, 0.0286; Av. 9.125 per cent.

Subs., 0.4866, 0.6743. Calcd.: Ge, 0.2662, 0.3689 = 54.71 per cent. Found: 0.2661, 0.3688; Av. 54.69 per cent.

*Density of Germanium Tetramethyl as Gas.* Vapor density determinations were made with the vacuum apparatus of Laubengayer and Corey in the manner described by Dennis, Corey and Moore.[2]

Two determinations gave for the weight of 1 liter under standard conditions, 5.932 g. and 5.936 g.; av., 5.934 g. The calculated density is 5.924 g.

*Density as Liquid.* The density of the liquid sample was determined at 0°. Two determinations gave 1.003 and 1.009 g. per cc. The density as liquid may therefore be regarded as 1.

*Vapor Tension.* The vapor tension was determined from $-89°$ to $+46.5°$ using the apparatus of Laubengayer and Corey.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Temp.,°C | −89.2 | −79.1 | −64.8 | −49.0 | −40.0 | −29.5 | −21.8 |
| Press., mm. | 0.0 | 0.8 | 2.3 | 7.0 | 11.8 | 24.3 | 41.4 |
| Temp.,°C | −12.4 | − 9.6 | 0.0 | 9.3 | 21.4 | 30.1 | 39.7 |
| Press., mm. | 73.2 | 87.9 | 139.3 | 209.5 | 342.3 | 473.2 | 679.5 |
| Temp.,°C | 41.8 | 43.0 | 46.5 | | | | |
| Press., mm. | 718.6 | 749.3 | 836.6 | | | | |

*Boiling Point.* The boiling point of germanium tetramethyl, as taken from the vapor-tension curve, is 43.4°.

*Index of Refraction.* This was determined with an Abbé refractometer. Four closely agreeing determinations gave 1.3868 at 23.5°.

[1] Dennis and Johnson: J. Am. Chem. Soc., **47**, 790 (1925).

[2] Dennis, Corey and Moore: J. Am. Chem. Soc., **46**, 657 (1924).

*Melting Point.* The melting point was determined in the tube R, Fig. 2, of the vacuum fractionation apparatus by observing the temperature at which the solid and liquid phases were coexistent. Agreeing results indicated that the melting point is in the neighborhood of −88°.

*Properties of Germanium Tetramethyl.* The substance is a colorless, oily liquid of a pleasant, sweetish odor somewhat resembling that of chloroform, but quite unlike that of germanium tetraethyl. It burns with a sooty flame which is yellow on the outer surface but shows a deep-red inner mantle.

Germanium tetramethyl is more readily acted upon by oxidizing agents than is the tetraethyl. Nitric acid slowly oxidizes it at 0°. Chlorine rapidly acts upon it in the cold, but bromine attacks it much more slowly. Iodine did not seem to affect it during a period of 48 hours. Concentrated hydrochloric acid and concentrated sulphuric acid do not act upon it in the cold.

Germanium tetramethyl is soluble without decomposition in alcohol, ether and benzene. It appears to form a constant boiling mixture with ether, boiling at a temperature slightly above 34°.

## Summary

This article deals with the preparation of germanium tetramethyl, its purification and analysis, density as gas, density as liquid, vapor tension, boiling point, index of refraction, melting point and some of its chemical properties. There is also described a method for analysis by combustion of a liquid containing carbon and hydrogen.

*Ithaca,*
*New York.*

# THE DISSOCIATION OF WATER IN POTASSIUM AND SODIUM BROMIDE SOLUTIONS*

BY HERBERT S. HARNED AND GEOFFREY M. JAMES

In the present investigation, the method used by Harned, Harned and Swindells, and Åkerlöf[1] for the determination of the activity coefficient of water as an electrolyte and therefrom its dissociation in neutral aqueous potassium, sodium, lithium chloride and sulphate solutions has been used for determining these same quantities in aqueous potassium and sodium bromide solutions. The data necessary for the evaluations of these quantities include measurements of the cells:

$$H_2 \mid HBr(m_o), MBr(m) \mid AgBr \mid Ag,$$
$$H_2 \mid MOH(m_o), MBr(m) \mid M_xHg \mid MOH(m_o) \mid H_2, \text{ and}$$
$$Ag \mid AgBr \mid MBr(m+m_o) \mid M_xHg \mid MBr(m_o) \mid AgBr \mid Ag.$$

In this study, measurements of the first of these cells containing 0.01 M and 0.1 M hydrobromic acid in potassium and sodium bromide solutions and measurements of the second of the above cells containing 0.1 M potassium hydroxide in potassium bromide solutions have been made. The necessary data on cells containing sodium hydroxide in sodium bromide solutions as well as the data for the third type of cells containing sodium bromide have been obtained from the yet unpublished work of Mr. Stuart D. Douglas. The data of the third type of cells containing potassium bromide were obtained from the measurements of Pearce and Hart,[2] supplemented by some values for the concentrated solutions obtained by Mr. Douglas.[3]

## (1) Materials

Potassium amalgam containing 0.01% potassium was made by the method described by MacInnes and Parker, Knobel, and Harned.[4]

Potassium hydroxide solutions were prepared from the purest grade of potassium hydroxide available by precipitating the carbonate present in a solution of about 20% strength by means of a saturated solution of barium hydroxide. The carbonate-free solution was titrated against standardized hydrochloric acid, diluted to 0.1 M by redistilled water, and finally titrated from time to time with a 0.1 M hydrochloric acid solution which had been standardized gravimetrically. It was preserved in a large bottle fitted with soda-lime tubes.

Potassium and sodium bromides and potassium iodide of the best grade obtainable were ground and dried at 105°. These were tested for neutrality.

* Contribution from the John Harrison Laboratory of Chemistry of the University of Pennsylvania.

[1] Harned: J. Am. Chem. Soc., 47, 930 (1925); Harned and Swindells: 48, 126 (1926); Åkerlöf: 48, 1160 (1926).

[2] Pearce and Hart: J. Am. Chem. Soc., 43, 2483 (1921).

[3] Douglas: Thesis, University of Pennsylvania (1926).

[4] MacInnes and Parker: J. Am. Chem. Soc., 37, 1445 (1915); Knobel: 45, 70 (1923); Harned: 47, 676 (1925).

Hydrobromic acid. Stock solutions of 0.01 M and 0.1 M acid were made and standardized by gravimetric analysis. The acid solutions containing the bromides were made from these solutions by adding to weighed portions the calculated amounts of the respective salts.

Hydrogen was prepared by electrolyzing a 15% sodium hydroxide solution in a suitable apparatus containing a nickel cathode and a platinum anode.

## (2) Experimental Procedure

(a) *Cells:*

$$H_2 \mid HBr(m_o), MBr(m) \mid AgBr \mid Ag$$

Measurements of cells of this type containing no salt and different hydrobromic acid concentrations have been obtained by Lewis and Storch[1] and more recently by Livingston.[2] The electromotive forces of similar cells containing hydrochloric acid of constant strength and chloride solutions of varying strength have been studied extensively,[3] and the technique need not be described in detail. Suffice it to say that the method of preparing silver—silver chloride electrodes employed by Noyes and Ellis[4] was found to be quite satisfactory for the preparation of the silver—silver bromide electrodes. The measurements were all carried out at 25°. The electromotive forces were corrected to a hydrogen pressure of one atmosphere.

(b) *Cells:*

$$H_2 \mid KOH(m_o), KBr(m) \mid K_xHg \mid KOH(m_o) \mid H_2$$
$$H_2 \mid KOH(m_o), KI(m) \mid K_xHg \mid KOH(m_o) \mid H_2$$

Flowing amalgam cells of this type have been recently studied by a number of investigators.[5] In the present study, the cell employed was the same design as that described by Åkerlöf and permitted washing and filling without removal from its position in the thermostat. The solutions were boiled in vacuum and vacuum technique was employed throughout in the manner described by the previous investigators. This insured the removal of all but the slightest traces of dissolved air from the apparatus and the solutions.

## (3) Measurement of the Cells

$$H_2 \mid HBr(m_o), MBr(m) \mid AgBr \mid Ag$$

and Discussion of the Activity Coefficient of Hydrobromic Acid in Potassium and Sodium Bromide Solutions.

If the electromotive force, E, of the above cell containing salt at a concentration (m) be subtracted from the electromotive force, $E_o$, of the same cell containing no salt and acid at a concentration ($m_o$), the electromotive force of the concentration cell without liquid junction, or

$$Ag \mid AgBr \mid HBr(m_o), MBr(m) \mid H_2 \mid HBr(m_o) \mid AgBr \mid Ag$$

---

[1] Lewis and Storch: J. Am. Chem. Soc., 39, 2544 (1917).

[2] Livingston: J. Am. Chem. Soc., 48, 45 (1926).

[3] Harned: J. Am. Chem. Soc., 38, 1986 (1916); 42, 1808 (1920); 48, 326 (1926); Harned and Brumbaugh: 44, 2729 (1922); Harned and Swindells: 48, 126 (1926).

[4] Noyes and Ellis: J. Am. Chem. Soc., 39, 2532 (1917).

[5] Knobel: J. Am. Chem. Soc., 45, 70 (1923); Harned: 47, 676 (1926); Harned and Swindells: 48, 126 (1926); Åkerlöf: 48, 1160 (1926).

is obtained. From this measurement, the free energy change of transfer from the acid to the acid—salt solution may be obtained and also the activity coefficient of the acid relative to its value at ($m_o$) concentration by the equation

$$-\frac{\Delta\bar{F}}{NF} = E_o - E = E' = 0.05915 \log \frac{\gamma_{H(s)}\gamma_{Br(s)}(m+m_o)m_o}{\gamma_{H(m_o)}\gamma_{Br(m_o)}m_o^2} \qquad (1)$$

whence, taking the square root of the fraction and rearranging,

$$\log \frac{\gamma_{HBr(s)}}{\gamma_{HBr(m_o)}} = \frac{E'}{0.1183} - \log \sqrt{\frac{(m+m_o)}{m_o}} \qquad (2)$$

is obtained since $\gamma_{HBr}$ equals $\sqrt{\gamma_H\gamma_{Br}}$. Tables I and II contain the data and the activity coefficients of the hydrobromic acid for the solutions containing the acid at 0.01 M and 0.1 M concentrations and potassium bromide, and for the 0.01 M and 0.1 M acid solutions containing sodium bromide, respectively. The activity coefficient of the acid was taken to be 0.914 at 0.01 M pure aqueous solution. All other values of $\gamma$ in the tables are referred to this one.

TABLE I

Activity Coefficients of Hydrobromic Acid in Potassium Bromide Solutions

$m_o = 0.1 \quad \gamma_o = 0.805$

| m | E | E′ | γ |
|---|---|---|---|
| 0.0 | 0.20050* | 0.00000 | 0.805 |
| 0.1 | 0.18532 | 0.01518 | 0.765 |
| 0.2 | 0.17611 | 0.02439 | 0.747 |
| 0.3 | 0.16922 | 0.03128 | 0.740 |
| 0.5 | 0.15924 | 0.04126 | 0.734 |
| 1.0 | 0.14218 | 0.05832 | 0.755 |
| 2.0 | 0.11948 | 0.08102 | 0.850 |
| 3.0 | 0.10234 | 0.09816 | 0.977 |

*Mean value of three determinations.

$m_o = 0.01 \quad y_o = 0.914$

| m | E | E′ | γ |
|---|---|---|---|
| 0.0 | 0.31342† | 0.00000 | 0.914 |
| 0.007 | 0.30107 | 0.01235 | 0.891 |
| 0.01 | 0.29730 | 0.01612 | 0.884 |
| 0.02 | 0.28792 | 0.02550 | 0.867 |
| 0.04 | 0.27637 | 0.03705 | 0.840 |
| 0.07 | 0.26573 | 0.04769 | 0.817 |
| 0.1 | 0.25869 | 0.05473 | 0.799 |
| 0.2 | 0.24400 | 0.06942 | 0.770 |
| 0.3 | 0.23530 | 0.07812 | 0.751 |
| 0.5 | 0.22295 | 0.09047 | 0.744 |
| 1.0 | 0.20466 | 0.10876 | 0.755 |
| 2.0 | 0.18130 | 0.13212 | 0.843 |
| 3.0 | 0.16384 | 0.14958 | 0.968 |

*Mean value of five determinations.

## TABLE II

### The Activity Coefficients of Hydrobromic Acid in Sodium Bromide Solutions

$m_0 = 0.1$ $\gamma_0 = 0.805$

| m | E | E′ | γ |
|---|---|---|---|
| 0.0 | 0.20050 | 0.00000 | 0.805 |
| 0.1 | 0.18478 | 0.01572 | 0.773 |
| 0.2 | 0.17509 | 0.02541 | 0.762 |
| 0.3 | 0.16790 | 0.03260 | 0.759 |
| 0.5 | 0.15676 | 0.04374 | 0.770 |
| 1.0 | 0.13753 | 0.06297 | 0.827 |
| 2.0 | 0.11001 | 0.09049 | 1.022 |
| 3.0 | 0.08742 | 0.11308 | 1.306 |

$m_0 = 0.01$ $\gamma_0 = 0.914$

| m | E | E′ | γ |
|---|---|---|---|
| 0.0 | 0.31342 | 0.00000 | 0.914 |
| 0.007 | 0.30094 | 0.01248 | 0.893 |
| 0.01 | 0.29711 | 0.01631 | 0.888 |
| 0.02 | 0.28771 | 0.02571 | 0.870 |
| 0.04 | 0.27625 | 0.03717 | 0.842 |
| 0.07 | 0.26538 | 0.04804 | 0.823 |
| 0.1 | 0.25854 | 0.05488 | 0.802 |
| 0.2 | 0.24337 | 0.07005 | 0.780 |
| 0.3 | 0.23412 | 0.07930 | 0.768 |
| 0.5 | 0.22112 | 0.09230 | 0.771 |
| 1.0 | 0.20047 | 0.11295 | 0.819 |
| 2.0 | 0.17207 | 0.14135 | 1.009 |
| 3.0 | 0.14925 | 0.16417 | 1.286 |

The activity coefficients of hydrobromic acid at 0.01 M and 0.1 M in potassium and sodium bromide solutions are plotted in Fig. 1 along with similar results for hydrochloric acid in potassium chloride solutions obtained from the data of Harned.[1] The activity coefficient of hydrobromic acid is greater in sodium than in potassium bromide solutions of equal strength which is similar to the behavior of hydrochloric acid in the corresponding chloride solutions. Further, the activity coefficient of hydrobromic acid in a bromide solution is greater than that of hydrochloric acid in the corresponding chloride solution. Since the activity coefficient of a pure bromide in aqueous solution is greater at a given concentration than the corresponding chloride, this follows the general rule that the activity coefficient of an acid—in contradistinction to an hydroxide—is greater in a solution containing a salt which has the greater activity coefficient. Finally, it is of interest to note that the curves of the 0.01 M series and the 0.1 M series are very nearly the same in all cases

[1] Harned: J. Am. Chem. Soc., 48, 326 (1926).

at the same total concentration. This would indicate that the law of the linear variation of the logarithm of the activity coefficient is not exactly valid for hydrobromic acid in these bromide solutions.[1]

### (4) Measurements of the Cells

$$H_2 \mid KOH(m_2),\ KBr(m) \mid K_xHg \mid KOH(m_1) \mid H_2$$
$$H_2 \mid KOH(m_2),\ KI(m) \mid K_xHg \mid KOH(m_1) \mid H_2$$

and the Activity Coefficients of Potassium Hydroxide in Potassium Bromide and Iodide Solutions.

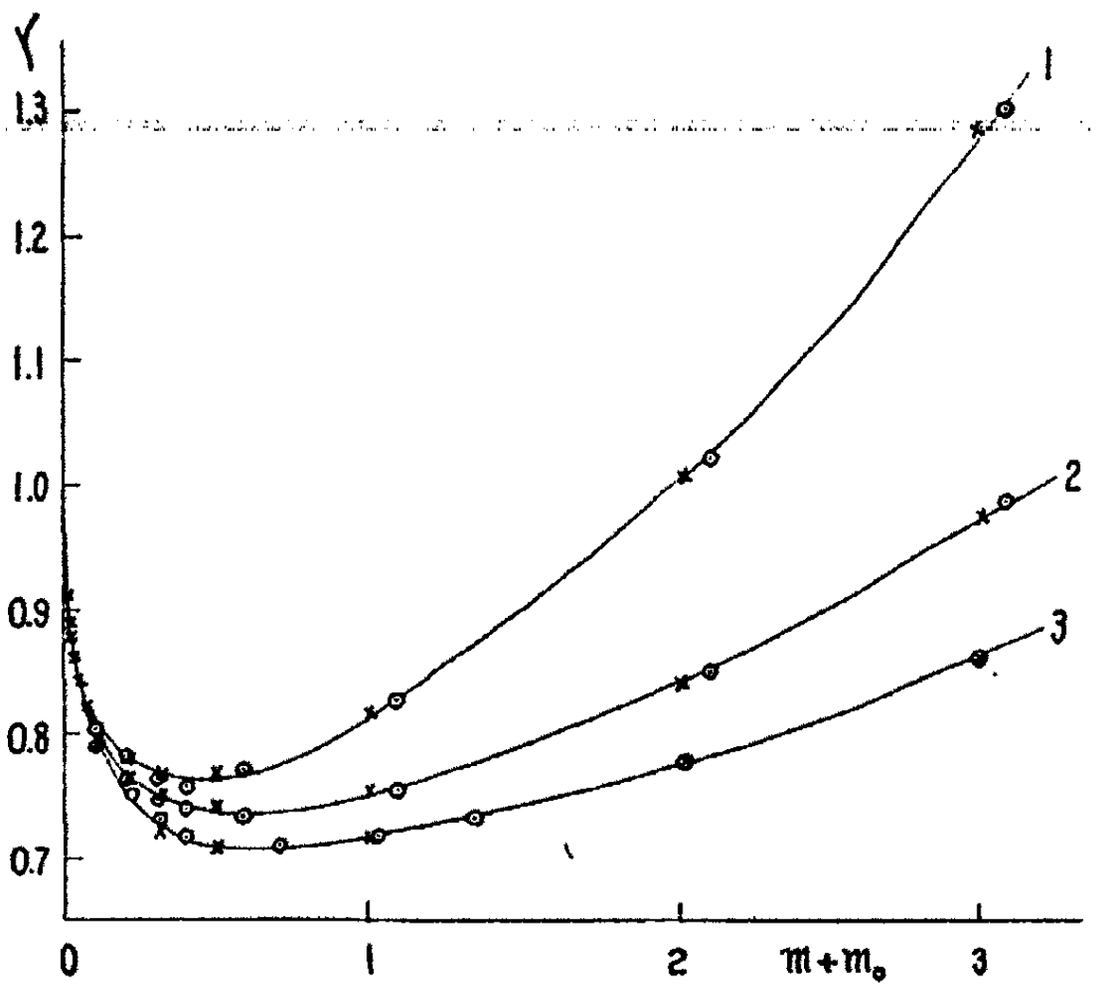



FIG. 1

Activity Coefficients of Hydrobromic Acid in Potassium and Sodium Bromide Solutions.

⊙ 0.1 M Acid Series
× 0.01 M Acid Series
1. HBr in NaBr
2. HBr in KBr
3. HCl in KCl.

Tables III and IV contain the results of the measurements of the above cells containing potassium hydroxide in potassium bromide solutions and potassium hydroxide in potassium iodide solutions, respectively. The first three columns show the concentrations of the solutions contained in the cells and the fourth column the observed electromotive forces. Since the exclusion of dissolved air was necessary which involved the process of boiling in vacuum,

[1] Harned: J. Am. Chem. Soc., 48, 326 (1926).

TABLE III

Electromotive Forces of the Cells:
$H_2 \mid KOH(m_2), KBr(m) \mid K_xHg \mid KOH(m_1) \mid H_2$

| $m_1$ | $m_2$ | m | E | $\Delta E$ | $E_{Corr.}$ |
|---|---|---|---|---|---|
| 0.1010 | 0.1009 | 0.2025 | 0.02263 | 0.00023 | 0.02286 |
| 0.1012 | 0.1014 | 0.5091 | 0.03767 | 0.00024 | 0.03791 |
| 0.1006 | 0.1008 | 1.012 | 0.05186 | 0.00003 | 0.05189 |
| 0.1008 | 0.1003 | 2.015 | 0.06899 | 0.00032 | 0.06931 |
| 0.1017 | 0.1007 | 3.103 | 0.08040 | 0.00067 | 0.08107 |

TABLE IV

Electromotive Forces of the Cells:
$H_2 \mid KOH(m_2), KI(m) \mid K_xHg \mid KOH(m_1) \mid H_2$

| $m_1$ | $m_2$ | m | E | $\Delta E$ | $E_{Corr.}$ |
|---|---|---|---|---|---|
| 0.1015 | 0.1016 | 0.2036 | 0.02152 | 0.00028 | 0.02175 |
| 0.1035 | 0.1025 | 0.5135 | 0.03565 | 0.00049 | 0.03614 |
| 0.1010 | 0.1019 | 1.022 | 0.05001 | 0.00001 | 0.05000 |
| 0.1031 | 0.1022 | 2.048 | 0.06668 | 0.00098 | 0.06766 |
| 0.1012 | 0.1012 | 3.044 | 0.07838 | 0.00029 | 0.07867 |

it was not convenient to make them up to exact round concentrations. For this reason, it was necessary to apply a small correction to the observed electromotive forces in order to obtain the electromotive forces of the cells containing exactly 0.1 M potassium hydroxide on both sides. This correction was made on the assumption that over the small ranges of concentration involved, the activity coefficients remained constant. The equation used for this correction is

$$\Delta E = 0.1183 \log \frac{m_1}{m_o} - 0.0591 \log \frac{m_2(m_2+m)}{m_o(m_o+m)} \qquad (3)$$

in which $m_o$ is the desired hydroxide concentration (in the present instance 0.1 M) and $\Delta E$ the correction to be applied. In the fifth columns of Tables III and IV are given the values of $\Delta E$ and in the sixth the corrected electromotive forces.

These electromotive forces are related to the activities of the ions and water by the equation

$$E = 0.05915 \log \frac{\gamma_{K(s)}\gamma_{OH(s)}\, a_{H_2O(m_1)}\ (m+m_o)m_o}{\gamma_{K(0.1)}\gamma_{OH(0.1)}a_{H_2O(s)}m_o^2} \qquad (4)$$

whence

$$E + 0.02568 \ln \frac{a_{H_2O(s)}}{a_{H_2O(0.1)}} = 0.05915 \log \frac{\gamma_{K(s)}\gamma_{OH(s)}\,(m+0.1)}{\gamma_{K(0.1)}\gamma_{OH(0.1)}\,0.1} \qquad (5)$$

where the subscript "s" refers to the solution of concentration $(m+0.1)$. Thus, if $\gamma_{K(0.1)}\gamma_{OH(0.1)}$ is known, $\gamma_{K(s)}\gamma_{OH(s)}$ and, therefore, $\gamma_{KOH(s)}$ or $\sqrt{\gamma_{K(s)}\gamma_{OH(s)}}$ may be calculated. Since the activity of water is proportional to its partial

vapor pressure, the second member on the left of this equation is equal to 0.02568 ln $p_s/p_{0.1}$. To compute the water activity ratios, the equation,

$$\ln \frac{p_0}{p_s} = \frac{m}{55.5}\left[2 + 2.303\alpha m - \frac{4.606\beta\alpha'}{\alpha'+1} m^{\alpha'}\right] \qquad (6)$$

which was shown by Harned[1] to be approximately valid over a considerable concentration range for strong uniunivalent electrolytes was found to be sufficiently accurate. $p_0$ is the vapor pressure of pure water and $p_s$ the vapor pressure of the solution. The values of the constants $\alpha$, $\alpha'$, and $\beta$ were obtained by the graphical method employed by Harned from the activity coefficients of potassium bromide and iodide which were calculated from the data of Pearce and Hart and Douglas. The values of the constants used were 0.08, 0.292, and 0.392 for $\alpha$, $\beta$, and $\alpha'$ in the case of potassium bromide, and 0.075, 0.263, and 0.353 for potassium iodide. It was assumed that the vapor pressures of the solutions containing the potassium halide at concentrations (m) and 0.1 M potassium hydroxide were the same as those of the salt solutions at concentrations (m+0.1). The value of ln $p_0/p_{0.1}$ was first computed, and then the values of ln $p_0/p_s$ at round concentrations, whence ln $p_s/p_{0.1}$ was obtained and, subsequently, 0.02568 ln $p_s/p_{0.1}$. These were plotted against the molal concentrations from which graphs the values in the third columns of Tables V and VI were obtained. The values of $\gamma$ calculated by equation (5) are given in the fifth columns of these tables. 0.772 at 0.1 M was taken as reference value.[2]

TABLE V

The Activity Coefficient of Potassium Hydroxide in Potassium Bromide Solutions KOH = 0.1 M

| m | E | 0.02568 ln $p_s/p_{0.1}$ | E+0.02568 ln $p_s/p_{0.1}$ | $\gamma$ |
|---|---|---|---|---|
| 0.0000 | 0.00000 | 0.000000 | 0.00000 | 0.772 |
| 0.2025 | 0.02286 | −0.000168 | 0.02269 | 0.690 |
| 0.5091 | 0.03791 | −0.000423 | 0.03749 | 0.649 |
| 1.012 | 0.05189 | −0.000850 | 0.05104 | 0.625 |
| 2.015 | 0.06931 | −0.001755 | 0.06756 | 0.625 |
| 3.103 | 0.08107 | −0.002856 | 0.07821 | 0.625 |

TABLE VI

The Activity Coefficient of Potassium Hydroxide in Potassium Iodide Solutions KOH = 0.1 M

| m | E | 0.02568 ln $p_s/p_{0.1}$ | E+0.02568 ln $p_s/p_{0.1}$ | $\gamma$ |
|---|---|---|---|---|
| 0.0000 | 0.00000 | 0.000000 | 0.00000 | 0.772 |
| 0.2036 | 0.02175 | −0.000172 | 0.02158 | 0.674 |
| 0.5135 | 0.03614 | −0.000437 | 0.03670 | 0.624 |
| 1.022 | 0.05000 | −0.000881 | 0.04912 | 0.600 |
| 2.048 | 0.06766 | −0.001861 | 0.06580 | 0.599 |
| 3.044 | 0.07867 | −0.002925 | 0.07574 | 0.601 |

[1] Harned: J. Am. Chem. Soc., 44, 252 (1922).
[2] Scatchard: J. Am. Chem. Soc., 47, 648 (1925).

The activity coefficients of potassium hydroxide in potassium bromide and iodide solutions as well as the values obtained by Harned[1] for this hydroxide in potassium chloride solutions are plotted in Fig. 2 whence it is seen that the hydroxide has the lower activity coefficient in the solutions of the salt which has the higher activity coefficient. As far as we are aware, this behavior is a general one and is just opposite to the behavior of acids in the salt solutions. To sum up, it is found that the activity coefficient of an acid and also the hydrogen ion is greater at a given concentration in a solution of a salt which itself possesses the greater activity coefficient whereas the reverse is true for the hydroxyl ion and hydroxides.

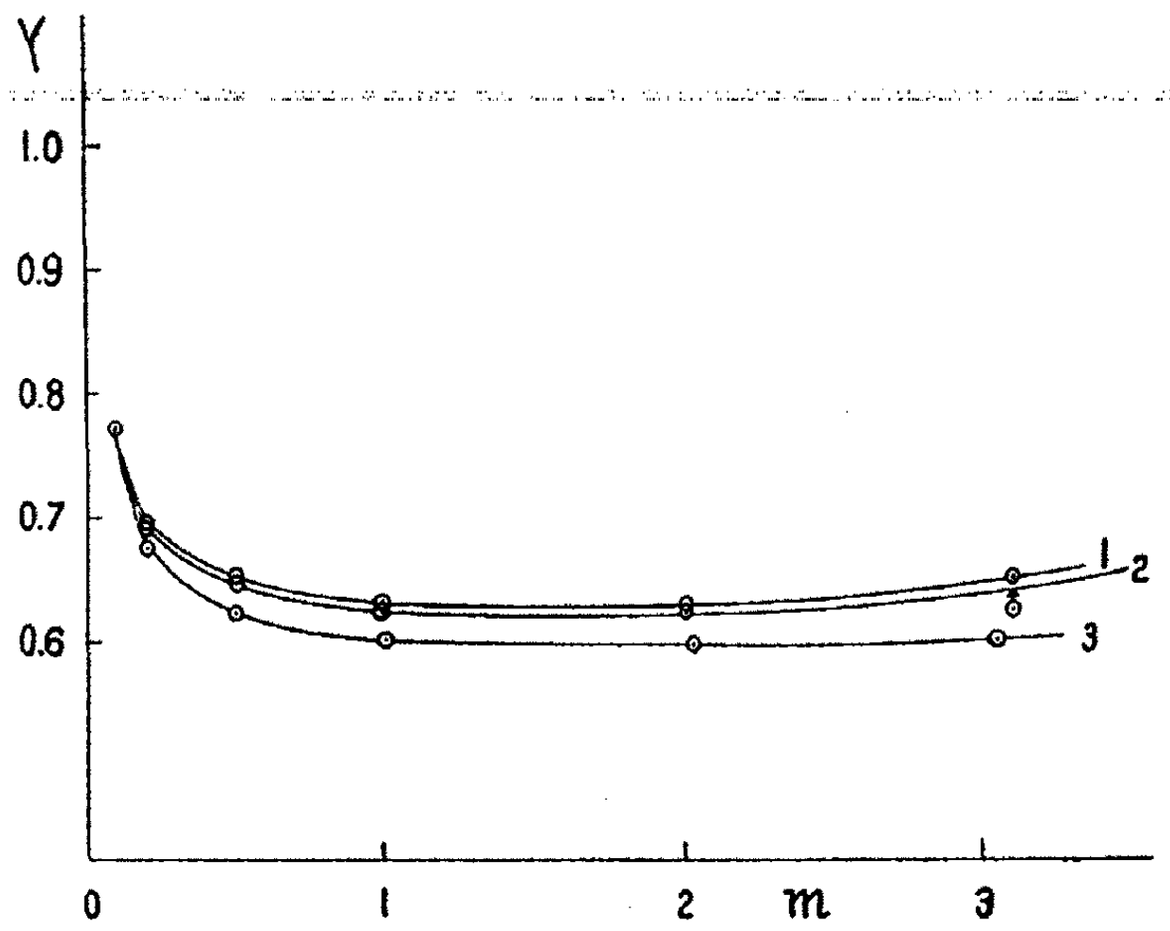



FIG. 2

The Activity Coefficient of KOH in KCl, KBr and KI Solutions.

1 KOH in KCl
2 KOH in KBr
3 KOH in KI

(5) The Ion Activity Coefficient and Ionic Concentration Product of Water in Potassium and Sodium Bromide Solutions.

The results of the measurements of the cells already described, together with the other data taken from the work of Douglas on cells of the type

$$Ag \mid AgBr \mid MBr(m_1) \mid M_xHg \mid MBr(m_2) \mid AgBr \mid Ag$$

permit the calculation of the activity coefficient of water as an electrolyte and the ionic concentration product of water in sodium and potassium bromide

[1] Harned: J. Am. Chem. Soc., 47, 689 (1925).

solutions by a method analogous to that used by Harned, Harned and Swindells, and Åkerlöf[1] for the alkaline chloride and sulphate solutions.

The electromotive forces of the cells of the type

$$Ag \mid AgBr \mid HBr(m_o), MBr(m) \mid H_2 \mid HBr(m_o) \mid AgBr \mid Ag$$

which are given in column five in Table I and II are related to the activity coefficients of the hydrogen and bromide ions by the equation

$$E_1 = 0.05915 \log \frac{\gamma_{H(s)}\gamma_{Br(s)}}{\gamma_{H(m_o)}\gamma_{Br(m_o)}} \frac{(m+m_o)m_o}{m_o^2} \qquad (1)$$

where the subscript "s" refers to the solution containing salt and acid, and $m_o$ to the solution containing acid only. The electromotive forces of the cells

$$H_2 \mid MOH(m_o), MBr(m) \mid M_xHg \mid MOH(m_o) \mid H_2$$

are related to the activity coefficients of the metal and hydroxyl ions and activities of the water molecules by the equation

$$E_2 = 0.05915 \log \frac{\gamma_{M(s)}\gamma_{OH(s)}\, a_{H_2O(m_o)}}{\gamma_{M(m_o)}\gamma_{OH(m_o)}\, a_{H_2O(s)}} \frac{(m_o+m)m_o}{m_o^2} \qquad (4)$$

Upon adding these two equations and rearranging the terms, we obtain

$$E_1+E_2 = 0.05915 \log \frac{\gamma_{M(s)}\gamma_{Br(s)}}{\gamma_{M(m_o)}\gamma_{Br(m_o)}} \frac{(m+m_o)^2}{m_o^2} + 0.05915 \log \frac{\gamma_{H(s)}\gamma_{OH(s)}a_{H_2O(m_o)}}{\gamma_{H(m_o)}\gamma_{OH(m_o)}a_{H_2O(s)}} \qquad (7)$$

The electromotive forces of the cells

$$Ag \mid AgBr \mid MBr(m+m_o) \mid M_xHg \mid MBr(m_o) \mid AgBr \mid Ag$$

are given by the equation

$$E_3 = 0.05915 \log \frac{\gamma_{M(m+m_o)}\gamma_{Br(m+m_o)}}{\gamma_{M(m_o)}\gamma_{Br(m_o)}} \frac{(m+m_o)_2}{m^{2o}} \qquad (8)$$

It can be seen that the right-hand member of this equation is identical with the first member on the right of equation (7). Subtracting (8) from (7) and rearranging terms we obtain

$$E_1+E_2-E_3 = 0.05915 \log \frac{\dfrac{\gamma_{H(s)}\gamma_{OH(s)}}{a_{H_2O(s)}}}{\dfrac{\gamma_{H(m_o)}\gamma_{OH(m_o)}}{a_{H_2O(m_o)}}} = 0.05915 \log \frac{K_{\gamma(s)}}{K_{\gamma(m_o)}} \qquad (9)$$

The calculation is shown in Tables VII and VIII in the case of potassium bromide and in Tables IX and X for sodium bromide.

[1] Harned: J. Am. Chem. Soc., **47**, 830 (1925); Harned and Swindells: **48**, 126 (1926); Åkerlöf: **48**, 1160 (1926).

## TABLE VII

### The Ionic Activity Coefficient Product of Water in Potassium Bromide Solutions 0.1 M Acid-Hydroxide Series

| m+0.1 | $E_1$ | $E_2$ | $E_3$ | $E_1+E_2-E_3$ | $K_{\gamma(s)}/K_{\gamma(0.1)}$ |
|---|---|---|---|---|---|
| 0.1 | 0.00000 | 0.0000 | 0.0000 | 0.0000 | 1.000 |
| 0.2 | 0.01518 | 0.0141 | 0.0323 | −0.0030 | 0.890 |
| 0.3 | 0.02438 | 0.0227 | 0.0513 | −0.0042 | 0.848 |
| 0.4 | 0.03128 | 0.0287 | 0.0643 | −0.0043 | 0.846 |
| 0.6 | 0.04126 | 0.0372 | 0.0830 | −0.0045 | 0.839 |
| 1.1 | 0.05832 | 0.0511 | 0.1110 | −0.0016 | 0.940 |
| 2.1 | 0.08102 | 0.0687 | 0.1435 | 0.0061 | 1.268 |
| 3.1 | 0.09816 | 0.0801 | 0.1637 | 0.0126 | 1.633 |

## TABLE VIII

### $\gamma_H\gamma_{OH}/a_{H_2O}$, $\sqrt{\gamma_H\gamma_{OH}}$, and $m_w$ of Water in Potassium Bromide Solutions

| m+0.1 | $K_{\gamma(s)}=\frac{\gamma_H\gamma_{OH}}{a_{H_2O}}$ | $0.02568 \ln p_s/p_{0.1}$ | $E_4=0.1183 \log \gamma_s/\gamma_{0.1}$ | $\gamma_s=\sqrt{\gamma_H\gamma_{OH}}$ | $m_w\times10^7$ |
|---|---|---|---|---|---|
| 0.1 | 0.569 | 0.000000 | 0.00000 | 0.754 | 1.329 |
| 0.2 | 0.507 | −0.000085 | −0.00309 | 0.710 | 1.408 |
| 0.3 | 0.484 | −0.000167 | −0.00437 | 0.693 | 1.442 |
| 0.4 | 0.482 | −0.000248 | −0.00455 | 0.690 | 1.445 |
| 0.6 | 0.478 | −0.000414 | −0.00491 | 0.685 | 1.450 |
| 1.1 | 0.535 | −0.000842 | −0.00244 | 0.719 | 1.371 |
| 2.1 | 0.721 | −0.001741 | 0.00436 | 0.821 | 1.180 |
| 3.1 | 0.842 | −0.002746 | 0.00985 | 0.913 | 1.093 |

## TABLE IX

### The Ionic Activity Coefficient Product Ratio of Water in Sodium Bromide Solutions 0.1 M Acid-Hydroxide Series

| m+0.1 | $E_1$ | $E_2$ | $E_3$ | $E_1+E_2-E_3$ | $K_{\gamma(s)}/K_{\gamma(0.1)}$ |
|---|---|---|---|---|---|
| 0.1 | 0.00000 | 0.0000 | 0.0000 | 0.0000 | 1.000 |
| 0.2 | 0.01572 | 0.0139 | 0.0331 | −0.0035 | 0.873 |
| 0.3 | 0.02541 | 0.0225 | 0.0524 | −0.0045 | 0.839 |
| 0.4 | 0.03260 | 0.0285 | 0.0663 | −0.0052 | 0.817 |
| 0.6 | 0.04374 | 0.0372 | 0.0862 | −0.0053 | 0.814 |
| 1.1 | 0.06297 | 0.0516 | 0.1175 | −0.0029 | 0.893 |
| 2.1 | 0.09049 | 0.0697 | 0.1546 | 0.0056 | 1.244 |

## TABLE X

### $\gamma_H\gamma_{OH}/a_{H_2O}$, $\sqrt{\gamma_H\gamma_{OH}}$, and $m_w$ of Water in Sodium Bromide Solutions

| m+0.1 | $K_{\gamma_s}=\frac{\gamma_H\gamma_{OH}}{a_{H_2O}}$ | $0.02568 \ln p_s/p_{0.1}$ | $E_4=0.1183 \log \gamma_s/\gamma_{0.1}$ | $\gamma_s=\sqrt{\gamma_H\gamma_{OH}}$ | $m_w\times 10^7$ |
|---|---|---|---|---|---|
| 0.1 | 0.551 | 0.000000 | 0.00000 | 0.742 | 1.351 |
| 0.2 | 0.481 | −0.000085 | −0.00358 | 0.692 | 1.445 |
| 0.3 | 0.462 | −0.000169 | −0.00467 | 0.678 | 1.475 |
| 0.4 | 0.450 | −0.000256 | −0.00676 | 0.663 | 1.494 |
| 0.6 | 0.449 | −0.000428 | −0.00573 | 0.664 | 1.497 |
| 1.1 | 0.492 | −0.000893 | −0.00379 | 0.689 | 1.429 |
| 2.1 | 0.685 | −0.001963 | 0.00364 | 0.796 | 1.211 |

Tables VII and IX contain in the first columns the molal concentrations, and in the next three columns the values of $E_1$, $E_2$ and $E_3$. The values of $E_1$ are those given in the fifth columns of Tables V and VI, respectively. The values of $E_2$ for potassium bromide were read off from large scale plots of the values given in the second column of Table V. In the case of sodium bromide the values shown for $E_2$ in Table IX were obtained in the same manner from the data of Douglas on sodium hydroxide in sodium bromide solutions. The values of $E_3$ for both neutral salt solutions were also derived from the work of Douglas by reading off the values at the required concentrations from large scale plots. In the fifth columns of Tables VII and IX are given the values of $E_1+E_2-E_3$ and in the sixth columns the values of $K_{\gamma(s)}/K_{\gamma(0.1)}$ calculated by means of equation (9). We have now to estimate $K_{\gamma(0.1)}$ in order to compute the absolute values of $K_{\gamma(s)}$ and of the activity coefficient of water as an electrolyte, $\gamma_s$ or $\sqrt{\gamma_H\gamma_{OH}}$. Since our chief interest lies in the comparison of these results with those obtained by Harned[1] on the ionic concentration of water in potassium and sodium chloride solutions, we have simply taken $K_{\gamma(0.1)}$ at the reference concentration, 0.1M, to be somewhat less than the values employed in the case of the chloride solutions. Therefore, we let $\gamma_{0.1}$ equal 0.754 and 0.742 for potassium and sodium bromides at 0.1 M, whereas Harned employed 0.764 and 0.752 for the respective chlorides. From these values, $K_{\gamma(0.1)}$ is found to be 0.569 and 0.551 for the potassium and sodium bromide solutions, respectively.

In the second columns of Tables VIII and X are given the values of $K_{\gamma(s)}$ calculated from the ratios in the sixth columns of Table VII and IX. In order to compute $\gamma_s$ or $\sqrt{\gamma_H\gamma_{OH}}$ it is necessary to eliminate $a_{H_2O}$. This has been done by the method previously employed in the calculation of the activity coefficient of the hydroxide in the bromide and iodide solutions. The third columns of Tables VIII and X contain the values of $0.02568 \ln p_s/p_{0.1}$ obtained by readings at the required concentrations from the appropriate large scale plots. The fourth columns of Tables VIII and X contain the values of $E_4$ obtained by adding the values of $0.02568 \ln p_s/p_{0.1}$ to those given in the fifth

[1] Harned: J. Am. Chem. Soc., 47, 930 (1925).

columns of Tables VII and IX. The fifth columns in Tables VIII and X contain the values of $\gamma_s$ calculated from the values of $E_4$ by means of the equation

$$E_4 = 0.1183 \log \gamma_s/\gamma_{0.1} \qquad (10)$$

The results obtained also permit the calculation of the dissociation of water, or the molal concentration of dissociated water molecules per 1000 gs.

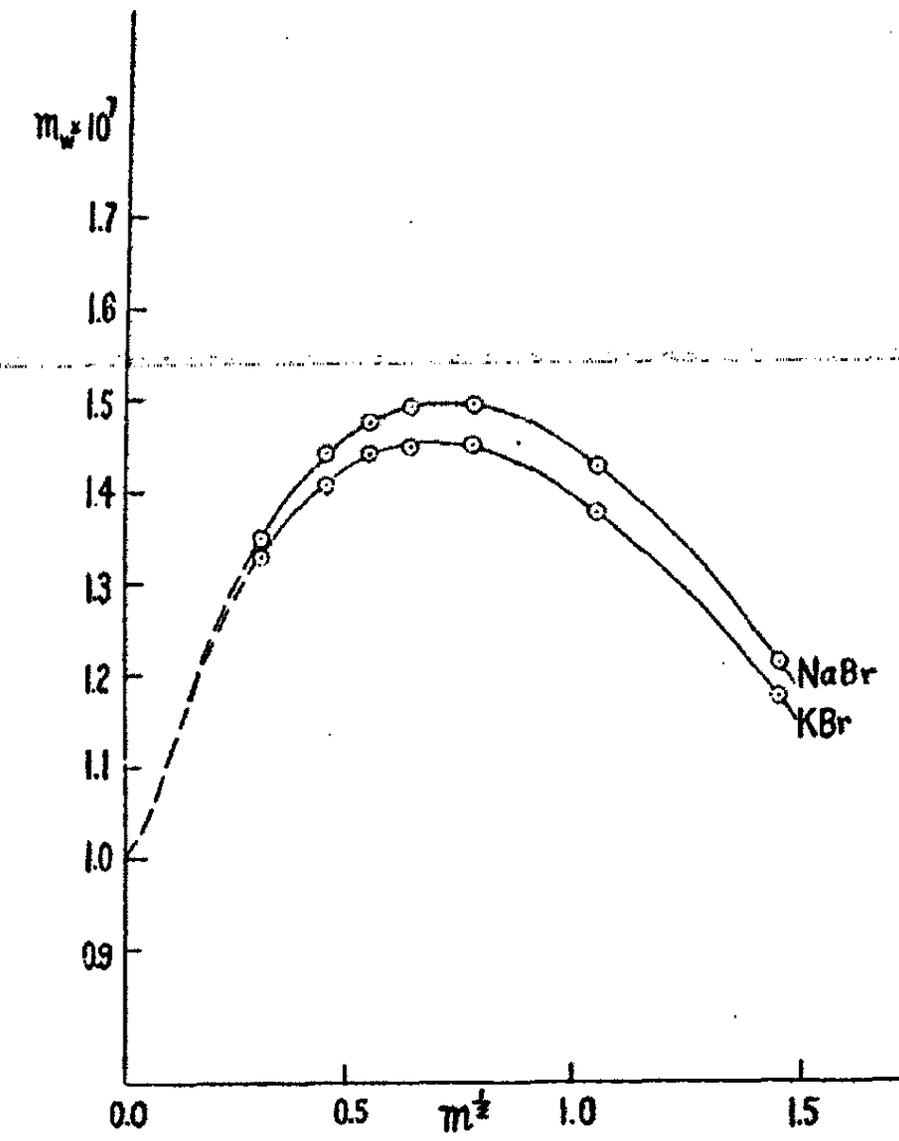



FIG. 3

The Dissociation of Water in Potassium and Sodium Bromide Solutions.

of water, $m_w$. The constant of equilibrium for the dissociation of water into ions is given thermodynamically by

$$K_w = \frac{a_H a_{OH}}{a_{H_2O}} = \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} m_w^2$$

where $k_w$ is the dissociation constant, and $m_w$ the concentration of the hydrogen and hydroxyl ions of water. Solving for $m_w$, we obtain

$$m = m_H = m_{OH} = \sqrt{\frac{K_w}{K_{\gamma(s)}}} \qquad (11)$$

The value of $K_w$ at 25° was taken to be $1.005 \times 10^{-14}$. The values of $m \times 10^7$ are shown in the sixth columns of Tables VIII and X.

In Fig. 3, the values of $m_w \times 10^7$ in potassium and sodium bromide solutions are plotted against the square root of the salt concentration. The

dashed curves at salt concentrations below 0.1 M were not determined but were estimated from the similar results obtained by Harned[1] in the cases of the corresponding chloride solutions. These plots are quite similar to those obtained by Harned, and are of the same order of magnitude. Sodium bromide produces a somewhat greater dissociation than potassium bromide and sodium chloride, and potassium bromide produces a somewhat greater dissociation than potassium chloride. The maxima of all these curves occur at approximately 0.5 M salt concentration.

## Summary

(1) Measurements of the following types of cells were made:

$H_2 \mid KOH(m_o), KBr(m) \mid K_xHg \mid KOH(m_o) \mid H_2$

$H_2 \mid KOH(m_o), KI(m) \mid K_xHg \mid KOH(m_o) \mid H_2$

$H_2 \mid KBr(m_o), KBr(m) \mid AgBr \mid Ag$

$H_2 \mid HBr(m_o), NaBr(m) \mid AgBr \mid Ag$

(2) From the results obtained, the activity coefficients of potassium hydroxide in solutions of potassium bromide and iodide, and of hydrobromic acid in solutions of potassium and sodium bromides have been calculated.

(3) A calculation of the activity coefficient of water as an electrolyte and the ionic concentration of water in potassium and sodium bromide solutions has been made.

*Philadelphia,*
*Pennsylvania.*

[1] Harned: J. Am. Chem. Soc., **47**, 930 (1925).

# THE NATURE OF "STANNIC ACIDS"

BY E. POSNJAK

Since the time of Berzelius the so-called stannic acids have been the subject of numerous investigations. Disregarding the various compositions which have at one time or another been assigned to "stannic acids," it had until recently been thought that there existed two isomeric compounds. Textbooks of inorganic and analytical chemistry usually still distinguish between $\alpha$ and $\beta$ or ortho- and meta-stannic acids. This distinction is based on the apparent differences in their behavior toward certain reagents and on their relative stability. The typical $\alpha$-stannic acid is usually formed by precipitation of stannic salts at ordinary temperature, while the typical $\beta$-stannic acid is formed by the action of strong hot nitric acid on tin.

A review of the work done on the so-called stannic acids has recently been given by H. B. Weiser.[1] Referring the reader to his paper for a more complete statement we shall briefly mention here only a few of the more significant results and discuss a paper by Willstätter and his collaborators, which has appeared since Weiser's publication.

Van Bemmelen[2] investigated the water content of the typical "stannic acids." He showed by means of dehydration experiments that there existed no definite hydrates, but that their composition varied according to the method of preparation, the surrounding water vapor pressure, and the temperature. He also studied the action of various reagents on "$\alpha$ and $\beta$ stannic acid" and came to the conclusion that their behavior was explainable on the basis of the colloidal character of the stannic acids ("colloidal modifications"), that is, adsorption and peptization were taking place (except where concentrated reagents were used) rather than formation of definite compounds and true solutions.

Lorenz[3] confirmed Van Bemmelen's observations of the variability of the water content which under certain conditions he found to be identical for $\alpha$ and $\beta$ stannic acid, but he thought that chemically they behaved as two different modifications.

More recently Mecklenburg[4] investigated the behavior of the "stannic acids." His leading thought was that if the differences between $\alpha$ and $\beta$ stannic acid were due to their colloidal nature they probably represent the end members of a series of possible preparations, whose properties and behavior would be intermediate between them. By preparing "stannic acids" at different temperatures Mecklenburg was able to show that a series of preparations could readily be made whose properties changed in a continuous

[1] J. Phys. Chem., 26, 654 (1922).

[2] Van Bemmelen's collected papers, published under the title, "Die Absorption," 54 (1910).

[3] Z. anorg. Chem., 9, 369 (1895).

[4] Z. anorg. Chem., 74, 207 (1912).

way, lying between the characteristic properties of $\alpha$ and $\beta$ stannic acids. He was thus able to demonstrate the colloidality of the "stannic acids" and, in a plausible way, attributed their differences to the difference in the size of their "primary" particles. Thus the "$\alpha$-stannic acid" which is formed at low temperature has smaller "primary" particles than the "$\beta$-stannic acid" and accordingly is much readier to peptize, shows greater adsorption values, etc. than the so-called meta-stannic acid. Weiser,[1] whose review of the work done on the "stannic acids" has been referred to above, confirmed and supplemented some of Mecklenburg's work, thus bringing the problem of the so-called isomery of stannic acids to a fairly definite conclusion on the basis of colloidal chemistry.

Recently, however, Willstätter and his collaborators[2] have, among a series of papers dealing with various hydrated oxides, published also one on "stannic acids." They consider that the colloidality of "stannic acids" and the conclusions drawn therefrom have been overemphasized and that the chemical nature of these substances has been neglected. They assume the existence of a large number of chemically definite stannic acids, which they divide into three groups: (1) mono-stannic acids, (2) a-stannic acids and (3) b-stannic acids. In the first group they include three simple hydrates, while the second and third groups are derived from the first one by various and progressively increasing degrees of polymerization and "intermolecular dehydration." They establish this classification and distinguish between these types of stannic acid by the strength of hydrochloric acid required to "either dissolve a stannic hydroxide as a tin base, or to convert it into a water-soluble compound." That such a distinction is not only arbitrary but meaningless, is self-evident. They further tried to establish the existence of definite hydrates by taking dehydration curves. Considering the usual method of determining the loss of water by heating a definite single sample through all temperatures as faulty, the authors used for each temperature "a new, previously not heated sample." Each of the four curves given, representing different preparations, shows a break which takes place for each preparation not only at a different temperature but also at different stages of hydration and which the authors think proves the existence of definite hydrates. The fact that preparations which had been air-dried prior to their use for dehydration experiments lost more water on heating to a certain temperature than those which were partially dehydrated at room temperature in a desiccator, is taken by the authors to indicate chemical changes on drying and is suggested as an explanation for the difficulties and the failures of previous experimenters to establish definite hydrates.

It seems that the conclusions drawn by Willstätter and his collaborators are to say the least very hasty. It is questionable whether such dehydration experiments represent more than rates of dehydration. In such cases it is always necessary to guard against the mistake of taking rates for equilibrium conditions, and unless some direct relation is found between the water lost

[1] J. Phys. Chem., **26**, 654 (1922).

[2] R. Willstätter, N. Kraut and W. Fremery: Ber. **57**, 63 (1924).

in a certain temperature interval and a parallel definite change in some other property, the assumption of hydrates is not sound. The method of using fresh samples for each temperature is hardly to be regarded as an improvement and the usual way of heating a single sample to constant weight for a sufficiently long time is probably more reliable.

Dehydration probably always causes crust formation which may greatly decrease the rate of dehydration. Such crust formation, rather than chemical changes on drying, may be responsible for the difference observed by Willstätter and his collaborators in the dehydration of air-dried preparations as compared with those dried over phosphorus pentoxide.

In conclusion one may say that Willstätter and his collaborators did not bring forth a single new fact, but rather take the problem back some fifty years and only add further to the confusion.

As has been stated above, the problem of the so-called stannic acids though not completely solved, has been greatly clarified by the application of the viewpoints of colloidal chemistry. We have now on hand, however, a method for obtaining the necessary direct proof provided these substances are crystalline. This is, of course, the application of the X-ray powder method[1] which has already in many similar cases furnished complete solutions. As is well known, it consists in passing a beam of monochromatic X-rays through a finely divided crystalline substance which causes diffraction effects to take place. In this way a number of lines are produced which may be registered on a photographic film. The spacing and the intensity of such lines are characteristic for each substance and may therefore serve for their identification as suggested by A. W. Hull.[2]

It seemed desirable to apply this method in the case of the "stannic acids." Accordingly preparations of the two "stannic acids" were made in the following way. The "$\alpha$-stannic acid" was prepared by nearly neutralizing a solution of sodium stannate with hydrochloric acid. The voluminous precipitate was first washed by decantation and finally brought on a filter where it was further washed and left to become air dry; all of course taking place at room temperature. The "$\beta$-stannic acid" was prepared by the usual method of letting strong hot nitric acid react with tin. The precipitate which formed was filtered off, washed, and as in the case of the other preparation was left to become air dry at room temperature. In addition to these two preparations, the X-ray examination included crystals of stannic oxide.

The results are given in Table I where for each substance the interplanar spacing $d/n$ and the relative intensity (I) are given. The first value is derived from the fundamental equation underlying X-ray reflection, $n\lambda = 2d \sin \Theta$, in which $n$ is the order of reflection, $\lambda$ the wave-length of X-rays used ($K_\alpha$ line of molybdenum, 0.712 A. U.), $d$ is the distance between the planes of atoms and $\Theta$ is the angle of reflection. The intensity (I) is a visual estimate with ten as a maximum value.

[1] Debye and Scherrer: Nachr. Ges. Wiss. Göttingen, 1916; A. W. Hull: Phys. Rev., 10, 661 (1917).

[2] J. Am. Chem. Soc., 41, 1168 (1919).

TABLE I

X-ray data[1]

| "α-stannic acid" d/n | I | "β-stannic acid" d/n | I | $SnO_2$ (crystals) d/n | I |
|---|---|---|---|---|---|
| 3.39 | 10 | 3.40 | 10 | 3.40 | 10 |
| 2.64 | 10 | 2.68 | 9 | 2.68 | 10 |
| | | 2.29 | 2 | 2.36 | 6 |
| 1.74 | 10 | 1.74 | 9 | 1.78 | 10 |
| | | | | 1.64 | 3 |
| 1.44 | 7 | 1.43 | 7 | 1.44 | 8 |
| | | | | 1.33 | 2 |
| 1.21 | 1 | 1.23 | 2 | 1.22 | 5 |
| | | | | 1.17 | 1 |
| | | | | 1.14 | 0.5 |
| 1.09 | 4 | 1.10 | 4 | 1.10 | 6 |
| | | | | 1.04 | 1 |

The X-ray spectra obtained from the α and β "stannic acids" were rather weak[2] and had broad diffuse lines. The lines from the "α-stannic acid" preparation were appreciably wider than those obtained from the "β-stannic acid." However, as seen from Table I the position of the lines and their intensities are the same, thus giving definite proof of the identity of the two. P. Scherrer[3] has shown that, for colloids, line-width is indicative of particle size and that with decreasing size of particles the lines become broader. The X-ray experiments therefore seem to confirm completely Mecklenburg's[4] colloidochemical studies, which led him to the conclusion that the so-called stannic acids differ only in the size of their "primary" particles, "α-stannic acid" having smaller primary particles than the "β-stannic acid."

The X-ray data obtained from the coarsely crystallized preparation of stannic oxide (identical with the mineral cassiterite) are given side by side with the others in Table I. This preparation of course gave a clear spectrum with sharp lines. A comparison of the data for stannic oxide with those for the so-called stannic acids readily shows the identity of the spectra, as it is perfectly obvious that the lines of lower intensity in the stannic oxide spectrum would not be discernible in the films obtained from the so-called stannic acids.

---

[1] The X-ray pictures were made in 1922. The results were not published at this time as it was intended to do some further work in this connection; but there was no opportunity to continue this work. However, judging from the abstract, these results have now been substantiated by Nabua Yamada: J. Chem. Soc. Japan, 33, 210 (1923); Chem. Abstracts 17, 2998 (1923).

[2] For this reason they could not be well reproduced here.

[3] Bestimmung der inneren Struktur und der Grösse von Kolloidteilchen mittels Röntgenstrahlen, in Zsigmondy's "Kolloidchemie," 387.

[4] Op. cit.

The X-ray experiments lead therefore to the definite conclusion that the so-called stannic acids are essentially stannic oxide in a state of extremely fine division, and, as judged from the width of the lines, the size of the particles in the $\alpha$-stannic preparations is smaller than in the $\beta$-stannic. This is a direct confirmation of the deductions drawn by others from the study of the colloidal properties and behavior of these substances.

**Summary**

By means of the X-ray powder method it has been shown that the so-called $\alpha$ and $\beta$ stannic acids are identical and are essentially stannic oxide. The width of the lines indicates that "$\alpha$-stannic acid" has finer particles than the "$\beta$-stannic acid." These results directly confirm the deductions drawn by others, especially Mecklenburg, from the study of the colloidal properties and behavior of the "stannic acids."

*Geophysical Laboratory,*
*Carnegie Institution of Washington,*
*Washington, D. C.*
*May, 1926.*

# THE MECHANISM OF REACTIONS PHOTOSENSITIZED BY MERCURY VAPOR*

BY ABRAHAM LINCOLN MARSHALL

## Pressure and Adsorption

An ever increasing body of facts is accumulating with respect to the behaviour of mercury vapor when stimulated by resonance radiation of wave length 2536.7 Å both in vacuo and in the presence of other gases. Füchtbauer and Joos[1] have determined the intensity and the broadening of the adsorption line at 2536.7 Å caused by a number of admixed gases. The relationship between the adsorption coefficient and the frequency is found to vary greatly with the nature of the gas added. Argon, nitrogen, water vapor, carbon dioxide, and hydrogen were the gases investigated. The frequency range over which the extinction coefficient has half its maximum value was taken to be a characteristic magnitude for the broadening. The half-value range was found to increase proportionally to the density of the added gas over the range 5–50 atmospheres. The total absorption however decreased with increasing density of added gas. In the case of nitrogen this decrease amounted to 25 percent. in the range 10–40 atmospheres. This means that while the absorption band is more spread out the maximum is much shallower.

A calculation of the total number of absorbing molecules based on the classical theory of dispersion and absorption showed that one mercury atom in thirty-five was acting as a resonator. This calculation was made by extrapolating to zero density of the added gas. All the measurements were with mercury vapor at one thousandth millimetre pressure.

## Extinction Coefficient

Goos and Meyer[2] have investigated quantitatively the extinction coefficient for saturated mercury vapor in the temperature range 0°-40°C. when illuminated with the 2536 Å line from a cold mercury arc. They found that at 0°C. in a distance of 16 mm. the intensity drops to half value. At 20°C. this decrease occurs in 6 mm. and at 40°C. in 5 mm. They also found that there were some deviations from the logarithmic law which could be explained as due to the non-homogeneous absorption of the exciting light.

Franck and Grotrian[3] have studied the absorption spectrum of mercury vapor at atmospheric pressure. They found complete absorption over the range 2540-2580 Å and a band at 1849 Å over 100 Å wide. The bands appeared to be quite continuous. These bands can be excited to fluorescence by light which does not correspond to that emitted by a mercury arc. Working

*Contribution from the Laboratory of Physical Chemistry, Princeton University.

[1] Physik. Z., 23, 73 (1922); Ann. Physik, 71, 204 (1923).

[2] Z., Physik, 35, 803 (1924).

[3] Z. techn. Physik, 3, 194 (1922).

at 35 mm. pressure of mercury vapor they studied the variation in the strength of absorption with temperature using a continuous source of radiation. From this data a value of 1 kg. cal. was calculated for the heat of dissociation of $Hg_2$ molecules which are assumed to be the cause of these absorption bands. This gives a partial pressure for $Hg_2$ of $2\ (10)^{-7}$ mm. at 10 cm. total pressure and 200°C.

### Extinction of Fluorescence

Wood[1] found that when mercury vapor at 0.001 mm. pressure was illuminated with light from a cold mercury arc it emitted a strong monochromatic fluorescence of wave length 2536.7 Å. The intensity of fluorescence decreased to half value in a distance of 5 mm. and obeyed the usual absorption laws.

A decrease was observed in the intensity of the resonance radiation on admitting air. Calling the intensity in vacuo 300 the following table illustrates the results obtained.

| air pressure (in mm.) | intensity | absorbed energy |
|---|---|---|
| 0.01 | 300 | 0 |
| .45 | 230 | 70 |
| 1.11 | 200 | 100 |
| 2.20 | 170 | 130 |
| 6.20 | 100 | 200 |
| 9.50 | 70 | 230 |
| 14.20 | 50 | 250 |
| 18.00 | 40 | 260 |
| 32.00 | 12 | 288 |

He described in this paper a resonance lamp which only emitted monochromatic radiation of wave length 2536.7 Å. Air at 30 mm. pressure saturated with mercury vapor at room temperature, and mercury in a high vacuum had the same absorption when illuminated by this light. With the air at atmospheric pressure however the absorption decreased to half its initial value. Füchtbauer's results agree with this observation.

Franck and Wood[2] working with mercury at 30 cm. pressure observed that oxygen at 3 mm. completely suppressed the fluorescence of the mercury while helium at 1 atmosphere had no effect. Wood[3] showed that argon at 0.5 mm. noticeably increased the intensity of the emitted resonance radiation while at 60 mm. the intensity was more than doubled. Helium at 330 mm. increased the intensity four-fold. He assumed that the effect was due to a broadening of the absorption line and stated that in helium or argon practically the entire energy of the line might be diverted. To support this conclusion, light of wave length 2536.7 Å from a monochromator was passed through a highly exhausted quartz tube containing a drop of mercury to remove the

[1] Physik. Z., 13, 357 (1912).
[2] Phil. Mag., 21, 314 (1911).
[3] Phil. Mag., 44, 1110 (1922).

"core" of the line. The emergent light produced no resonance radiation in a second exhausted mercury tube although the intensity was still nearly the same as in the original beam. When, however, helium was admitted to the second tube an intense emission appeared.

Van der Lingen and Wood[1] have examined the absorption spectrum of mercury and give the following results: (1) strong absorption line at 2536 Å and a weaker one at 2539 Å; (2) four lines at 2346, 2339, 2334, 2331 Å which fuse together with rise of temperature forming a band which gradually pushes towards the side of shorter wave lengths with increasing vapor density; (3) a strong absorption line at 1849 Å; (4) two strong and very asymmetric absorption bands, one with its head in close proximity to the 2539 line and the other with its head near 1849 Å. These bands creep out gradually with increasing vapor density towards longer wave lengths.

The complete fluorescence spectrum excited by a zinc spark consists of (1) a symmetrical structureless band extending from the red to 3700 with a maximum at 4850; (2) a similar band with a maximum at 3300, the two fusing together with increasing exposure; (3) an asymmetric faint band coinciding with the absorption band just above 2539 and another extending between 2349 and 2100. In addition there are the lines 2536 and 1849. Absorption of light in the 1849 band causes emission of the green-violet band and the 2536 Å line. Wood[2] finds that when liquid mercury is absent one does not observe fluorescence at any density or temperature. It occurs only in the presence of vapor freshly liberated from the liquid. The absorption, however, he states appears to be characteristic of the atom as he has never been able to distinguish any difference between the absorption of freshly forming vapor and that in the static condition.. The time interval between absorption and subsequent luminescence has been found to be of the order of $10^{-4}$ sec. Niewadniczanski[3] reports experiments on the fluorescence of mercury vapor which are apparently a contradiction of the results of van der Lingen and Wood. At constant temperatures above 155°C. a green fluorescence limited to the beam of the exciting light was definitely observable. The intensity diminished with local cooling instead of increasing as reported by Wood. The intensity of fluorescence seems to be a function of temperature only.

Phillips[4] working with a column of distilling mercury vapor showed that visible luminosity extended 18 inches from the point of illumination. He found this to consist of the 2536 Å line and four continuous bands—one about 2600, another between 3100-3500 and another in the range 4350-4500 Å.

Compton and Turner[5] have experimented with methods of producing the band spectrum in mercury and confirm the conclusions of Hulthen, Kratzer and Mulliken that these bands are due to mercury hydride molecules. These

[1] Astrophys. J., 54, 149 (1921).
[2] Proc. Roy. Soc., 99, 362 (1921).
[3] Nature, 117, 555 (1926).
[4] Proc. Roy. Soc., 89, 44 (1913).
[5] Phil. Mag., 48, 360 (1924).

ideas are based on calculations of moments of inertia obtained from an analysis of the structure of the bands. In addition to these mercury hydride bands with resolvable structure there are the green and ultra-violet unresolvable bands. They believe that the spectrum arises when the molecules are formed by reaction of hydrogen with excited mercury molecules, the primary effect being the formation of a hydrogen atom and an excited mercury hydride molecule.

H. A. Stuart[1] has studied the effects of a number of gases in quenching the resonance emission of excited mercury vapor. He claims that Wood used a strongly self-reversed and broad line to excite fluorescence in his experiments. In such cases additions of other gases would not only weaken the reemission by impacts of the second kind but would also cause a broadening of the absorption line so that more of the energy of the incident radiation would be diverted. An increase or decrease in fluorescence would depend on which of these effects predominated. Stuart avoided the latter effect by using the light from a resonance lamp as his source of excitation. Malinowski has shown that the 2536 Å line thus obtained is a fine doublet each component having a width of about $2.3\ (10)^{-4}$Å.

The following table gives a brief summary of the results obtained.

| gas added | pressure in mm. to decrease intensity to half value | percent yield for impacts of second kind |
|---|---|---|
| $H_2$ | 0.2 | 70 |
| $O_2$ | 0.35 | 100 |
| CO | 0.4 | 80 |
| $CO_2$ | 2.0 | 20 |
| $H_2O$ | 4.0 | 10 |
| $N_2$ | 30 | 1.3 |
| Ar | 240 | 0.2 |
| He | 760 | 0.03 |
| air | 1.2 | |

The second column gives the pressure in mm. which caused the fluorescence to be decreased to one half the value observed with mercury in vacuo. The final column gives the percentage of collisions which are effective in causing radiationless dissipation of energy. The calculations have been made on the assumption that for oxygen all collisions are effective. This leads to a value for the mean life of excited mercury atoms in agreement with that obtained from other sources.

Wood[2] has recently shown that the 2536.7 Å line from a water-cooled quartz mercury arc consists of five components with an average separation of 0.011 Å. When this light is passed through mercury vapor at 0°C it is found that each of the components has been split into two. With mercury at room temperature only the edges of the lines remain. With nitrogen at 3 cm. pressure and mercury at 0°C. a ten-fold increase in absorption was observed.

[1] Z. Physik, 36, 262 (1925).
[2] Phil. Mag., 50, 761 (1925).

Under ordinary circumstances, even with a water-cooled arc the five components of the line are strongly reversed and it is necessary to use a strong transverse magnetic field to press the discharge against the wall of the tube to avoid reversal.

In a study of the optical excitation of the mercury spectrum in the presence of foreign gases Wood concludes that there are two effects present: the apparent accumulation of electrons on the metastable $2p_3$ orbit in a very large number of atoms and the emission of lines not present in the exciting light. Nitrogen purified by phosphorus when admitted to the resonance tubes causes an immense increase in the intensity of the light emitted, a green glow being visible. The presence of water vapor is apparently necessary for this effect. If the nitrogen contains a little hydrogen the effect is not observed. This enhanced emission was shown to be accompanied by strong absorption of the 4046 line in the excited vapor. This indicates that in the presence of nitrogen a large number of electrons in the excited atoms are in the $2p_3$ state. Some of the evidence given seems to point to excitation of some of the frequencies emitted by impact with nitrogen after it has been excited by optically excited mercury.

Donat[1] has observed that when a mixture of mercury and thallium vapor is illuminated by the resonance radiation of mercury the thallium fluoresces although it does not absorb this radiation. With only mercury vapor present the addition of 60 mm. argon reduced resonance fluorescence to 25 percent. of value in vacuo. 70 mm. of nitrogen depressed emission to 1 percent. while 12 mm. of hydrogen reduced it to 0.1 percent. The mercury pressure was 0.25 mm. and the temp. 100°C.

With thallium also present low pressures of argon cause a strong increase of the sensitized fluorescence of thallium followed by a gradual decrease as the pressure is further increased. With nitrogen the effect is similar. Hydrogen however causes the fluorescence to decay in a manner similar to that observed with only mercury present.

Loria[2] has reinvestigated the effect of argon and nitrogen in order to remove certain objections from the experimental technique of Donat. He found that a pressure of $2\ (10)^{-3}$ mm. nitrogen was sufficient to cause the 5350 Å line of thallium to show up strongly. The effects of both argon and nitrogen were very sensitive to traces of oxygen which destroyed the fluorescence. The role of the inert gas is said to be to change the excited mercury atom from the $2p_2$ to the metastable $2p_3$ state.

Olsen and Meyers[3] attempt to explain the results of Donat and Loria on the basis of diffusion of the resonated thallium atoms. The inert gas acts to prevent the diffusion of the excited thorium atoms from the region of formation and therefore the re-emission of the energy occurs nearer the point of observation with a corresponding increase in the intensity of the light.

[1] Z. Physik, 29, 345 (1924).
[2] Phys. Rev., (2) 26, 573 (1925).
[3] J. Am. Chem. Soc., 48, 389 (1926).

## Quantitative Measurement of Absorption

The first object of the present work was to attempt to develop a method for measuring in absolute units the amount of energy absorbed by mercury vapor at various saturation temperatures in vacuo and in the presence of other gases. Taylor and Marshall[1] have shown that a variety of gas reactions could be photosensitized by mercury vapor to the resonance light from a cold mercury arc. To interpret these reactions it was necessary to obtain some knowledge of the amount of light absorbed.

A number of experiments were necessary to determine if this quantity could be directly measured as the results of Harrison and Forbes[2] on the energy radiated from a mercury arc led one to expect that one would be dealing with extremely small differences. A large surface Moll thermopile was used in connection with a Moll galvonometer. Each had an internal resistance of 50 ohms and with 1.5 amps. in the magnet coil of the galvanometer one obtained maximum sensitivity. This combination can be arranged to have a period of 2 seconds but it was found necessary to work with a period of 15-20 secs. to obtain maximum sensitivity. With this arrangement it was found that the absorption was measurable but a considerable amount of effort was still necessary to determine the best working conditions.

The absorption cell used was the specially designed quartz apparatus described by Marshall.[3] The water-cooled mercury arc in the central compartment was operated on 10 amps. and 23 volts. The temperature of the cooling water was 15°C. The cell was mounted in a water bath whose temperature could be regulated. One side of the thermostat had a quartz window inserted which was 5 cm. wide and 20 cm. long. The cell was placed 1 cm. from this window, the arc being in the plane normal to the middle of the window. A chlorine-bromine filter as described by Robinson and Anderson[4] was placed between the thermopile and the absorption cell. The filter was 3 cm. long and completely covered the thermopile surface. The spectrogram furnished with the filter showed that it transmitted a narrow band at 2536 and the yellow and green lines of the mercury arc. The transmission of $\lambda = 2536.7$ Å is given as 80 percent. The initial experiments were made with the vessel free from mercury vapor and with mercury vapor saturated at 20°C. together with nitrogen at one atmosphere. A zero-point reading was taken with the thermopile darkened and the shutter was then opened. There seemed to be a small difference with and without mercury present but it was masked by fluctuations which gave unsteady and not very reproducible readings. An attempt was next made to improve the sensitivity of the arrangement. This was accomplished by using a glass plate between the cell and the thermopile instead of a shutter and taking the zero point when the thermopile was illuminated by the visible light transmitted by the filter. It was thus possible to bring the

[1] J. Phys. Chem., **29**, 1140 (1925).
[2] J. Optical Soc., **10**, 1 (1925).
[3] J. Phys. Chem., **30**, 34 (1926).
[4] J. Am. Chem. Soc., **47**, 718 (1925).

pile closer to the cell and obtain full scale reading for the light transmitted in the narrow band about 2536.7 Å. When this was done it at once became apparent that the light absorbed by mercury was easily measurable. The absorption at room temperature was small but at 60°C. became quite large. In one of the first experiments the deflection was 246 scale divisions without mercury present and 107 scale divisions with mercury (saturated at 60°C.) and nitrogen at one atmosphere. The final arrangement is illustrated in Fig. 1. A is the compartment containing the water cooled quartz arc; B is an evacuated compartment which enables the temperature of the reaction chamber C to be controlled independently from A. H is a light-filter compartment which was used in some experiments. D is a ground and polished fused quartz window in the side of the thermostat. It was free from all air bubbles and clear as a piece of optical glass. E was a clear glass plate used as a shutter; F a chlorine bromine filter and G a Moll large surface thermopile. The Moll galvanometer with lamp and scale was enclosed in a black box which enabled good readings to be easily made in a light room. It was unnecessary to make any correction for light reflected by the glass plate since in any series of experiments this was always constant and cancelled out in taking difference to obtain the value for the absorption.

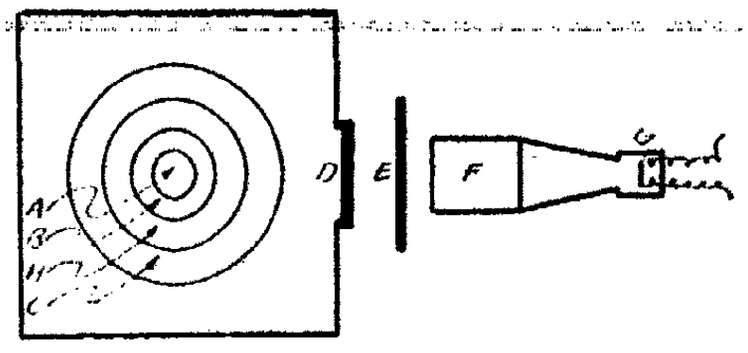



FIG. 1

Numerous experiments were carried out under these conditions to determine the effect of hydrogen, nitrogen and oxygen at various temperatures on the adsorption of mercury. The results obtained were of extreme interest but the degree of reproducibility was far from being what one might desire. The chief cause of trouble was ultimately found to be in the mercury arc itself. Mercury was continually condensing in droplets on the cooled quartz walls and as these drops increased in size they would run down the walls so that the amount of light which could escape from the arc through any small part of the surface was continually changing. At times the fluctuations would be extremely large. The difficulty was avoided by only cooling the arc to a distance of about 2 cm. above the level of the mercury cathode and allowing the rest of the tube to run hot thus preventing mercury from condensing on it.

Three readings were taken of the zero point at intervals of 10 secs. and then three with the glass screen removed after the reading became steady; this took about 30 seconds. This procedure was repeated about ten times for each value obtained and the mean of these determinations is the one given.

In the initial part of this work it was found that when an old arc was used the amount of energy emitted in the region about 2536 Å fell off fairly rapidly after the arc was first struck. On examining one of these arcs after an experiment a great deal more mercury was found condensed on the walls than was

the case with a new arc. The drops were much larger and it is quite likely that tungsten from the anode is the cause of the trouble. These variations in transmission from time to time will undoubtedly account for all the variations observed by Marshall[1] in the rate of combination of electrolytic gas ($2H_2+O_2$).

A very beautiful effect was observed when pure nitrogen was present with mercury at the higher temperatures. This consisted of an intense green fluorescence which extended for only a fraction of a millimeter from the inner surface of the reaction chamber C. (Fig. 1). In the presence of traces of hydrogen or oxygen in the nitrogen no fluorescence was observed. On lowering the temperature the fluorescence gradually extended to a greater distance from the surface but fell off rapidly in intensity. This same effect was observed by Wood[2] with pure nitrogen and mercury vapor at room temperature. He also showed that this emission was accompanied by strong absorption of the 4046 Å line.

### Calibration of Thermopile

The thermopile was calibrated by means of a standard carbon filament lamp supplied by the Bureau of Standards. The lamp was operated with several currents at a distance of 3 metres from the thermopile. The operating conditions specified for the lamp were rigidly adhered to. The following table gives the current through the lamp filament; the energy flux per cm.$^2$ at a distance of 3 metres from the lamp; the number of scale divisions corresponding to this flux density, and finally, the ratio flux density/deflection.

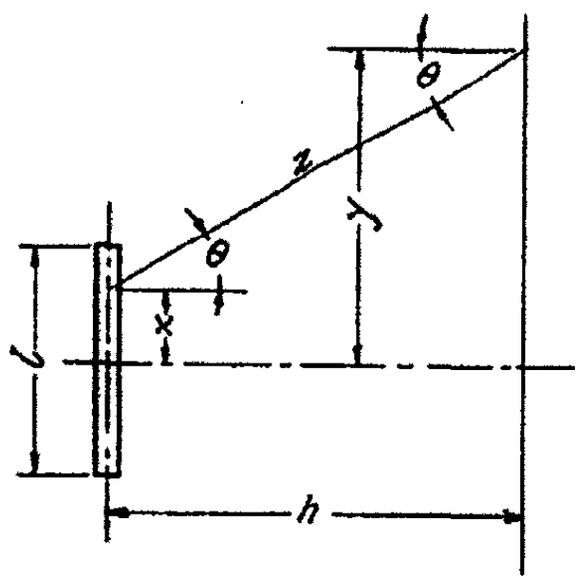



FIG. 2

| amps | flux cm.$^{-2}$ | deflection | flux deflection |
|---|---|---|---|
| 0.250 | 18.4 $(10)^{-6}$watt | 152 mm. | 1.21 $(10)^{-7}$ |
| 0.300 | 26.3 $(10)^{-6}$watt | 220 mm. | 1.20 $(10)^{-7}$ |
| 0.350 | 36.3 $(10)^{-6}$watt | 307 mm. | 1.18 $(10)^{-7}$ |
| 0.400 | 47.9 $(10)^{-6}$watt | 399 mm. | 1.20 $(10)^{-7}$ |

From the average of these measurements it is found that 100 scale divisions = 120 ergs sec.$^{-1}$ cm.$^{-2}$.

1 quantum 2536 Å = 9 $(10)^{-12}$ ergs. hence

100 scale divisions = 8 $(10)^{14}$ quanta min.$^{-1}$ cm.$^{-2}$

[1] J. Phys. Chem., 30, 42 (1926).

[2] Phil. Mag., 50, 770 (1925).

In order to determine the total energy emitted from the arc and incident on the reaction chamber from the thermopile reading it was necessary to make a mathematical analysis of the conditions existing in this case.[1]

## Calculation of Total Energy Emitted by Arc

Consider the lamp as a line source at the axis of an infinite cylinder of radius $h$ (Fig. 2). It is assumed that the inverse square law and the cosine laws hold. Then the intensity of radiation at a point $y$ due to a length of arc $dx$ at a point on the arc distant $x$ from the centre is given by the equation

$$dI_y = \frac{I\,dx}{z^2}\cos^2\Theta$$

where for the present I is taken as the proportionality factor and will be evaluated later.

$$\cos\Theta = \frac{h}{\sqrt{(y-x)^2+h^2}}.$$

and

$$I_y = \int_{-l/2}^{+l/2} \frac{I\,h^2dx}{[(y-x)^2+h^2]^2} \qquad (1)$$

$$= \frac{I}{2h}\left[\frac{h(y+l/2)}{y^2+h^2+l/4^2+yl} - \frac{h(y-l/2)}{y^2+h^2+l/4^2-yl} + \tan^{-1}\frac{lh}{h^2+y^2-l/4^2}\right] \qquad (2)$$

This equation will enable one to calculate relative intensities at various points on the cylinder of radius $h$. The total radiation from the lamp onto the cylinder is given by the expression

$$\int_{-\infty}^{+\infty} 2\pi h I_y dy \qquad (3)$$

where $I_y$ is a function of $y$ defined by equation (1). The equation may be solved graphically or integrated by substituting in the value for $I_y$.

$$\text{total radiation from arc} = \int_{-l/2}^{+l/2} 2\pi h^3 I \int_{-\infty}^{+\infty} \frac{d(y-x)}{[(y-x)^2+h^2]^2}\,dx$$

$$= 2\pi h^3 I \int_{-l/2}^{+l/2}\left[\frac{y-x}{\{(y-x)^2+h^2\}2h^2} + \frac{1}{2h^3}\tan^{-1}\frac{y-x}{h}\right]_{-\infty}^{+\infty} dx$$

$$= \pi I \int_{-l/2}^{+l/2}\left[o-o+\pi/2-(-\pi/2)\right]dx = \pi^2 Il.$$

$$\text{hence } I = \frac{\text{total radiation from arc}}{\pi^2 l} \qquad (4)$$

Substituting the value of I given in equation (4) into equation (2) one obtains

[1] I am indebted to Mr. F. C. Blake of L'Azote Inc., Wilmington, Del. for suggesting the method of approach which led to the successful solution of this calculation.

$$I_y = \frac{\text{total radiation}}{2\pi^2 lh}\left[\frac{h(y+l/2)}{y^2+h^2+l/4^2+yl} - \frac{h(y-l/2)}{y^2+h^2+l/4^2-yl} + \tan^{-1}\frac{lh}{h^2+y^2-l/4^2}\right] \tag{5}$$

In the present experiments the arc was 10 cm. long, the cell was the same length and distant 3 cm. from the arc. The surface of the thermopile was opposite the middle of the arc and 24 cm. away. The thermopile reading gives directly a value for $I_y$ at this point.

Substituting this value in equation (5) one obtains directly a measure of the number of quanta absorbed in the cell.

In making this calculation it has been assumed however that the cell is an infinite cylinder and it is necessary to integrate equation (3) graphically between the limits $+l/2$ and $-l/2$ to determine the fraction of the total energy intercepted by the cell.

Table I gives the value calculated for $I_y$ for various values of $y$.

TABLE I

| y | $I_y$ |
|---|---|
| 0 | 0.491 I |
| 1 | 0.486 I |
| 2 | 0.469 I |
| 3 | 0.432 I |
| 4 | 0.362 I |
| 5 | 0.259 I |

When these values are plotted the area under the curve is found to be 4.25 I. Substituting this value in equation (3) one obtains 80.0 I as the value for the amount of radiation intercepted by the cell. If all the radiation were intercepted this value would have been 98.6 I as calculated from equation (4). Hence about 80 percent. of the total energy emitted is intercepted by the cell. It is thus necessary to multiply the values obtained from equation (5) by a factor 0.80 in order to obtain actual values for the energy absorbed. This equation reduced to

$$\text{total radiation absorbed} = \frac{1.6\,\pi^2\, lh\, I_y}{\frac{lh}{h^2+l/4^2} + \tan^{-1}\frac{lh}{h^2-l/4^2}} \tag{6}$$

or per 100 scale divisions

$$\text{total energy absorbed} = \frac{1.6\,\pi^2 .\, 10 . 24 . 8(10)^{14}}{\frac{240}{576+25} + \tan^{-1}\frac{240}{576-25}} = 3.74(10)^{18} \text{ quanta min.}^{-1}$$

Only 80 percent. however of the energy in the region 2536 Å is transmitted by the filter and of this energy another 25 percent. is lost by reflection from the quartz surfaces before reaching the thermopile. It is thus necessary to multiply the above value by a further factor 1.66 to obtain the best value

for the energy corresponding to 100 scale divisions deflection. The value then becomes 6.23 $(10)^{18}$ quanta absorbed per minute.

### Temperature Coefficient of Absorption with Hydrogen and Nitrogen

Table II gives some preliminary results obtained at a number of temperatures on the absorption in the presence of several different gases. In all these experiments the arc was operated on 6 amps. at 22 volts. It was found that the decrease in current from 10 to 6 amps. caused a very small decrease in the amount of energy absorbed.

TABLE II

| gas | temp. | deflection | absorption (in scale divisions) |
|---|---|---|---|
| vacuum | | 286 | |
| $H_2$ | 40°C | 178 | 108 |
| $N_2$ | 40°C | 162 | 124 |
| $H_2$ | 64°C | 128 | 158 |
| $N_2$ | 70°C | 180 | 106 |

Another series of similar experiments is illustrated in Table III.

TABLE III

| gas | temp. | deflection | absorption (in scale divisions) |
|---|---|---|---|
| vacuum | | 286 | |
| $N_2$ | 65°C | 148 | 138 |
| $H_2$ | 68° | 142 | 144 |
| $H_2$ | 40° | 152 | 134 |
| $N_2$ | 41° | 155 | 131 |
| $N_2$ | 14° | 250 | 36 |
| $H_2$ | 16° | 251 | 35 |
| $H_2$ | 25° | 215 | 71 |
| $O_2$ | 25° | 281 | 5 |

The experiments listed above are merely illustrative of many performed and show the general trend of the results obtained. Absorption with hydrogen or nitrogen present was approximately the same at a given temperature but much smaller in the case of oxygen. Subsequent results indicate that the low results with oxygen are due to an actual removal of the mercury vapor by oxidation. The effect of temperature is very interesting and corresponds roughly to that observed in the combination of electrolytic gas ($2H_2+O_2$).[1]

This seems to indicate that the real temperature coefficient of the photochemical reaction is unity as was previously surmised by the author.

### Absorption by Mercury in Vacuo

The next experiments to be described relate to an attempt to determine the absorption of mercury vapor in vacuo. Some experiments gave positive

[1] J. Phys. Chem., 30, 34 (1926).

results and some negative. It was only when a diffusion pump was used to exhaust the cell that reproducible results were obtained. The results obtained with the cell at 30°C. are given in Table IV. Higher temperatures were not employed since it had been found in previous work that excited mercury in vacuo rapidly darkened the surface of the quartz thus changing its transmission.

TABLE IV

| vessel empty | Hg in vacuo | absorption (in scale divisions) |
|---|---|---|
| 439 | 401 | 38 |
| 392 | 348 | 44 |
| 388 | 362 | 26 |
| 379 | 348 | 31 |
| 405 | 369 | 36 |
| 400 | 368 | 32 |
| 398 | 358 | 40 |
| | average | 35 |

The mercury was removed from the cell by filling it with concentrated nitric acid until the mercury was all dissolved. The cell was then washed carefully with distilled water and dried by drawing through it air obtained from outside the laboratory to avoid contamination by mercury vapor.

Table V shows the influence of hydrogen on the absorption at a number of temperatures. The conditions obtaining for the experiments listed in this table were as favorable as any realised in this work and it is felt that these results are particularly reliable and show the degree of reproducibility obtainable.

TABLE V

Influence of $H_2$ at 760 mm.

| | temp. | deflection | absorption (in scale divisions) |
|---|---|---|---|
| mercury absent | | 440 | |
| | 34 | 277 | 163 |
| mercury absent | | 439 | |
| | 34 | 278 | 161 |
| mercury absent | | 392 | |
| | 34 | 258 | 134 |
| mercury absent | | 406 | |
| | 35 | 265 | 141 |
| | 50 | 220 | 186 |
| | 70 | 239 | 167 |
| | 4 | 370 | 36 |
| | 20 | 320 | 86 |
| | 35 | 264 | 142 |
| mercury absent | | 405 | |

The results within the bracket are for a single filling of the cell.

## Production of Hydrogen Peroxide

The next part of this work deals with another factor in determining the mechanism of these reactions. It was suggested by Taylor[1] and Marshall[2] that the mechanism of the reaction between hydrogen and oxygen might involve a stage giving hydrogen peroxide and that if this were the case it should be possible to remove this material unchanged from the reaction zone by the use of a rapid flow of gas. The cell as originally described was modified to permit circulating gas through it. It was found when this was done that large quantities of hydrogen peroxide could be detected in the effluent gas. It was necessary however to saturate the gas with mercury vapor before passing it through the cell. In fact it was found that this was all that was necessary to cause these reactions to proceed and in all subsequent experiments no liquid mercury was used in the cell. By employing a sufficient rapid rate of flow it appeared to be possible to cause the reaction to stop at the hydrogen peroxide stage. The results obtained are summarised in Table VI.

TABLE VI

| rate of flow litres hr.$^{-1}$ | | time in minutes | amt. $H_2O_2$ formed in c.c. gas at N. T. P. |
|---|---|---|---|
| $H_2$ | $O_2$ | | |
| 11.7 | 5.8 | 30 | 10.9 |
| 11.7 | 5.8 | 67 | 18.0 |
| 190 | 110 | 30 | 61.0 |
| 190 | 110 | 20 | 30.0 |
| 340 | 130 | 15 | 29.4 |
| 11.7 | 5.8 | 15 | 14.6 |
| 11.7 | 5.8 | 15 | 12.1 |
| vessel throughly cleaned | | | |
| 11.7 | 5.8 | 15 | 15.2 |

In the last three experiments which are bracketed the gas was mixed with nitrogen flowing at 120 litres per hour. It is observed that this very large dilution with nitrogen does not appear to have much effect on the rate of reaction. This is in agreement with the results of Stuart[3] who found that only 1.3 percent. of impacts between excited mercury and nitrogen molecules were efficient in deactivating the mercury. A similar effect was observed in some experiments using the original static method with helium. The rate of reaction was the same for electrolytic gas at one atmosphere or when diluted by helium at one half atmosphere pressure.

It was observed that with gas flowing at 17 litres per hour practically no mercuric oxide deposited in the outlet tube but that at the faster rates there was a very heavy deposit.

[1] Trans. Faraday Soc., 21, 560 (1926).
[2] J. Phys. Chem., 30, 44 (1926).
Z. Physik, 36, 262 (1925).

Rideal and Hirst[1] criticise the viewpoint advanced from this laboratory concerning the chain mechanism involved in these reactions and state that the combination between these gases is promoted by a mercury surface when the latter is illuminated at ordinary temperatures with the resonance light 2536 Å. Following up this idea they have radiated other metals such as iron, copper, cadmium and silver, with the light from arcs struck between electrodes of these various metals but have observed no catalytic effect in promoting any reactivity.

They did observe in the case of mercury-sensitised reactions that the rate at room temperature was very roughly proportional to the area of the mercury surface exposed. They strongly uphold the idea that the high rate of combination observed is due to the catalytic effect of the mercury surface and that the Cario and Franck mechanism is not necessary.

The results which have just been given in connection with this work are an ample refutation of this whole idea as there was no liquid mercury present in the reaction system. They have recently[2] abandoned completely their original point of view and now agree that the mercury atoms in the liquid play no role in the photosensitization. They have also observed that hydrogen peroxide is formed as one of the stages in the combination of hydrogen and oxygen and suggest that these reactions involve simple addition of *active* hydrogen molecules to the molecules of the other reactants. The primary process according to them is the activation of hydrogen by the excited mercury molecules. This point of view seems a rather retrograde step and ignores a number of facts collected in diverse ways which have led us to consider the reactive form of hydrogen as the atom. The burden of proof for such a conception must lie with its originators. Bonhoeffer[3] has shown that atomic hydrogen produced by Wood's method will cause a mixture of hydrogen and oxygen to combine giving hydrogen peroxide as the product. H. Senftleben[4] has given what appears to be certain proof for the existence of hydrogen atoms under our experimental conditions. A system containing hydrogen and mercury vapor was illuminated with the resonance radiation from a mercury arc and an increase was observed in the thermal conductivity of the gas which could only be explained by assuming the presence of H-atoms. The effect was absent when mercury vapor was absent, when a hot mercury arc was used and when the walls of the vessel were at the same temperature as the filament. Cario and Franck showed that the hydrogen gas "cleaned up" on the walls of the vessel when illuminated under these conditions, an effect which had previously been ascribed by Langmuir to the adsorption of hydrogen atoms. The results of Olsen and Meyers[5] on the hydrogenation of ethylene at low pressures give additional evidence for a mechanism via atomic

[1] Nature, 116, 899 (1925).
[2] Nature, 117, 449 (1926).
[3] Z. Electrochem. 31, 521 (1925).
[4] Z. Physik, 32, 922 (1925).
[5] J. Am. Chem. Soc., 48, 389 (1926).

hydrogen. They found that the initial rate of reaction over a pressure range for hydrogen from 1.50 to 11.80 mm. was proportional to the square root of the hydrogen pressure.

## Probable Mechanism of Reaction

Subsequent results will show definitely that one is dealing with a chain mechanism in the combination of hydrogen and oxygen and the most probable mechanism from the data at present available seems to be:

$$Hg' + H_2 = 2H + Hg \quad (1)$$
$$H + O_2 = HO_2 \quad (2)$$
$$HO_2 + H_2 = H_2O_2 + H \quad (3)$$
$$2H_2O_2 = 2H_2O + O_2 \quad (4)$$

It is at present uncertain whether the primary reaction is according to (1) or involves the formation of mercurous hydride. There is some physical and chemical evidence to support the latter conclusion. The exact mechanism for the decomposition of hydrogen peroxide vapor is uncertain at present.

## Quantum Yield for $2H_2+O_2$

The next step taken to elucidate the mechanism of this reaction was a determination of the quantum yield while the reaction was proceeding. It was evident that this would involve several difficulties since it was necessary to work at about 50°C. to obtain an absorption that was readily measurable with a fair degree of precision and this would involve a reaction rate that would only allow ten minutes for the entire series of measurements. Also the deposition of mercuric oxide on the walls would complicate the absorption measurements. These difficulties were overcome by the use of a circulatory system with a large volume external to the cell to slow down the rate of pressure change and extend the reaction over a considerably longer period. By this means it was also possible to avoid the use of liquid mercury in the cell. A closed system was used with a mercury circulating pump which was able to circulate the gases at a rate of 100 litres per hour. A water jacketed glass coil was used as a mercury saturator. A small amount of mercury was placed in each of the fifteen coils to ensure saturation. In all these experiments the saturator was kept at 50°C. and the reaction cell at 70°-80°C. to prevent condensation of any mercury in the cell. The gas circulator used was similar to one described by Chatterji and Finch.[1] It was modified by using a small rod with a short piston attached which was immersed in the mercury column. With this device one could operate at any speed desired independent of the natural period of the mercury column. The volume of the whole apparatus was about 1950 cc. The gases were circulated through a liquid air trap and gas bubbler. A tube containing powdered pyrolusite was also inserted in the system to decompose the ozone formed and prevent fouling of the mercury in the pump.

[1] J. Chem. Soc., 127, 2464 (1925).

The results obtained with electrolytic gas are summarised in Table VII.

TABLE VII

Rate of Reaction from Electrolytic Gas

| Time (mins.) | pressure (mm.) | $\Delta p$ in mm. $min.^{-1}$ |
|---|---|---|
| 0 | 667 | 24 |
| 10 | 643 | 29 |
| 20 | 614 | |

The readings obtained with the thermopile during the reaction were very steady and averaged around 247 scale divisions. No visible film of mercuric oxide deposited in the cell during the twenty minutes of the run although there was a very considerable deposit formed in the outlet tube. The reading obtained with the mercury arc with no mercury vapor in the cell was 368 scale divisions. The absorption thus amounted to 121 scale divisions. Calibration of the thermopile gave a deflection of 235 scale divisions for an energy density of 47.9 $(10)^{-6}$ watt $cm.,^{-2}$ $sec.^{-1}$. In this experiment the thermopile was 30 cm. from the arc. The number of quanta absorbed as calculated from equation (6) is thus 1.98 $(10)^{19}$ per minute. A pressure decrease of 2.6 mm. per minute would correspond to the disappearance of 1.82 $(10)^{20}$ molecules per minute. The mechanism postulated requires the disappearance of 4 molecules for a pair of hydrogen atoms in each stage. Thus the length of the chain initiated by each hydrogen atom would be

$$\frac{1.82\ (10)^{20}}{4 \times 1.98\ (10)^{19}} = 2.3$$

This means that on the average the change postulated would repeat itself 2.3 times for each hydrogen atom formed or 4.6 times for every quantum absorbed. This however is assuming that the final product is hydrogen peroxide. Experiment has shown that hydrogen peroxide is formed in appreciable quantities and this would be removed in the gas bubbler which was filled with water. It is probable however that a considerable amount was used in oxidising the mercury to mercuric oxide and that still more was catalytically decomposed at the glass and mercuric oxide surfaces. This last step would tend to increase the number of molecules reacting per quantum absorbed as determined by pressure change. Due to the shape of the cell it would be impossible to circulate the gases uniformly and there would certainly be some channeling effect at the rapid rates of flow used. It is impossible at present even to estimate the amount of this effect but the net result would be to decrease the number of quanta absorbed in the flowing gas stream and hence to lengthen the reaction chains. Another factor in increasing the length of the chains is found in Stuart's results on the quenching of the fluorescence. Hydrogen and oxygen are equally efficient in quenching fluorescence and presumably only the energy taken up by hydrogen is used in forming hydrogen atoms and in this particular experiment this would be about 66 percent. of the total energy absorbed.

Another series of measurements was made with the entire arc water cooled. In this case it was observed that the rate of reaction was about 60 percent. faster while the absorption increased about 10 percent. The reason for this increase is at present unknown. Table VIII gives the results obtained.

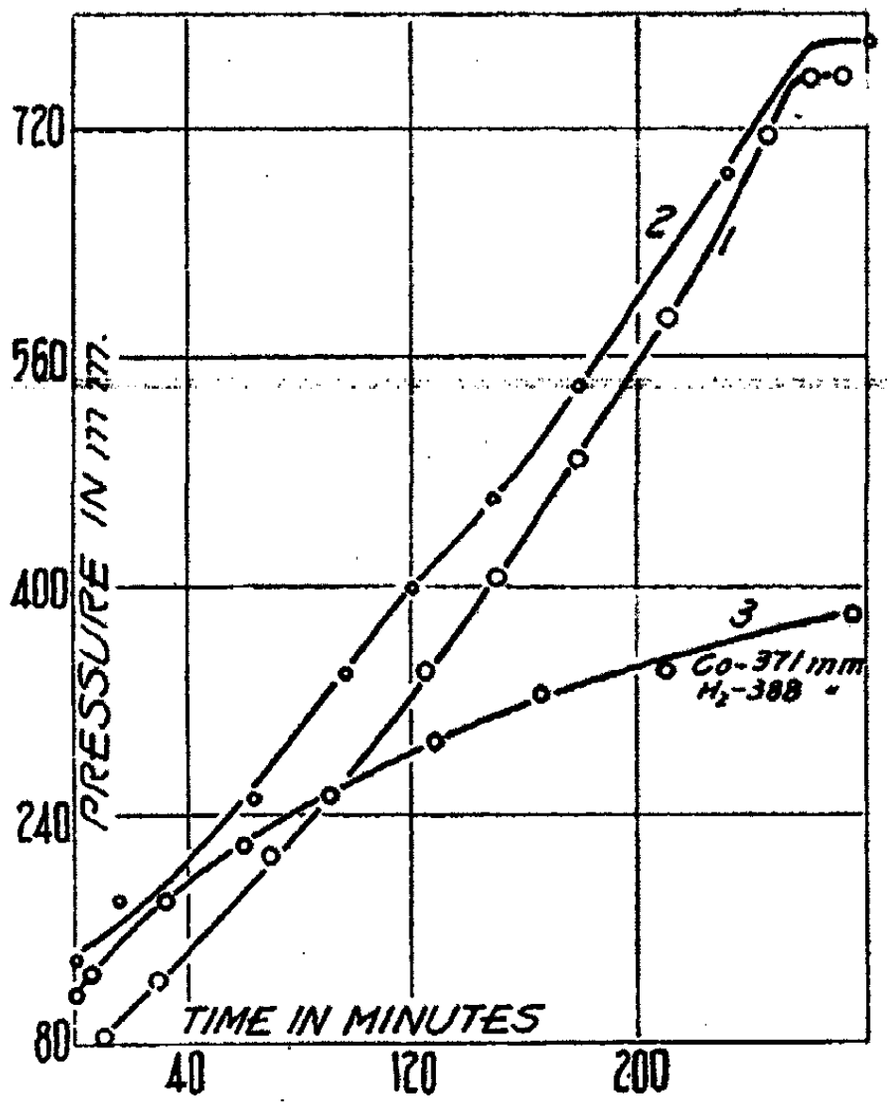



FIG. 3

TABLE VIII

| time (mins.) | pressure | p (in mm.) |
|---|---|---|
| 0 | 750 | 22 |
| 5 | 728 | 24 |
| 10 | 704 | 24 |
| 15 | 680 | 57 |
| 30 | 623 | 37 |
| 40 | 586 | |

This gives an average pressure change of 4.1 mm. per minute. It was more difficult to obtain a reliable value for the absorption but the best value appeared to be 132 scale divisions or 2.16 $(10)^{19}$ quanta per minute. The pressure decrease of 4.1 mm. per minute corresponds to 2.87 $(10)^{20}$ molecules disappearing. Assuming four molecules to disappear in each link of the chain per pair of hydrogen atoms the chain contains 3.3 members.

Some results obtained for electrolytic gas under the same temperature conditions are illustrated in Fig. 3. In curve (1) 61 cc. of $H_2O_2$ gas were removed as such while the remainder of the pressure decrease was due to formation of water and mercuric oxide. In curve (2) 30.6 cc. of $H_2O_2$ was collected undecomposed. The slight increase observed in the rate of reaction was due to a relative increase in the concentration of hydrogen as the reaction proceeded.

Curve (3) shows results obtained with a mixture of CO and $H_2$.

## Quantum Yield for $H_2+CO=HCOH$

A number of experiments have been performed with mixtures of CO and $H_2$ to determine the relationship between quanta absorbed and molecules reacting. It has been found that the energy absorbed is approximately constant over the entire range of the reaction independent of the relative concentration of the reacting gases. During the course of the reaction the rate decreased to 30-50 percent. of its initial value. The mechanism of this reaction has not been closely investigated as yet but an intensive study is now in progress. Samples were taken from the reacting system from time to time during the course of the reaction and analysed. These analyses seemed to indicate that CO and $H_2$ were disappearing in the ratio 1 : 1 and that no hydrocarbon was being formed. The results will be set forth in a number of tables. The thermopile calibration was checked after each experiment. The reaction products were removed from the system by means of a liquid air trap.

TABLE IX

composition of gas 379 mm. CO
318 mm. $H_2$
thermopile readings—no mercury present—347 scale divisions
reaction proceeding—233 " "
absorption 114 " "

| time (mins.) | pressure (mm.) |
|---|---|
| 0 | 681 |
| 9 | 666 |
| 19 | 652 |
| 29 | 637 |
| 39 | 624 |
| 49 | 612 |
| 69 | 590 |
| 89 | 565 |
| 119 | 538 |
| 229 | 455 |

114 scale divisions is equivalent to 1.86 $(10)^{19}$ quanta absorbed. The initial rate of reaction was 1.6 mm. $min.^{-1}$. This is equivalent to 11.0 $(10)^{19}$ molecules disappearing per minute. Since two molecules disappear for each step in the

chain per hydrogen atom and there are two hydrogen atoms formed per quantum absorbed the length of the chain initiated by a hydrogen atom is 1.48.

TABLE X

composition of gas 204 mm. CO
500 mm. $H_2$
thermopile readings no mercury present 267 scale divisions
reaction proceeding 193 " "
absorbed 74
thermopile 20 cm. from arc

| time (mins.) | pressure (mm.) | ratio $CO/H_2$ |
|---|---|---|
| 0 | 656 | 0.49 |
| 15 | 643 | |
| 60 | 617 | |
| 120 | 586 | |
| | sample taken | 0.33 |
| | 541 | |
| 180 | 516 | |
| 240 | 494 | |
| 260 | 487 | |
| | sample taken | 0.24 |
| | 451 | |
| 330 | 434 | |
| 420 | 413 | |
| | sample taken | 0.18 |
| 510 | 360 | |
| | sample taken | 0.18 |

thermopile calibration gave 242 scale divisions equivalent to 47.9 $(10)^{-6}$ watt sec.$^{-1}$ cm.$^{-2}$.

74 scale divisions are thus equivalent to 5.33 $(10)^{18}$ quanta absorbed per minute. The initial rate was 0.87 mm. per minute which is equivalent to 6.0 $(10)^{19}$ molecules disappearing. This gives a yield per hydrogen atom formed of 2.8 molecules of formaldehyde or 5.6 molecules per quantum absorbed.

64 cc. of formaldehyde gas were removed from the liquid air trap after the reaction. There was also some solid product left in the trap which was probably a polymer of formaldehyde.

The results given in Table X are the most reliable obtained for CO and $H_2$. The thermopile and arc emission were checked both before and after the experiment and it was found that conditions had remained steady during the course of the experiment.

TABLE XI

composition of gas 372 mm. CO
346 mm. $H_2$
thermopile readings no mercury present 254 scale divisions
reaction proceeding 187 " "
67 " "

253 scale divisions = 47.9 $(10)^{-6}$ watt sec.$^{-1}$ cm.$^{-2}$

| time (mins.) | pressure (mm.) | ratio $CO/H_2$ |
|---|---|---|
| 0 | 631 | |
| 10 | 622 | |
| 30 | 607 | |
| 60 | 586 | |
| | sample taken | |
| | 535 | |
| 120 | 501 | |
| 150 | 489 | |
| | sample taken | 1.00 |
| | 456 | |
| 180 | 439 | |
| 210 | 425 | |
| 270 | 404 | |
| | sample taken | 1.03 |
| | 366 | |
| 300 | 359 | |
| 360 | 340 | |
| 420 | 325 | |
| | sample taken | 0.88 (uncertain) |

67 scale divisions = 5.0 $(10)^{18}$ quanta absorbed per minute. The initial rate of the reaction was 6.02 $(10)^{19}$ molecules per minute. This gives a yield per hydrogen atom of 3.0 molecules product. This means that 6 molecules were formed for every quantum absorbed.

Rideal and Hirst[1] have sought to explain the decreasing velocity of combination in these reactions as originally observed by Marshall and Taylor[2] as due to a covering of the liquid mercury surface with solid polymerisation products of formaldehyde. This was supposed to inhibit the surface reaction, or, more recently, to slow down the rate of evaporation of mercury. It is apparent however from the above results that it is intimately connected in some manner with the chain mechanism involved in this reaction.

A few measurements were made screening the reaction vessel with a layer 1 cm. thick of 1.7 percent. tartaric acid solution as described by Dickinson and Sherrill.[3] Within the accuracy of observation the quantum yield appeared to

[1] Nature, **116**, 899 (1925).
[2] J. Phys. Chem., **29**, 1140 (1925).
[3] Proc. Nat. Acad. Sci., **12**, 175 (1926).

be unchanged. This would indicate that the amount of energy from the 1849 Å line reaching the reaction system was very small compared to that from the 2536 Å line.

A rough calculation from the rate of circulation, the vapor pressure of mercury at 50°C. and the rates of reaction found indicates that from 50 to 100 molecules of product are formed for each mercury atom passing through the reaction zone.

It must again be emphasized here that the values given for the length of the chains are the very lowest values obtainable taking into account all known correction factors. Any further correction introduced for channeling which means incomplete absorption, or for effective use of absorbed energy will tend to increase the length of the chain. If the primary process is $Hg' + H_2 \longrightarrow H + HgH$ and in subsequent reactions only the free H is able to initiate reaction the length of the chain would be doubled.

## Summary

1. A full discussion has been given of the qualitative data available on the absorption by mercury vapor of light of wave length 2536.7Å. Measurements on the extinction of fluorescence in mercury vapor fn the presence of various foreign gases have also been tabulated.

2. A method has been developed for measuring the amount of energy absorbed by mercury vapor from a water cooled quartz murcary arc.

3. A method is given for calculating the total energy radiated by a quartz mercury arc.

4. Quantitative data are presented concerning the absorption by mercury in vacuo and with hydrogen or nitrogen at one atmosphere pressure.

5. The temperature coefficient of the absorption by mercury in the presence of hydrogen and nitrogen has been measured.

6. Hydrogen peroxide has been shown to be the first isolable product of the photochemical reaction between hydrogen and oxygen when sensitized by mercury vapor.

7. The following mechanism is given for this reaction:

$$\begin{aligned} Hg' + H_2 &= 2H + Hg \\ H + O_2 &= HO_2 \\ HO_2 + H_2 &= H_2O_2 + H \\ 2H_2O_2 &= 2H_2O + O_2. \end{aligned}$$

8. The maximum yield measured for a mixture of $2H_2+O_2$ was 6.6 molecules of $H_2O_2$ formed per quantum of 2536.7 Å absorbed.

9. The maximum yield observed for the reaction $CO+H_2=HCOH$ was 6 molecules per quantum for a mixture of composition 37 cm. CO and 34.6 cm. $H_2$.

10. Care is taken to point out that the above values for the quantum yield represent minimal values and that all further corrections applied would increase the length of the chains.

11. These reactions must therefore have some "chain mechanism" and the Einstein-Stark Photochemical Equivalence Law does not hold.

12. With an energy input of 120 watts into the mercury arc 0.39 percent. is absorbed by the reacting system under optimum conditions.

*Research Laboratory,*
*General Electric Co.,*
*Schenectady, N. Y.*

# AQUEOUS SOLUTIONS OF SODIUM SILICATES. PART IV. HYDROLYSIS.

BY R. W. HARMAN

## Introduction

No theory as to the possible number and constitution of sodium silicates and their behaviour in aqueous solution can be formulated without an accurate and extensive study of their hydrolytic dissociation. There are comparatively few investigations on the subject.

Kohlrausch[1] from his conductivity measurements concluded that $Na_2SiO_3$ was practically completely hydrolysed even in moderately dilute solution and that a solution of $Na_2O \cdot 3{\cdot}4SiO_2$ was also considerably hydrolysed.

Kahlenberg and Lincoln[2] from freezing point measurements considered that $Na_2SiO_3$, $NaHSiO_3$ and $Na_2Si_5O_{11}$ (they had no grounds for assigning the latter two formulae) hydrolysed into NaOH and colloidal silicic acid, being completely hydrolysed at concentrations containing 1 gm. mol. per 48, 48 and 125 litres respectively; but their conclusions are obviously wrong if there are any free silicate ions in solution. Neither they nor Kohlrausch considered this possibility, but assumed all the silica to exist as colloidal sol even in very dilute solution.

Loomis[3] found that the molecular depression of the freezing point of aqueous solutions of $Na_2SiO_3$ was too large to be accounted for by ionic dissociation alone, yet too small to correspond to complete hydrolytic dissociation and suggested that $Na_2SiO_3$ possessed the properties of a mixture of NaOH and $SiO_2$ where the presence of the silica appeared to diminish the degree of dissociation of the NaOH.

Apart from these few earlier investigations little was done on this subject until Bogue[4] carried out a fairly extensive investigation of the hydrolysis of these silicates. Bogue determined by E.M.F. measurements, the hydroxyl ion concentration of ratios approximately 1:1, 1:1.5, 1:2, 1:2.5, 1:3, 1:3.5, and 1:4, at five concentrations ranging from 0.6 to 0.02 gm. equiv. per liter. Contrary to the work of previous investigators, his results indicate only a low percentage hydrolysis even in ratio 1:1. Bogue's experimental work appears to have been done very carefully, but he made no correction for the liquid-liquid potential differences, evidently considering that the saturated KCl which he used as a connecting liquid would eliminate them. His metasilicate, also, which he says is "unquestionably the pure compound $Na_2SiO_3$" contained 3% excess $SiO_2$ and this in concentrated solution may exert a consider-

[1] Z. physik. Chem., 12, 773 (1893).
[2] J. Phys. Chem., 2, 77 (1898).
[3] Wied. Ann., 60, 531 (1897).
[4] J. Am. Chem. Soc., 42, 2575 (1920).

able influence. In order to calculate the degree of hydrolysis from his experimentally found values of hydroxyl ion concentration, Bogue made three assumptions:—

(1) If no hydrolysis had occurred, the hydroxyl ion concentration would be the same as that of water at the same temperature.

(2) If hydrolysis had proceeded to completion the hydroxyl ion concentration would be the same as in an equivalent solution of NaOH.

(3) The hydroxyl ion concentration is a linear function of the degree of hydrolysis.

Assumptions (1) and (3) seem quite justifiable. Bogue himself queries assumption (2) on the grounds that, if true, it is necessary to admit

(a) Non-existence of any ionisable silicic acid (silicate ions).

(b) Absence of any influence of the colloidal silica on the hydroxyl ions.

He thought (a) to be true, but (b) to be unlikely, i.e. he supposed there were no free silicate ions in the solutions but that the sodium silicates were completely hydrolysed and that the colloidal silicic acid sol either adsorbed the hydroxyl ions or exerted some retarding influence on their movements.

If complete hydrolysis does take place and subsequent adsorption of the hydroxyl ions by the colloidal silica, then this adsorption is very considerable even in ratio 1:1, while there must be almost complete adsorption in ratio 1:3 and higher. But from freezing point measurements this adsorption seems unlikely. At the time Bogue's paper was published, the only work on freezing points was the few measurements of Loomis and of Kahlenberg and Lincoln, but his suggestion does not at all agree with their results.

Bogue also calculated the degree of hydrolysis of all these silicates, by assuming that the concentration of NaOH in the silicate solution would have the same hydroxyl ion concentration as it would have in a pure solution of NaOH. This is not true if silicate ions are present, as then the dissociation of the NaOH formed by hydrolysis will depend upon the total sodium ion concentration.

In view of the importance of the degree of hydrolysis of silicates in any investigation as to their molecular behaviour in solution, it was thought advisable to repeat and if possible, confirm Bogue's results. In addition several other ratios have been studied and over a wider range of concentration, and an attempt has also been made to determine the liquid-liquid potential differences.

## Experimental

*Method:*—The degree of hydrolysis is best obtained by measuring the hydroxyl ion concentration directly. The hydroxyl ion concentration of silicate solutions cannot be found by means of indicators, as quite different results are obtained with different indicators. In this connection Suida[1] has shown that hydrated silica and silicates adsorb basic dyestuffs but not acidic ones. However, the most direct and accurate method, that of measuring the hydrogen ion concentration by means of the hydrogen electrode, can quite

[1] Monatsheft, **25**, 1107 (1904).

correctly be used. Preliminary experiments with the same and different electrodes gave reproducible results when tested with solutions of different concentrations and ratios, showing that no poisoning or other effects took place at the electrode.

*Hydrogen Cell:*—The usual laboratory type suggested by Walpole, with a platinum electrode platinised in the usual manner, was used. The hydrogen was taken from a commercial cylinder and was purified by passing through (1) an alkaline solution of potassium permanganate (2) caustic potash (3) conc. sulphuric acid (4) dilute solution of barium chloride, and then through distilled water and a column of glass tubing about 4 feet long immersed in the thermostat, before entering the electrode vessel. The hydrogen was bubbled through the apparatus for two to three hours, depending on the solution, the E.M.F. remaining quite steady for the last half hour at least.

*Standard Cells.*—The half cell used was a saturated KCl calomel cell, made up with great care from purified materials. Two normal calomel cells were also made up and agreed with each other and with several others prepared in this laboratory. The saturated calomel cell was tested against these normal cells from time to time and found to keep in good agreement with them. The hydrogen cell, calomel cell, and connecting liquid of saturated KCl were immersed in a water thermostat electrically heated and regulated to 25°C ± 0.01.

The measurements were made with a Cambridge and Paul potentiometer of latest design, the current being supplied by an accumulator which was balanced just before and after each reading against a Weston cell. This Weston cell was prepared with much care from purified materials and was tested from time to time against a standard Weston cell. Adjustment of the current was made by a sensitive reflecting galvanometer.

The connecting liquid was in all cases KCl, generally saturated KCl but this is fully discussed under the heading "Liquid-liquid potential difference".

From time to time throughout the course of these experiments, the whole system was checked by the use of certain standard solutions, whose pH values are accurately known. The E.M.F.'s obtained agreed within 0.1 millivolt with those cited and agreed upon in the literature for these standard solutions.

The silicate solutions were prepared as previously described[1].

## Liquid—Liquid Potential Difference

The E.M.F. of the following combination, viz.,

Pt . $H_2$ | Na sil. | sat. KCl | sat. KCl . $Hg_2Cl_2$ | Hg. was observed for 6 different values of the ratio $Na_2O$: $SiO_2$ and at various concentrations.

It is well known that the use of saturated KCl as a bridge liquid considerably reduces the liquid P.D. but does not entirely eliminate it; especially is this so where one of the solutions, as here, contains a very mobile ion e.g. OH ion.

[1] Harman: J. Phys. Chem., 29, 1155 (1925).

This liquid P.D. may be determined experimentally by the Bjerrum extrapolation method[1] by measuring the E.M.F. using first 3.5N.KCl and then 1.75N.KCl as the connecting liquid, the difference in E.M.F. observed in the two cases being equal to the P.D. Care was taken to make the liquid connections always in the same manner by dipping the arms of the hydrogen electrode and calomel cell into a wider tube containing the KCl solution. The E.M.F. was observed at definite time intervals after the connection had been made, so that differences due to changes in the liquid potential which occur with time, were eliminated. Duplicate measurements of the P.D. agreed within 0.1 millivolt.

The liquid P.D. has also been calculated by means of Henderson's formula, by making use of the mobilities of the Na, OH and $SiO_3$ ions found from conductivity and transport number experiments and the values of the ion concentrations found by the lowering of the freezing point of the same solutions. These ion concentrations will be discussed in a paper on osmotic activity of aqueous solutions of sodium silicates shortly to be communicated.

In Table I are given a few of the experimental results obtained in measuring the liquid P.D.'s by the Bjerrum extrapolation method, in order to show their general nature and magnitude. The P.D.'s calculated by means of Henderson's formula are given in the last column.

The sign of the E.M.F. due to the liquid P.D. has been designated negative or positive where it opposes or aids respectively, the general E.M.F. of the cell; i.e. a negative P.D. is to be added to the E.M.F. observed for the whole cell, and a positive P.D. is to be subtracted from the E.M.F. of the cell.

### Liquid—Liquid Potential Differences

TABLE I

| Ratio | $N_w$. | $E_{3.5N.}$ | $E_{1.75N.}$ | Exptl. Liq. P. D. (Bjerrum Method) | P. D. calculated (Henderson) |
|---|---|---|---|---|---|
| 2:1 | 2 | 1.0440 | 1.0401 | −.0039 volts | −.0051 |
| | 1 | 0.9850 | 0.9848 | −.0002 | −.0003 |
| 1:1 | 2.4 | 1.0456 | 1.0426 | −.0030 | −.0047 |
| | 0.1 | 0.9794 | 0.9794 | −.0000 | −.0001 |
| 1:1.5 | 2 | 1.0132 | 1.0122 | −.0010 | −.0016 |
| | 1 | 0.9570 | 0.9570 | −.0000 | −.0000 |
| 1:2 | 1 | 0.9674 | 0.9673 | −.0001 | −.0002 |
| | 0.1 | 0.9286 | 0.9286 | −.0000 | −.0000 |
| 1:3 | 2 | 0.9200 | 0.9208 | +.0008 | +.0010 |
| | 1 | 0.8950 | 0.8950 | +.0000 | +.0000 |
| 1:4 | 2 | 0.8950 | 0.9000 | +.0050 | +.0063 |
| | 1 | 0.8868 | 0.8871 | +.0003 | +.0005 |

[1] Z. Elektrochem., 17, 389 (1911).

The P.D.'s calculated from the Henderson formula are higher than those found experimentally by the Bjerrum extrapolation. This does not necessarily mean that the values for ionic concentrations and conductances used in the calculations are grossly wrong, for most cases in the literature where these two methods are compared show no closer agreement.

It is seen that in ratios 2:1 and 1:1 the P.D. is 4 and 3 millivolts respectively at concentrations $_2N_w$, and that this E.M.F. opposes the general E.M.F. of the cell. This is to be expected from the relatively high concentration of the OH ions of these solutions. In ratios 1:3 and 1:4 the P. D. is just as large but is in the opposite direction. Here there is no OH ion, probably only sodium and silicate ions; hence, either the silicate ion is much less mobile than the sodium or there is a much larger concentration of sodium than silicate ions present.

## Method of Calculation

In the following treatment of the subject the assumption is made that the E.M.F. gives us a measure of the actual hydrogen ion concentration instead of the more thermodynamically correct ion activity.

From the Nernst equation, applying the barometric correction for the partial pressure of the hydrogen, we get at 25°C the following,

$$pH = \frac{\text{E.M.F. obs.} + \text{E.M.F. bar.} - \text{E.M.F. cal.}}{0.05911}$$

wnere E.M.F. obs. stands for the observed E.M.F. of the cell corrected for the liquid P.D. The values for the barometric pressure correction have been taken from Clark's "Determination of Hydrogen Ions". (Table, p. 457).

From the values of hydrogen ion concentration so found the values of OH ion concentration have been obtained from $K_w$. The value of $K_w$ for water at 25°C has been taken as $1.00 \times 10^{-14}$. Since $K_w = [H] \times [OH]$, $K_w = 1.00 \times 10^{-14}$ only for pure water. The activity of the water, $[H] \times [OH]$ will be different in a solution.

Since $a_1/a_o = f_1/f_o$ where $a_1$ and $a_o$ are the activities of water in a solution and in pure water, and $f_1$ and $f_o$ the respective fugacities,

$$a_1 = a_o \cdot f_1/f_o.$$

Assuming the vapour to conform to the laws of an ideal gas, we get

$$a_1 = a_o \cdot p_1/p_o$$

where $p_o$ and $p_1$ are the respective vapour pressures of water and solution.

Hence we get

$$[OH] = \frac{1.00 \times 10^{-14}}{[H]} \times p_1/p_o$$

When $p_o - p_1 = 1$ mm., then $K_w$ becomes $0.955 \times 10^{-14}$. The values for $p_1$ have been taken from the work on vapour pressures shortly to be communicated.

## Calculation of Degree of Hydrolysis

Omitting for the present the possibility of hydrolysis taking place in two stages, the interaction of sodium metasilicate and water may be represented as follows:—

$$\begin{array}{ccccc} Na_2SiO_3 & \rightleftarrows & 2Na^{\cdot} & + & SiO_3''. \\ + & & + & & + \\ 2HOH & \rightleftarrows & 2OH' & + & 2H^{\cdot} \\ & & \uparrow\downarrow & & \uparrow\downarrow \\ & & 2NaOH & & H_2SiO_3. \end{array}$$

According to the classical theory of the ionisation of electrolytes there should be in the above solution an equilibrium represented by,—

$$Na^{\cdot} + OH' \rightleftarrows NaOH.$$

and the NaOH is usually considered practically completely dissociated, in such cases of hydrolysis. If the NaOH is not completely dissociated then the degree of hydrolysis can only be correctly calculated from the measured OH ion concentration plus the concentration of the undissociated NaOH. Most investigators in such a case, take the NaOH concentration as equal to that which would give rise to the same OH ion concentration in a pure NaOH solution. This is how Bogue, in his work on the hydrolysis of these silicates, calculated his results. But if, as here, the OH ion concentration is small, and the sodium ion concentration is large, this view is not strictly correct. If the total sodium ion concentration were known then it would be possible to calculate the percentage of undissociated NaOH. Noyes' rule regarding mixtures of electrolytes is also not strictly applicable, as NaOH and $Na_2SiO_3$ are not of the same valence type.

The same difficulty applies to the other salts or ratios. Whether they are definite salts or not, NaOH is a product of hydrolysis and this NaOH is largely ionised. It is only in the more concentrated solutions that undissociated NaOH is likely to exist as such, and it is also in these more concentrated solutions that the applicability of the Nernst equation, and the concept of hydrogen ion concentration, rather than hydrogen ion activity, are doubtful, so that the values of hydrolysis for $2N_w$ and $1N_w$ solutions of ratios 2:1 and 1:1, where the hydroxyl ion concentration is about 0.2 – 0.3 N, must be regarded as only very approximate.

However, the change in diesociation of NaOH due to the addition of an equivalent of sodium ion, e.g. to 0.1N . NaOH, is, very approximately, on account of the very doubtful application of the mass action law to such a case, from 90% to 85%. This 85% is the degree of ionisation of 0.2N . NaOH, and that which one would obtain by applying Noyes' rule of mixture of electrolytes, where the degree of either constituent depends upon the total concentration of the common ion.

Taking, e.g., 2N . $Na_2SiO_3$, where the experimentally found OH ion concentration is 0.256N, we see that,—

(1) calculating the degree of hydrolysis from the OH ion concentration alone gives us $0.256/2 \times 100 = 12.8\%$

(2) calculating it from the NaOH concentration i.e. 0.3N which gives this 0.256N OH ion concentration we get $0.30/2 \times 100 = 15\%$.

(3) taking into account the fact that in the silicate solution there is approximately double the sodium ion concentration, which according to the above rather doubtful assumption would alter the ionisation of NaOH here from 85% to 80% we get the NaOH concentration equal to 0.32N, which gives $0.32/2 \times 100 = 16\%$.

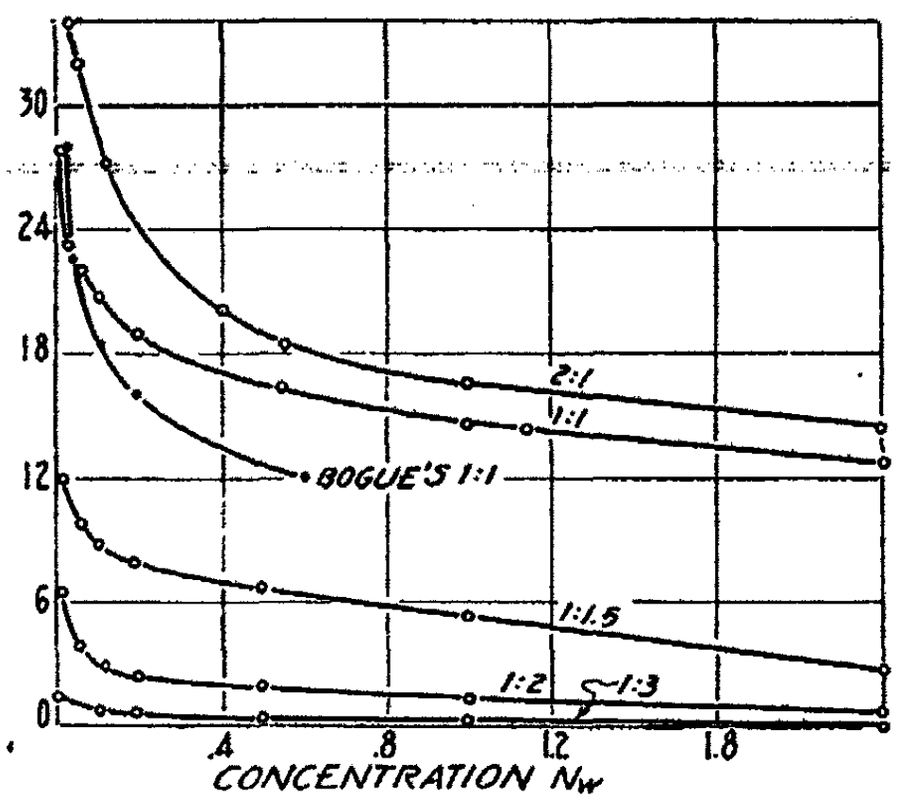



FIG. 1

Percentage Hydrolysis against Concentration

It has been thought most advisable, in view of what might be called the present transition state of knowledge regarding the theory of solution, to calculate the degree of hydrolysis by both methods (1) and (2) above, and to reject method (3) on account of its very doubtful applicability. Therefore in Table II two sets of values for ratios 2:1, 1:1, etc. are given for the percentage hydrolysis.

For method (2) above, given in column 6, the values for the degree of ionisation of NaOH at 25°C have been taken from A. A. Noyes[1] and one or two values for concentrated solutions from Frary and Nietz[2].

In dilute solutions and in ratios 1:3 and 1:4, where the OH ion concentration is very small, the two sets of values are the same.

The results given in Table II below are shown graphically in Fig. 1, where percentage hydrolysis is plotted against concentration.

[1] Carnegie Inst. Pub., **63**, 177, 340 (1908).

[2] J. Am. Chem. Soc., **37**, 2263 (1915).

TABLE II

| $N_w$ | E.M.F. corrd. | pH' | [H'] | [OH'] | % hydrolysis calc. from [NaOH] which gives expt. [OH] | % hydrolysis calc. from exptly. found [OH] ion alone' |
|---|---|---|---|---|---|---|
| | | | **Ratio 2 : 1.** | | | |
| 2.0 | 1.483 | 13.48 | $0.33\times10^{-13}$ | 0.29 | 17.5 | 14.5 |
| 1.0 | 1.0334 | 13.23 | 0.59 | 0.165 | 19.0 | 16.5 |
| 0.398 | 1.059 | 12.93 | $0.12\times10^{-12}$ | 0.0804 | 22.6 | 20.2 |
| 0.159 | 0.9981 | 12.63 | 0.235 | 0.0424 | 28.3 | 26.6 |
| 0.0398 | 0.9697 | 12.12 | 0.77 | 0.01297 | 32.6 | 32.6 |
| 0.0159 | 0.9455 | 11.74 | $0.18\times10^{-11}$ | 0.0056 | 36.0 | 35.0 |
| | | | **Ratio 1 : 1.** | | | |
| 2.435 | 1.0490 | 13.49 | $0.325\times10^{-13}$ | 0.295 | 14.8 | 12.1 |
| 1.133 | 1.0328 | 13.22 | 0.600 | 0.163 | 16.3 | 14.3 |
| 0.547 | 1.0181 | 12.97 | $0.11\times10^{-12}$ | 0.0896 | 18.7 | 16.3 |
| 0.204 | 0.9956 | 12.59 | 0.255 | 0.0388 | 20.0 | 19.0 |
| 0.1 | 0.9798 | 12.32 | 0.48 | 0.0207 | 21.8 | 20.7 |
| 0.05 | 0.9628 | 12.04 | 0.91 | 0.011 | 22.6 | 22.0 |
| 0.02 | 0.9406 | 11.67 | $0.215\times10^{-11}$ | 0.00465 | 23.25 | 23.25 |
| 0.01 | 0.9274 | 11.44 | 0.36 | 0.00278 | 27.8 | 27.8 |
| | | | **Ratio 1 : 1.5.** | | | |
| 2.0 | 1.0046 | 12.74 | $0.18\times10^{-12}$ | 0.054 | 3.0 | 2.7 |
| 1.0 | 1.0040 | 12.73 | 0.185 | 0.0532 | 5.9 | 5.3 |
| 0.5 | 0.9915 | 12.52 | 0.30 | 0.0329 | 7.0 | 6.6 |
| 0.2 | 0.9724 | 12.20 | 0.63 | 0.0158 | 8.25 | 7.9 |
| 0.1 | 0.9574 | 11.95 | $0.115\times10^{-11}$ | 0.00868 | 8.7 | 8.9 |
| 0.05 | 0.9424 | 11.69 | 0.205 | 0.00488 | 9.7 | 7.7 |
| 0.02 | 0.9218 | 11.34 | 0.46 | 0.0022 | 11.0 | 11.0 |
| 0.01 | 0.9064 | 11.08 | 0.83 | 0.0012 | 12.0 | 12.0 |
| | | | **Ratio 1 : 2.** | | | |
| 2.450 | 0.9720 | 12.19 | $0.645\times10^{-12}$ | 0.0152 | 0.65 | 0.62 |
| 1.110 | 0.9677 | 12.12 | 0.76 | 0.013 | 0.21 | 1.01 |
| 1.0 | 0.9678 | 12.12 | 0.76 | 0.013 | 1.35 | 1.3 |
| 0.5 | 0.9584 | 11.96 | $0.11\times10^{-11}$ | 0.0091 | 1.88 | 1.8 |
| 0.204 | 0.9424 | 11.69 | 0.205 | 0.00486 | 2.38 | 2.4 |
| 0.1 | 0.9290 | 11.46 | 0.35 | 0.00285 | 2.85 | 2.8 |
| 0.05 | 0.9180 | 11.28 | 0.53 | 0.0019 | 3.8 | 3.8 |
| 0.021 | 0.9034 | 11.03 | 0.935 | 0.00107 | 5.1 | 5.1 |
| 0.011 | 0.8924 | 10.84 | $0.14\times10^{-10}$ | 0.000714 | 6.5 | 6.5 |

TABLE II (continued)

| $N_w$ | E.M.F. corrd. | pH | (H·) | (OH') | % hydrolysis: (same in both methods) |
|---|---|---|---|---|---|
| | | | Ratio 1 : 3. | | |
| 2.0 | 0.9196 | 11.31 | $0.49\times10^{-11}$ | 0.00202 | 0.101 |
| 1.0 | 0.9190 | 11.29 | 0.515 | 0.00192 | 0.192 |
| 0.5 | 0.9170 | 11.27 | 0.55 | 0.00180 | 0.36 |
| 0.2 | 0.9060 | 11.07 | 0.85 | 0.00117 | 0.57 |
| 0.1 | 0.8954 | 10.89 | $0.13\times10^{-10}$ | 0.00768 | 0.77 |
| 0.05 | 0.8854 | 10.73 | 0.185 | 0.00054 | 1.10 |
| 0.02 | 0.8651 | 10.38 | 0.42 | 0.00024 | 1.20 |
| 0.01 | 0.8324 | 9.83 | $0.14\times10^{-9}$ | 0.000069 | 1.38 |
| | | | Ratio 1 : 4. | | |
| 2.0 | 0.8904 | 10.81 | $0.155\times10^{-10}$ | 0.000638 | 0.032 |
| 1.0 | 0.8934 | 10.86 | 0.14 | 709 | 0.071 |
| 0.5 | 0.8916 | 10.84 | 0.14 | 711 | 0.14 |
| 0.2 | 0.8921 | 10.84 | 0.14 | 712 | 0.35 |
| 0.1 | 0.8869 | 10.75 | 0.175 | 57 | 0.57 |
| 0.05 | 0.8818 | 10.67 | 0.215 | 464 | 0.93 |
| 0.02 | 0.8675 | 10.42 | 0.38 | 26 | 1.30 |
| 0.01 | 0.8534 | 10.18 | 0.66 | 15 | 1.50 |

## Discussion of Results

The results are on the whole the same as those obtained by Bogue, but there are a few differences, especially in the more concentrated solutions of ratio 1:1 where the author's values for the percentage hydrolysis are higher. This is partly accounted for by the fact that the correction for the liquid P.D. which Bogue did not apply, increases the percentage hydrolysis by over 3% and by the fact that Bogue's metasilicate, according to his own analysis, was of ratio 1:1.03 instead of 1:1. In ratio 1:2 the author's values are slightly higher at all concentrations. The values in dilute solutions for ratios 1:1 and 1:1.5 and at all concentrations for ratios 1:3 and 1:4 are practically the same as those obtained by Bogue.

In Table III are given the hydroxyl ion concentrations, at round concentrations, for the purposes of comparison, these values being plotted against the ratio in Fig. 2.

TABLE III

**Hydroxyl Ion Concentration**

| $N_w$ | NaOH | 2:1 | 1:1 | 1:1.5 | 1:2 | 1:3 | 1:4 |
|---|---|---|---|---|---|---|---|
| 2.0 | ——— | 0.29 | 0.256 | 0.054 | 0.0160 | 0.00202 | 0.000638 |
| 1.0 | 0.725 | 0.165 | 0.147 | 0.053 | 0.013 | 0.00192 | 709 |
| 0.5 | 0.405 | 0.096 | 0.0875 | 0.033 | 0.0091 | 0.0018 | 711 |
| 0.2 | 0.175 | 0.048 | 0.038 | 0.0158 | 0.00486 | 0.00117 | 712 |
| 0.1 | 0.090 | 0.028 | 0.0207 | 0.0087 | 0.00285 | 0.000768 | 57 |
| 0.05 | 0.046 | 0.016 | 0.011 | 488 | 19 | 54 | 464 |
| 0.02 | 0.0196 | 0.0068 | 0.00465 | 22 | 107 | 24 | 26 |
| 0.01 | 0.0094 | 0.0036 | 0.00278 | 12 | 0.000714 | 134 | 15 |

From Fig. 2 it can be seen that in concentrated solution there is a large and sudden fall in OH ion concentration from NaOH to ratio 2:1 which has only a little larger OH ion concentration than 1:1. Then another large and sudden drop to ratio 1:2, after which the pressure in OH ion concentration is small, until from 1:3 onwards it is practically constant. In dilute solutions below $0.05N_w$ the fall is more gradual after ratio 1:1.

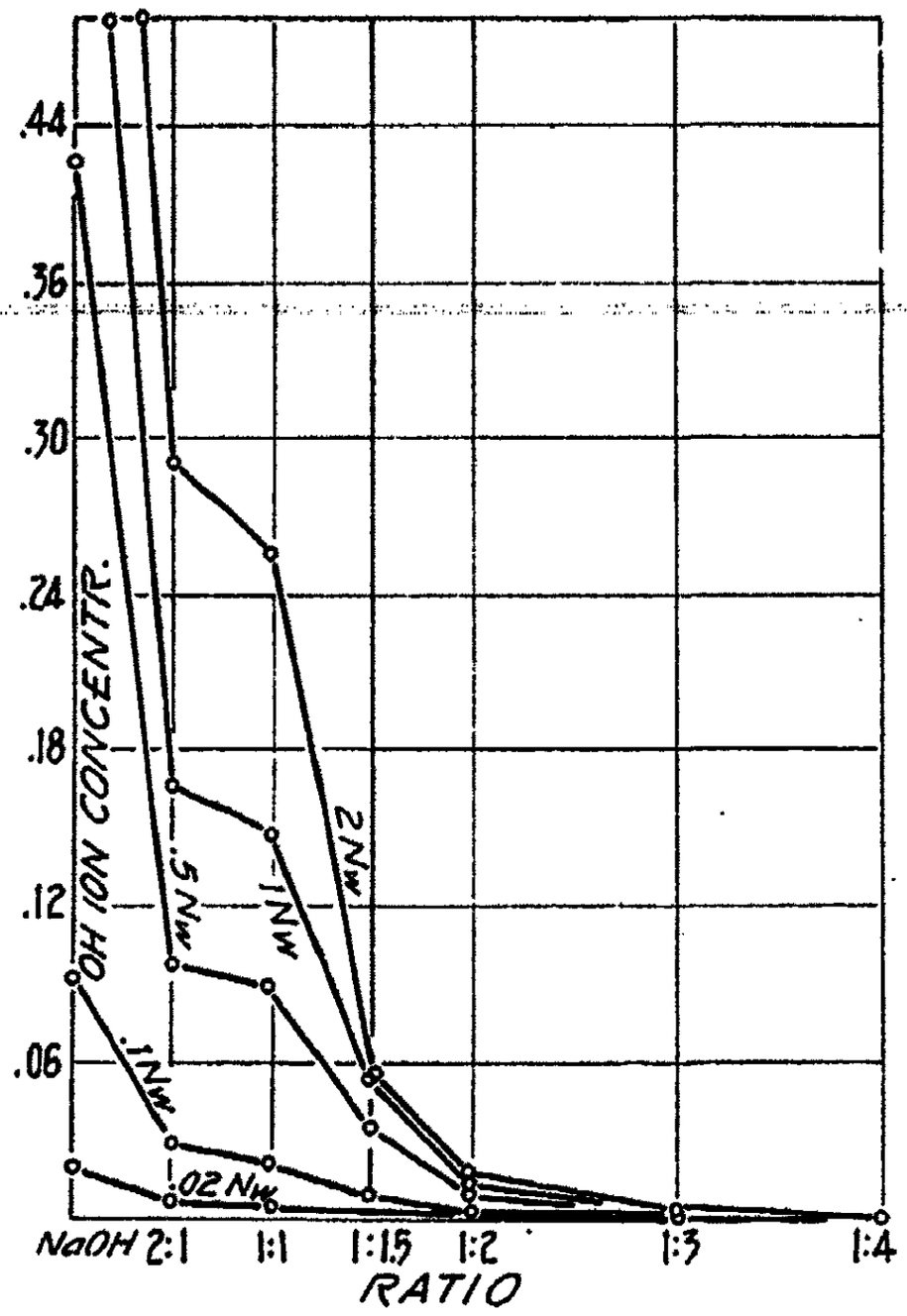



FIG. 2
OH Ion Concentration against Ratio

Whether the points are joined by straight lines, as in the figure, or whether a smooth curve is attempted to be drawn through the points, we observe in the more concentrated solutions changes of direction at ratios 2:1, 1:1 and in the neighbourhood of 1:2.

This variation of OH ion concentration with ratio, between NaOH and ratio 1:2, is very similar to the change of conductivity with ratio remarked upon in the first paper of this series[1]. So we may conclude that the variations

[1] Harman: J. Phys. Chem., 29, 1155 (1925).

in conductivity noted, in the more concentrated solutions of ratios containing relatively little silica, are mainly due to changes in the OH ion concentration. However, the OH ion concentration alone does not account for the high conductivity in ratios rich in silica, i.e. in ratios 1:3 and 1:4, as in these the OH ion concentration is practically negligible. Neither does it wholly account for the very high conductivity exhibited by ratios 1:2 and 1:1.

In Table IV the values of percentage hydrolysis at comparable concentrations have been given. These values are plotted against the ratio in Fig. 3, the results being much the same as in the case where the OH ion concentration is plotted against the ratio.

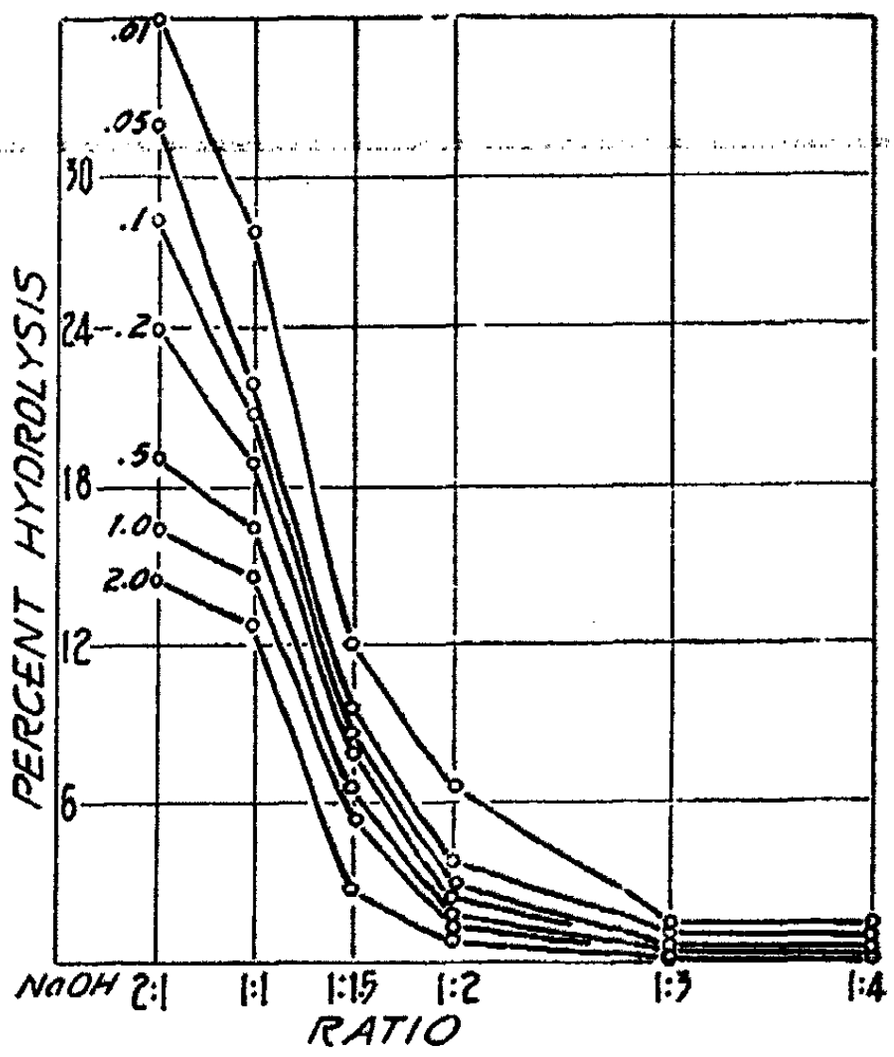



FIG. 3
Percentate Hydrolysis against Ratio

## TABLE IV

### Percentage Hydrolysis

(calculated from NaOH)

| $N_w$ | 2:1 | 1:1 | 1:1.5 | 1:2 | 1:3 | 1:4 |
|---|---|---|---|---|---|---|
| 2.0 | 17.5 | 15.25 | 3.0 | 1.0 | 0.101 | 0.032 |
| 1.0 | 19.0 | 16.5 | 5.9 | 1.35 | 0.192 | 0.071 |
| 0.5 | 19.7 | 19.1 | 7.0 | 1.88 | 0.36 | 0.14 |
| 0.2 | 24.2 | 20.0 | 8.25 | 2.40 | 0.58 | 0.35 |
| 0.1 | 28.4 | 21.8 | 8.7 | 2.85 | 0.77 | 0.57 |
| 0.05 | 31.6 | 22.6 | 9.76 | 3.8 | 1.10 | 0.93 |
| 0.02 | 34.2 | 23.25 | 11.0 | 5.1 | 1.20 | 1.30 |
| 0.01 | 36.0 | 27.8 | 12.0 | 6.5 | 1.34 | 1.50 |

The results of hydrolysis experiments thus show that one of the principal factors concerned is the existence of the stable salt $Na_2SiO_3$. Contrary to previous belief this salt is not completely hydrolysed even in dilute solution. In ratio 1:2 hydrolysis is very low, and in ratios 1:3 and 1:4 it is practically absent, hence some other theory is necessary to account for the general properties of these silicates in solution.

From the fact that all the solutions exhibit a relatively low degree of hydrolysis we can conclude that,—

(1) If this is not the true value of hydrolysis i.e. if these silicates are more or less completely hydrolysed, then OH ion adsorption by the colloidal silica sol takes place to a very large extent. Hence we should expect these solutions to show a very low osmotic activity.

or (2) silica exists in the solutions as simple or complex silicate ions and ionic micelles, and is not present wholly as colloidal silica sol as previously supposed.

## Summary

(1) Hydroxyl ion concentrations and percentage hydrolyses of silicate solutions of ratios, $Na_2O$: $SiO_2$, 2:1, 1:1., 1:1.5, 1:2, 1:3, 1:4 and at concentrations ranging from 2—0.01$N_w$ have been found by the hydrogen electrode method.

(2) The values of OH ion concentration and percentage hydrolysis have been plotted against the concentration and against the ratio $Na_2O$: $SiO_2$.

(3) None of these silicates are largely hydrolysed. At 0.01$N_w$, $Na_2SiO_3$ is only 27.8% hydrolysed, while ratios 1:3 and 1:4 at the same concentration show only 1.5% hydrolysis.

(4) In concentrated solution the percentage hydrolysis is very low.

(5) The liquid—liquid P.D.'s between these silicate solutions and KCl have been found by the Bjerrum extrapolation method.

(6) It appears probable that much of the silica is present as simple and complex silicate ions (and ionic micelles). This also accounts for the good conductivity and the high transport numbers.

I wish to express my thanks to the Commissioners of the 1851 Exhibition for a scholarship which enabled me to carry out this work, and to Professor Donnan for his constant kindly interest and advice.

*The Sir William Ramsay Laboratories of Physical and Inorganic Chemistry,*
*University College, London,*
*April 7, 1926.*

# EXPERIMENTS ON THE ELECTROLYSIS OF RADIUM D AND RADIUM E

BY JOHN P. McHUTCHINSON

That extraction of radio-elements by electrolysis of their solutions is possible when the E.M.F. employed is lower than the decomposition potential of their ordinary isotopes, was proved by the experiments of von Hevesy[1]. It was further indicated that the single electrode potential between the solution and the electrode on which the decomposition was taking place, was of fundamental importance, since in the electrolysis of pure aqueous solutions the quantity of active ions present is not sufficient to carry an appreciable current. Thus, successful extractions of the active deposit of radium have been accomplished by the use of much lower potentials and current densities than would be required for the deposition of lead (isotopic with the B and D members) or of bismuth (isotopic with the C and E members). In particular, from a solution of radium E and radium F, containing bismuth to prevent the deposition of radium E, radium F was deposited with a cathode potential of .08 volts and a current density of .16 milliamperes per sq. cm.[2] Also, from a lead acetate solution containing radium D and its products, radium F was deposited on the cathode with a current density of 4 microamperes per sq. cm., radium E and radium F together at ten microamperes, while with larger currents all the products were deposited.

These current densities being extremely small and not readily obtainable for any ordinary extraction, and since no data seemed to be available as regards what extraction of radium D and radium E would be obtained when the conditions as regards voltage and current density were arranged exactly as given ordinarily for their isotopes, lead and bismuth, the following experiments were undertaken, and certain unlooked-for results emerged.

## Experimental

A solution of radium D, radium E, and radium F in equilibrium was obtained by dissolving the deposit from old, cleaned emanation tubes in concentrated nitric acid, evaporating to dryness in a platinum basin, and then dissolving in distilled water. Care was taken on the completion of each electrolysis not to interrupt the current, which would send any deposited matter back into solution again: but in every case, the electrodes were washed by siphoning off the solution, at the same time adding distilled water till the solution was really one of water only, the electrolysis being finished when the level of the water fell below the lower ends of the electrodes. Measurements of activity were made with a $\beta$-ray electroscope having a base of gold-beater's skin, through an air-space of 2 cm. in addition, so as to cut off all the $\alpha$-radiation of radium F.

[1] Phil. Mag., (6), 23, 628 (1912); 25, 390 (1913).

[2] Paneth and von Hevesy: Monatsheft, 34, 1605 (1913).

1. To a quantity of the active solution 20 c.c. conc. $HNO_3$ were added, the volume being made up to 100 c.c. with water: and this solution was electrolysed between the usual plate platinum electrodes with a potential difference of 3 volts and a current density of 15 milliamperes per sq. cm. at a temperature of 65°.[1] The conditions were therefore such as would deposit lead (the isotope of radium D) as peroxide on the anode. Numerous experiments were made, the electrolysis being continued for periods varying between 1 hour and 24 hours. In no case was any deposit with an appreciable $\beta$ activity found on the anode even after the lapse of several days, which indicated that no radium D as peroxide had been deposited. In the same electrolysis, the cathode possessed a slight activity amounting only to about 1 per cent of the total activity present in electrolysed solution. Since von Hevesy and Paneth[2] had found that the peroxide of radium D behaved electrochemically like lead peroxide, this failure to extract was unexpected, and is an interesting result.

In a paper by Mlle. Curie[3] there was obtained, under similar conditions, an activation of the gold electrodes employed: but this, as is suggested in another part of the same paper, may have been due to traces of lead present as impurities in the mercury present on the radon tubes, from which the solution of the active deposit was obtained. She also found that the lead peroxide film on the anode contained radium E, which agrees with the result reported in section 2. It may be that this is a question of obtaining an adherent deposit, since the possible active layer would be only about one molecule thick; and it was therefore thought that, if a small trace of a lead salt were added, the radium D would be held fast in a layer of lead peroxide, a few hundred molecules thick.

2. Several experiments were therefore conducted with conditions exactly as stated above except that small quantities of lead as nitrate varying from 1 to 10 milligrams were added to the solution. In every case the anode was strongly active, but observations of its activity from day to day showed that radium E in large proportions was also present in the anodic depsoit. Now radium E, like bismuth, in nitric acid solution might be expected on the cathode, but in every case the cathode was inactive.

The likeliest reason for this anomalous result would appear to be that some of the radium E ions had been adsorbed by the lead peroxide surface on the anode: and this was tested by arranging the electrolytic conditions so as to deposit bismuth on the cathode and observing if radium D was present along with the radium E.

3. The active solution containing two milligrams of bismuth as nitrate, was electrolysed with the conditions as for bismuth. (Potential difference: 1.8 volts: Current density .2 milliamperes per sq. cm. at 50° in 100 c.c. solution containing 1 c.c. conc. $HNO_3$: 2 c.c. conc. $H_2SO_4$ and 1 gm. $K_2SO_4$). In this

[1] Smith: "Electro-analysis", 6th edition, p. 110 (1919).
[2] Wien. Ber., 113, 1909 (1914).
[3] J. Chim. phys., 22, 484 (1925).
[4] Smith: *op. cit.* p. 106.

case no activity was found on the anode, but the cathode was strongly active with large quantities of radium D present along with the radium E. This seems to indicate that the bismuth film on the cathode had in the absence of any adsorptive film on the anode adsorbed a certain proportion of the radium D ions.

4. With conditions as for the deposition of lead as element on the cathode in caustic soda solution and with quantities of about 10 milligrams of lead present as nitrate, the extraction of radium D and radium E was practically complete if electrolysis was continued long enough, both these elements being obtained in their equilibrium proportions on the cathode. In this case the tendency of the radium E ions was the same as that of the radium D ions, and complete deposition of all the active matter occurred on the cathode, though in cases 1, 2, and 3 where the mass of added material did not exceed a few milligrams, the average extraction obtained was not more than 50%.

5. The influence of adsorption on this electrolytic extraction was further noted when a 10% nitric acid solution of the active matter containing 2 milligrams of lead and of bismuth as nitrates was electrolysed. The cathode deposit consisted of practically radium E alone, but the anode deposit of lead peroxide with radium D still contained a quantity of radium E, due perhaps to the more strongly adsorptive surface provided by the spongy peroxide film than by the metallic bismuth deposit. This method will permit of some of the radium E being separated for the most part pure, the complete extraction of which was found by Mlle. Curie (loc. cit.) to present great difficulties.

6. When electrodes, which held previously deposited films, e.g. of lead peroxide and copper, were employed in the electrolysis of a nitric acid solution of radium D and radium E, without the addition of any other substance such as salts of lead or bismuth, extractions of the radioactive matter were obtained. The cathodic deposit was radium E alone, and traces of this element were present also on the anode with the radium D. It would appear therefore that the failure to extract as reported in section 1 was due to the absence of a suitable surface for the infinitesimal mass of the radio-elements present to adhere to.

It is not considered that the failure to extract by ordinary electrolytic conditions as for lead or bismuth, in any way contradicts the well-known fact that radio-elements will deposit on an electrode even with no current passing. In the experiments described above, the liberation of gases at anode and cathode would, in the absence of any substance to act as a nucleus, prevent the deposition of the radioactive matter.

## Summary

The results enumerated above may be summarised as follows:—

1. It has not been found possible to extract radium D or radium E on ordinary platinum electrodes from nitric acid solution with the electrolytic

conditions required for the extraction of their isotopes lead and bismuth respectively.

2. Extraction becomes possible under these conditions if traces of lead or bismuth are present: but the active matter obtained on any one electrode is due to adsorption effects as well as to electrolytic deposition.

*The Radiometric Laboratory,*
*The University,*
*Glasgow.*
*February 13, 1926.*

97-45
94-194

# THE PEPTIZATION OF PYROXYLIN*

BY MILTON L. BYRON

## History

Pelouze[1] first used the name "Pyroxylin" with reference to collulose nitrate. His product, however, and the guncotton that Schönbein[2] discovered in 1846, were almost identical. At the present time England and the United States use the name "Pyroxylin"[3] to designate those soluble cellulose nitrates used in the manufacture of collodion and lacquers, while in Germany it is used to designate the insoluble and explosive variety.

In 1846, F. Domonte and Henard[4] submitted guncotton to alcohol-ether and obtained incomplete solution: they claimed the soluble cellulose nitrate was identical with the xyloidine that Braconnot[5] had discovered in 1883 while the insoluble cellulose nitrate contained more nitrogen.

Lunge and Bebie[6] working with the influence of water on the nitrating process, incidentally showed the fallacy of attempting to judge the ether-alcohol solubility of cellulose nitrate from the nitrogen content as illustrated in Table I.

TABLE I

| Percent nitrogen | Solubility in ether-alcohol 2:1 | Percent nitrogen | Solubility in ether-alcohol 2:1 |
|---|---|---|---|
| 13.65 | 1.50% | 11.59 | 100.02 |
| 13.21 | 5.40 | 10.93 | 99.82 |
| 12.76 | 22.00 | 9.76 | 74.22 |
| 12.58 | 60.00 | 9.31 | 1.15 |
| 12.31 | 99.14 | 8.40 | 0.61 |
| 12.05 | 99.84 | 6.50 | 1.73 |

According to Worden,[7] "the nitrogen content is not a trustworthy criterion of solubility, for nitrocelluloses are known to contain 10% and 11% nitrogen which are, or are not, soluble in amyl acetate. For example, a cotton may be nitrated at a comparatively low temperature, and after nitration is substantially complete so far as nitrogen content of the nitrocotton is concerned, if a sample be withdrawn, and washed to neutrality in the usual manner, while the bulk of the nitrated cotton remains in the nitrating mixture, the temperature of which is considerably elevated, it is possible to produce two nitrocottons, in which the sample first withdrawn is completely soluble in alcohol-

---

* A thesis submitted for the degree of M.Chem. at Cornell University.

[1] Am. J. Sci., (2) 5, 142, 259 (1842).

[2] Worden: "Technology of Cellulose Esters", 1, III, 1570.

[3] Worden: "Technology of Cellulose Esters", 1, III, 1696.

[4] Jahrbuch der Chemie, 1, 1136 (1846-48).

[5] Worden: "Technology of Cellulose Esters", 1 III, 1567.

[6] J. Am. Chem. Soc., 23, 528 (1901).

[7] Worden: "Technology of Cellulose Esters", 1, III, 1721.

either mixture, while the latter sample is substantially insoluble therein, both containing approximately the same nitrogen content."

In view of the fact that the temperature is considerably elevated, the nitrogen content of the second sample should be somewhat higher, and this might account for the difference in solubility.

The "soluble" cellulose nitrates are distinguished from the highly nitrated guncottons by a solubility in ether-alcohol, i.e. ethyl ether and ethyl alcohol, but not in any ether or any alcohol.

A. Matteoschat[1] has made an extensive study of the solvent action of alcohol-ether mixtures on cellulose nitrate. In the case of the completely soluble cellulose nitrate, the proportion of ether to alcohol may be varied widely without altering the solubility figure. The solubility depends upon the cellulose nitrate, proportions of solvent, and strength of solvent used. The sample of cellulose nitrate used contained 12.95% nitrogen which is not completely soluble in alcohol-ether. Matteoschat's data are given in Table II.

TABLE II

| Ether-Alcohol | Strength of Alcohol, Percent by Wt. | | | |
|---|---|---|---|---|
| | 99.5 | 95 | 90 | 80 |
| 1 : 2 | 34.4 | —— | —— | —— |
| 1 : 1 | 52.3 | 42.3 | 28.7 | 14.2 |
| 2 : 1 | 40.5 | 52.4 | 53.9 | 45.0 |
| 3 : 1 | 25.0 | 42.4 | 53.0 | 57.5 |
| 0 : 1 | 3.1 | 1.7 | —— | —— |

This shows that the weaker alcohol gives the best results provided the ether is in excess.

T. Chandelon[2] explains this in the following conclusions, drawn from his experiments:—

"(1) The greater solubility of moist cellulose nitrate in a mixture of ether and alcohol does not depend on the existence of a hydrate, but simply on the dilution of the solvent by the water in the moist substance.

"(2) It is immaterial whether this water is contained in the moist cellulose nitrate, or previously added to the solvent."

G. Lunge and J. Bebie[3] determined how far the mixture of ether (0.720) and alcohol (0.810) might be varied from the usual proportion of three to one.

"A cellulose nitrate of 11.54% nitrogen dissolved easily in ether-alcohol six to one, only 95% dissolving in nine parts ether to one of alcohol, and only 7.3% in twenty-seven parts of ether to one of alcohol.

In the other direction, one-third of ether to one part of alcohol acted as a complete solvent. One sixth ether to one part of alcohol dissolved only 93%.

---

[1] Worden: "Technology of Cellulose Esters", 1, III, 2291; Chem. Abs., 8, 1669 (1914)
[2] J. Chem. Soc., 104 I, 18 (1913).
[3] Z. angew. Chem., 14, 538 (1901); J. Am. Chem. Soc., 25, 568 (1901).

From this, one sees that a decrease of the ether content has less effect on the solubility of the cellulose nitrate than that of the alcohol, and also that the more important rôle of the solution must be ascribed to the alcohol. Thus the solubility may vary in wide limits from the usual proportion of 3 : 1."

Bancroft[1] states that in a number of cases, mixed solvents will peptize a solid much better than either solvent alone; cellulose nitrate in ether-alcohol being a good example.

He also says[2] that "cellulose nitrate swells in alcohol and not in ether, but it is not known whether this is universal nor whether the alcohol peptizes the cellulose nitrate at higher temperatures."

## Purpose

The purpose of this thesis is to determine whether either ethyl alcohol or ethyl ether peptizes pyroxylin, and if so, why the mixture peptizes the pyroxylin better than either the alcohol or the ether.

## Experimental

*Materials*

The pyroxylin was made by the E. I. duPont de Nemours and Company. It is used in making collodion and consequently the commercial name is "Collodion Cotton."

The nitrogen content of the pyroxylin was found to be 12.1%, using a Dennis improved nitrometer.

The absolute alcohol was made by the United States Industrial Chemical Company; using an alcoholmeter, the alcohol tested 99.8% at 15°C.

The ether was made by Kahlbaum. It was acetone-free and had been distilled over sodium. It was kept in a glass-stoppered bottle in contact with metallic sodium.

*Preliminary Experiments*

According to the Pharmacopeias,[3] pyroxylin is slowly but completely soluble in twenty-five parts of a mixture of three parts ethyl ether, one part ethyl alcohol.

In making up this solution 62.5 gm. of absolute alcohol was added to 10 gm. of pyroxylin, and 187.5 gm. of anhydrous ether was then added.

In order to determine whether the alcohol or the ether is the peptizing agent, five cubic centimeter samples of the solution were taken at the start. To one set an excess of alcohol was added slowly and to the other an excess of ether as shown by Table III:

---

[1] Bancroft: "Applied Colloid Chemistry", 167 (1921).
[2] By private communication from Professor Chamot.
[3] Worden: "Technology of Cellulose Esters", 1, III, 1696.

TABLE III

| Sample No. | Volume Pyroxylin in Ether-Alcohol | Volume Alcohol added |
|---|---|---|
| 1 | 5 cc | 1 cc |
| 2 | 5 cc | 2 cc |
| 3 | 5 cc | 3 cc |
| 4 | 5 cc | 4 cc |
| 5 | 5 cc | 5 cc |
| 6 | 5 cc | 8 cc |
| 7 | 5 cc | 12 cc |
| 8 | 5 cc | 15 cc |
| 9 | 5 cc | 20 cc |
| 10 | 5 cc | 125 cc |
| | | Volume of Ether added |
| 11 | 5 cc | 1 cc |
| 12 | 5 cc | 2 cc |
| 13 | 5 cc | 3 cc |
| 14 | 5 cc | 4 cc |
| 15 | 5 cc | 5 cc |
| 16 | 5 cc | 6 cc |

The addition of the alcohol had no effect on the colloidal pyroxylin except as a diluent.

Sample No. 10 containing 25 parts of alcohol to one part of the colloidal solution was distilled to less than half of the original volume in order to remove all traces of ether, and the colloidal pyroxylin remained unchanged.

On adding ether, however, the results were quite different. For samples No. 11, 12, 13, no change was apparent, but sample No. 14 turned cloudy.

On the addition of an equal volume of ether to the original volume of the colloid, the sample began to coagulate; in sample No. 16 complete coagulation was obtained.

This would tend to prove that ether has no effect on the peptization of the pyroxylin; while alcohol should peptize it at some temperature because it swells in alcohol at room temperature.

If the pyroxylin is peptized at high temperatures, the peptization is due to the dissociated alcohol, whereas, if the pyroxylin is peptized at low temperatures, the peptization is due to associated alcohol. In either case the peptization will be due to adsorbed alcohol, the adsorbed film distintegrating the pyroxylin so that a colloidal solution results. When[1] a liquid is adsorbed by a solid, it will tend to peptize it and in some cases will do so. At higher temperatures the peptizing action increases.

Mardles[2] states that "although a liquid may be a non-solvent of a cellulose ester, at temperatures at and below its boiling point at atmospheric pressure, it often happens, for example with alcohol, benzene, methyl ketone, for cellu-

[1] Bancroft: "Applied Colloid Chemistry". 167 (1921).
[2] J. Phys. Chem., 30, 348 (1926); J. Soc. Chem. Ind. 42, 128T (1926).

lose acetate that it becomes a solvent at higher temperatures. Anhydrous alcohol becomes a solvent for a particular sample of cellulose acetate at 120° C and industrial at 100°C. Thus alcohol cannot be considered merely a diluent, since in mixtures, especially when dissociated, it must contribute greatly to the solvent action."

In order to determine the effect of high temperatures on the peptization of pyroxylin by the ethyl alcohol; samples weighing 0.1 and 0.01 gm. respectively, were placed in 5 cc of ethyl alcohol in pyrex tubes, the alcohol frozen in liquid air, suction applied and the tubes sealed. The tubes were heated in an asbestos box using 220 watt lamps as the heating medium, the thermometer being placed beside the tube.

The temperature was slowly raised, the tubes being removed and thoroughly shaken every 15°-20° C. rise in temperature.

Between 155° and 165° C. two of the tubes exploded. There had been no apparent change below 155° C.

Two other samples were heated to 145° C. for over an hour with thorough shaking every ten minutes with no apparent peptization in either case.

L. E. Smith,[1] in McBain's laboratory, "sealed nitrocotton and alcohol in a glass tube and heated to 100° C. for two or three hours, but no gelatinization appeared to take place in this time. The tube was then heated at 120° for upwards of 12 hours and at the end of that time most of the nitrocotton had dissolved leaving a slight residue. The solution obtained was yellow and very mobile even when 10% of nitrocotton had gone into solution. Alcohol containing varying amounts of water also dissolved nitrocotton, but the greater the proportion of water the greater the amount of residue, and the darker the solution."

Smith says: "It is obvious that this solvent action is not due to unchanged alcohol alone, but partly to the products obtained by the nitration of the alcohol by the nitrocotton. The solution smelled strongly of esters. The residue was probably nitrocotton but this has not been tested."

In view of the fact that the alcohol and cellulose nitrate were heated at 120° for upwards of twelve hours before solution was obtained while heating at 100° for two or three hours, or at 145° for over one hour had no effect, it would seem that a chemical reaction had taken place. This also would be indicated by the yellow solution, the smell of esters, and by the fact that a mobile solution was obtained even when 10% of the cellulose nitrate had gone into solution. The cellulose nitrate might be peptized by the ethyl nitrate formed; the ethyl nitrate might polymerize the ethyl alcohol which in turn would peptize the pyroxylin or a cellulose nitrate with a lower nitrogen content and soluble in ethyl alcohol might be formed in the chemical reaction.

I. N. Kugelmass[2] made a study of solutions of cellulose nitrate in alcohol, in ether, and in a mixture of the two. At room temperature neither ether nor alcohol peptized the pyroxylin. At lower temperatures, however, using car-

[1] J. Phys. Chem., 30, 348 (1926).
[2] Rec. Trav. chim., 41, 751 (1922).

bon dioxide snow and ether as the cooling medium, he obtained a colloid in ether which analyzed 13.75 nitrogen: and one in alcohol, which analyzed 14.02 nitrogen, while the original pyroxylin only analyzed 11.9 nitrogen.

According to these results, Kugelmass must have worked with a mixture of cellulose nitrates, some of high and some of low nitrogen content. The more highly nitrated cotton was peptized, leaving a residue of cellulose nitrate of low nitrogen content.

Kugelmass found that the pyroxylin-ether system formed suspensoids which gave a blue opalescence; with the pyroxylin-alcohol, he observed a series of distinctly separate layers. With regard to the peptization and protection of collulose nitrate in ether, he says: "The dissolved cellulose nitrate reduces the superficial surface tension of the same cellulose nitrate and, as a result, it is strongly adsorbed. The effect of the adsorption is to produce a more advanced reduction in the superficial tension, thereby diminishing the tendency of the particles of cellulose nitrate to unite."

It has already been shown that the addition of ether will precipitate cellulose nitrate from colloidal solution in ether-alcohol. In attempting to confirm the observations made by Kugelmass, the usual ratio of one part pyroxylin to twenty-five parts of solvent was used.

Anhydrous ether will not peptize pyroxylin at room temperature. To determine whether the ether would peptize the pyroxylin at low temperatures or not, 0.288 gm. of pyroxylin and 10 cc of anhydrous other were cooled in carbon dioxide snow and ether. The pyroxylin remained unaffected even after alternate shaking and cooling for several hours. In order to be certain that the temperature was low enough, the mixture was cooled in liquid air with no apparent result.

L. E. Smith[1] tested ether to see if it exerted a solvent action on cellulose nitrate at low temperatures. A sample of ether which was in contact with cellulose nitrate for eighteen months, showed that it had dissolved 0.004.

He could not confirm the results and observations of Kugelmass that ether at low temperatures dissolves cellulose nitrate forming suspensoids showing a blue opalescence, and a series of distinctly separate layers in alcohol. The results of our experiments agree with Smith's results and this tends to corroborate the statement that Kugelmass worked with a mixture of cellulose nitrates.

In determining the effect of lower temperatures on the peptization of pyroxylin by absolute alcohol alone, the same proportions of one part pyroxylin to twenty-five parts of solvent were used. 0.317 gm. of pyroxylin and 10 cc. (7.925 gm.) of absolute alcohol were cooled in carbon dioxide without apparent change. This solution, being 4% cellulose nitrate, was obviously too concentrated, and 10 cc. more of the absolute alcohol was added, giving a 2% solution.

On cooling with carbon dioxide snow and ether, and after considerable shaking the alcohol began to peptize the pyroxylin. In order to hasten the

[1] J. Phys. Chem., 30, 348 (1926).

action 10 cc. more of the absolute alcohol was added, giving 1.33% cellulose nitrate. After standing at the low temperature for some time, the alcohol completely peptized the pyroxylin.

On warming to room temperature, the sol became viscous. By increasing the temperature to 35° C. for some time, the sol set to a flowing jelly.

Another sol containing 4% pyroxylin completely peptized by alcohol alone, set to a stiff jelly at room temperature. On cooling, the jelly formed a sol and, on warming, went back to a jelly again, showing that this change is reversible.

L. E. Smith[1] carried out the following experiments on the gelatinizing power of alcohol. "It was found that the nitro cotton containing 12.1% nitrogen was soluble at room temperature to the extent of 0.35% in 95% alcohol. Experiments were devised to find the solubility of the same nitro cotton at low temperatures in anhydrous alcohol. The alcohol was thoroughly dried and then distilled into tubes already containing the nitro cotton. Solutions of various concentrations were prepared. The tube containing the smallest quantity of nitro cotton was first cooled in a mixture of solid carbon dioxide and ether: and the nitro cotton formed a solid compact mass which could not be broken up by shaking. The other tubes were well shaken before cooling to prevent this from happening. On cooling, the second tube containing approximately 0.8% nitro cotton the liquid became more viscous and dissolved the nitro cotton, forming a viscous sol which on warming to room temperature set to a flowing jelly or gel. The change from sol to gel was reversible, for, on cooling the gel, it reverted to the sol form. Two other solutions showed the same phenomenon. The gels became more turbid as the concentration of the nitro cotton was increased. The solution containing 5% nitro cotton was a stiff and a very turbid gel. These gels are stable at room temperature and even after a period of 18 months still show the reverse change on cooling. They show the phenomenon of syneresis to a marked degree. It is impossible to measure the actual solubility of nitro cotton under such conditions."

It is apparent then from the results of our experiments and those of L. E. Smith[2] that, despite the statement made by Kugelmass,[3] anhydrous ether, free from alcohol and acetone, has no apparent peptizing effect on pyroxylin. Absolute alcohol will cause pyroxylin to swell but will not peptize it at room temperatures or at higher temperatures.

From the experiments of Ramsay and J. Shields[4] we know that ethyl alcohol is polymerized as liquid, the degree of polymerization increasing with falling temperature.

When a sample of pyroxylin in alcohol is cooled for some time in carbon dioxide snow and ether shaking every few minutes, it is not completely peptized immediately, as the low temperature does not polymerize all of the alcohol

[1] J. Phys. Chem., 30, 347 (1926).
[2] J. Phys. Chem., 30, 347 (1926).
[3] Rec. Trav. chim., 41, 751 (1922).
[4] Phil. Trans., 184 A, 647-673 (1893).

and swelling precedes peptization. The best results are obtained by cooling, shaking as the alcohol warms up to room temperature, and repeating two or three times.

Alcohol polymerizes as the temperature is lowered, and it would seem that the lower the temperature, the greater the peptization. However, if liquid air is substituted for carbon dioxide snow and ether, the alcohol freezes, but the peptization is not enhanced. The reason why warming to room temperature gives better results is not as yet clear; but it is probable that the same results would be obtained if the alcohol could be vigorously shaken at the lower temperature.

According to L. E. Smith[1] there are very few instances of a gel formed from a sol on heating and re-forming the sol on cooling. Szegvari[2] thought he had discovered the first one; namely, nitrocotton dissolved in a mixture of amyl acetate and benzine (not benzene). He said that at a lower temperature the amyl acetate combined with nitrocellulose rather than the benzine, whereas at higher temperatures a compound was formed between amyl acetate and benzine to the exclusion of the former combination.

In the case of absolute alcohol and pyroxylin, the alcohol polymerizes when the temperature is lowered; it is then adsorbed by the pyroxylin. The pyroxylin is completely peptized at this temperature; then, as the temperature is raised, the sol slowly changes to a gel, due to the depolymerization of the alcohol, i. e. the finely divided pyroxylin is suspended throughout the sol or gel.

When pyroxylin is peptized in ether-alcohol mixtures, the ether apparently polymerizes the alcohol, which then peptizes the pyroxylin.

The conclusions from A. Matteoschat's[3] work are summarized as follows:

"(1) The difference in the solubility at different volume relations of the same components of the solvent mixture within relatively small limits of 1 : 1 and 3 : 1 and also by the use of different concentrations of alcohol in the same ratio mixtures is considerable.

(2) The mixture 1 : 1 is only favorable when alcohol of the highest concentration is employed; with technical alcohol better results are obtained with a 2 : 1 and 3 : 1 mixture.

(3) Adding the alcohol and allowing it to thoroughly saturate the cellulose nitrate, before adding the ether, gives a much better result than the direct use of ether-alcohol.

(4) The results of Matteoschat agree with the opinion of Schwalbe as well as Lunge and Bebie, i. e. decrease in alcohol decreases the solubility of nitrocellulose in ether-alcohol, in so far as highly concentrated alcohol is concerned. Yet the increase of alcohol above the 1 : 1 ratio does not increase the solubility, but lowers it."

Applying the theory of polymerization:

(1) An excess of ether polymerizes more of the alcohol, and also acts as a diluent.

---

[1] J. Phys. Chem., 30, 349 (1926).
[2] Kolloid-Z., 34, 34 (1924).
[3] Worden: "Technology of Cellulose Esters", 1, III, 2292.

(2) Water tends to depolymerize the alcohol and requires more ether to counteract this tendency.

(3) When the alcohol is added first, the ether polymerizes the alcohol already on the pyroxylin and gives complete peptization in a shorter time.

(4) Decreasing the alcohol should have the same effect that increasing the ether has, provided the solution was not already saturated with cellulose nitrate, in which case the solubility would decrease.

Pyroxylin is peptized very readily by acetone and by methyl alcohol at room temperature. It is not peptized by a mixture of alcohol and benzene either in hot water or in carbon dixoide snow and ether.

Cellulose acetate is not affected by ether-alcohol mixtures. Absolute alcohol does not peptize it either in carbon dioxide snow or in water bath. It is readily peptized, however, by acetone. A mixture of absolute alcohol and tetrachloroethane will peptize cellulose acetate after long heating in a water bath. On cooling the cellulose acetate precipitates, on warming it is again peptized, showing the change is reversible.

Cellulose acetate gives a jelly in tetrachloroethane after heating in a water bath for two or three days. If the heating is continued for twice this period, a very viscous mass is obtained.

## Conclusions

As a result of these experiments, the following conclusions are drawn:

(1) Pyroxylin is not peptized by anhydrous ether at any temperature.
(2) It is peptized by absolute alcohol at low temperatures.
(3) The peptization is due to the adsorption of polymerized alcohol.
(4) The alcohol is polymerized in ether-alcohol mixtures by the ether.

The author wishes to take this opportunity to thank Professor W. D. Bancroft, who suggested this problem, and under whose direction the work, was carried out.

*Cornell University.*

# ACTION OF NITRIC ACID ON METALS IN PRESENCE OF CATALYSTS

BY C. C. PALIT AND N. R. DHAR

In a previous paper[1] we have shown that if we start with dilute nitric acid and mercury at the ordinary temperature, we always get crystals of mercurous nitrite after some hours. Moreover we have established that the maximum yield of mercurous nitrite is obtained when nitric acid of 26% concentration reacts with mercury at a temperature of 30°. We have also observed that ferric nitrate is a retarder in the action of nitric acid and mercury, though we have observed that ferrous sulphate accelerates the reaction between mercury and nitric acid. We also have observed an interesting fact that, though the amount of mercury dissolved in dilute nitric acid in presence of ferric nitrate is less than in its absence, we have in all our experiments with nitric acid of 26% concentration, got much larger quantities of mercurous nitrite formed in presence of ferric nitrate than in its absence. This observation contradicts the previous observation of Rây[2] who stated that in presence of ferric salts no crystal of mercurous nitrate is obtained in four hours. We also have observed that in presence of mercurous nitrate, the yield of mercurous nitrite is much greater than in its absence.

In this paper we have investigated the influence of various nitrates on the formation of mercurous nitrite by the action of nitric acid on mercury. The amount of mercury taken in each case was approximately 17.4 grms. in a

TABLE I

Formation of crystals of mercurous nitrite in presence of various nitrate solutions of practically equivalent strength.

Volume of $HNO_3$ = 25 c.c. of 26%. Reaction = 24 hours. Temp. = 28°C.

| No. of experiment | Name of nitrate solution added as catalyst | Amount of nitrate in grm. in 1 c.c. of the solution taken | Amount of mercurous nitrate formed in grm. |
|---|---|---|---|
| 1 | Blank | ——— | 0.95 |
| 2 | Mercurous Nitrate | 0.5000 | 3.00 |
| 3 | Ferric Nitrate | 0.0142 | 2.95 |
| | | Trace (one drop only) | |
| 4 | Do Do | | 2.60 |
| 5 | Manganous Nitrate | 0.0157 | 2.93 |
| 6 | Nickel Nitrate | 0.0250 | 2.03 |
| 7 | Uranium Nitrate | 0.0340 | 1.42 |
| 8 | Chromium Nitrate | 0.0140 | 1.20 |
| 9 | Cobalt Nitrate | 0.0250 | 1.18 |
| 10 | Copper Nitrate | 0.0164 | 1.06 |

[1] Z. anorg. Chem., 134, 191 (1924).
[2] J. Chem. Soc., 99, 1012 (1911).

beaker and one cubic centimetre of approximately equivalent solutions of various nitrates was first added to the mercury and then 25 c.c. of nitric acid of 26% concentration were added. The reaction was allowed to continue for 24 hours, the temperature being 28°. The results obtained are given in Table I.

The order of efficiency of the various nitrates is the following:—

Mercurous nitrate > Ferric nitrate > Manganous nitrate > Nickel nitrate > Uranium nitrate > Chromium nitrate > Cobalt nitrate > Copper nitrate.

It seems probable that the decomposition of mercurous nitrite according to the equation $Hg_2(NO_2)_2 \rightleftarrows Hg(NO_2)_2 + Hg$ is retarded by the presence of substances like ferric nitrate, nickelous nitrate, manganous nitrate etc., and hence in their presence the yield of mercurous nitrite is greater than in their absence.

In a foregoing paper[1], it has been proved that ferric salts can be reduced to the ferrous state by nitric oxide. Moreover ferric salts are also reduced by metallic mercury. Consequently the added ferric nitrate becomes ferrous nitrate which in its turn possibly reduces the mercuric nitrite into the mercurous state and thus the concentration of mercurous nitrite in the solution is increased. It seems probable that manganous nitrate, nickelous nitrate, etc., are also capable of reducing the mercuric nitrite to the mercurous state and hence the yield of mercurous nitrite is greater in their presence than in their absence.

In a previous paper[2], the following remarks were made:—

"It seems certain that nitric acid is at first reduced to nitrous acid by the action of metals like bismuth, mercury, copper and silver and ferrous sulphate, sugar, and other substances".

In this paper, we have made further experiments on the reaction of nitric acid on metals in order to find out whether nitrous acid is a product of the reaction between the different substances and nitric acid. The results are given in Table II.

In experiments with silver, lead and bismuth, crystals of nitrates were deposited after 48 hours. In case of tellurium, a grey deposit of telluric acid was formed. In experiments with arsenic and antimony, a white deposit of $As_2O_3$ and $Sb_2O_3$ was formed. After 3 hours each of the above solutions was tested colorimetrically for the amount of nitrous acid present. For this, equal volumes (2 c.c.) of each of the solutions were taken and then to each of them 2 c.c. of 5% solution of potassium iodide and 1 c.c. of starch solution were added to liberate iodine. The intensity of the colour developed was now compared and it was found that the amount of nitrous acid liberated was in the following order:—

Fe > Cu > Cd > Ag > Zn > Co > Ni > Mn > Al > Pb > As > Sb > Bi > Te > Se.

---

[1] Proc. Akad. Wet. Amsterdam, 28, 545 (1919).

[2] J. Phys. Chem., 29, 142 (1925).

## TABLE II

### Volume of $HNO_3$ added = 20 c.c. Temperature = ordinary.

| No. of expt. | Name of elements used in the experiment | Strength of nitric acid used in per cent. three hours | Nature of chemical reaction during first hours of the reaction | Presence of nitrous acid during the first three | Presence of nitrous acid after 24 hours of the reaction | Amount of the element dissolved in 24 hours |
|---|---|---|---|---|---|---|
| 1(a) | Silver | 13 | Very slow | Slight | Nil | Complete |
| (b) | do | 26 | Quick | Copious | do | do |
| 2(a) | Lead | 13 | Very slight | Slight | do | Slight |
| (b) | do | 26 | Slight | do | do | do |
| 3(a) | Cadmium | 13 | Vigorous | Copious | do | Complete |
| (b) | do | 26 | do | do | do | do |
| 4(a) | Bismuth | 13 | Very slow | Slight | do | Slight |
| (b) | do | 26 | Slow | do | do | do |
| 5(a) | Aluminium | 13 | No action | Nil | Slight | Slight |
| (b) | do | 26 | Very slight | Very slight | Copious | Fair |
| 6(a) | Zinc | 13 | Quick | Copious | Nil | Complete |
| (b) | do | 26 | Vigorous | do | do | do |
| 7(a) | Cobalt | 13 | Quick | do | do | do |
| (b) | do | 26 | Vigorous | do | do | do |
| 8(a) | Nickel | 13 | Quick | do | do | do |
| (b) | do | 26 | Vigorous | do | do | do |
| 9(a) | Manganese | 13 | Quick | do | do | do |
| (b) | do | 26 | do | do | do | do |
| 10(a) | Copper | 13 | Slow | Copious | Slight | do |
| (b) | do | 26 | Quick | do | do | do |
| 11(a) | Iron | 13 | do | do | Fair | do |
| (b) | do | 26 | Vigorous | do | do | do |
| 12(a) | Chromium | 13 | No action | Nil | Nil | Nil |
| (b) | do | 26 | do | do | do | do |
| 13(a) | Sulphur | 13 | do | do | do | do |
| (b) | do | 26 | do | do | do | do |
| 14(a) | Selenium | 13 | do | do | do | do |
| (b) | do | 26 | Very slight | Very slight | do | Very slight |
| 15(a) | Tellurium | 13 | do | do | Very slight | Slight |
| (b) | do | 26 | Slow | Slight | Slight | Fair |
| 16(a) | Arsenic | 13 | Very slight | do | do | do |
| (b) | do | 26 | Slow | Copious | Fair | do |
| 17(a) | Antimony | 13 | No action | Nil | Slight | Slight |
| (b) | do | 26 | Slow | Slight | Very slight | do |

In case of sulphur and chromium, no colour developed showing the absence of nitrous acid. Consequently the above experiments conclusively prove that in all cases nitrous acid is the first product between the reaction of the elements and nitric acid and the above experiments confirm our view that nitrous acid is the primary product of the reaction between nitric acid and the metals.

In several papers[1] published from these laboratories, we have shown that slow oxidation of substances like sodium sulphite, ferrous hydroxide, phosphorus etc., is markedly retarded by the presence of reducing agents like sugar,[2] sodium arsenite, and organic substances. Moreover in a previous paper it has been shown that substances like tartaric acid, urea, ether, acetic anhydride, benzoic anhydride, etc., retard the action of nitric acid on copper whilst substances like strychnine sulphate, phthalic anhydride, arsenious oxide, carbon tetrachloride, etc., accelerate the reaction between nitric acid and copper. We have made further experiments on the action of nitric acid on copper and mercury in presence of reducing agents and the experimental results are given in Table III.

TABLE III

Volume of $HNO_3$ = 20 c.c. of 26%. Volume of reducing agent = 5 c.c.
Reaction = 4 hrs.

| No. of experiment | Substance used as reducing agent | Strength of reducing agent | Total volume of the solution in c.c. | Amount of copper dissolved in grm. at a temperature of 24°C | Amount of copper dissolved in grm. at a temperature of 20°C | Amount of mercury dissolved in grm at 20°C | Amount of mercurous nitrate formed in 20°C |
|---|---|---|---|---|---|---|---|
| 1 | Blank | ——— | 25 | 0.6464 | 0.3146 | 4.6924 | 0.52 |
| 2 | Tartaric Acid | Molar solution | do | 0.3588 | 0.2324 | 4.6880 | 0.42 |
| 3 | Citric Acid | do | do | 0.2804 | 0.2718 | 4.1858 | 0.43 |
| 4 | Glucose | do | do | 0.2402 | 0.1168 | 4.3510 | 0.48 |
| 5 | Formic Acid | do | do | 0.2270 | 0.1486 | 4.8640 | 0.46 |
| 6 | Cane Sugar | do | do | 0.1646 | 0.0892 | 4.5118 | 0.37 |
| 7 | Glycerine | do | do | 0.0876 | 0.0816 | 4.2024 | 0.28 |
| 8 | Oxalic Acid | do | do | 0.0058 | 0.0028 | 0.9780 | 0.00 |

In each of the above experiments the volume of nitric acid used was 20 c.c. of 26% concentration and the volume of the reducing agent added was 5 c.c. the total volume being 25 c.c. In the blank experiment only 5 c.c. of distilled water were added to make the total volume 25 c.c. The duration of reaction was 4 hours.

It will be seen from Table III that all the reducing agents used in our experiments, namely tartaric acid, citric acid, formic acid, oxalic acid, glycerine, glucose and cane sugar, act as marked retarders in the reaction between nitric acid on copper or mercury and the order of the retarding action is the following:—

In the case of copper at 24°C, tartaric acid > citric acid > glucose > formic acid > cane sugar > glycerine > oxalic acid and at 20°C, citric acid > tartaric acid > formic acid > glucose > cane sugar > glycerine > oxalic acid.

In the case of mercury at 20°C, formic acid > tartaric acid > cane sugar > glucose > glycerine > citric acid > oxalic acid.

[1] J. Chem. Soc., 111, 707 (1917); Proc.Akad. Wet. Amsterdam, 23, 1074 (1921); Trans. Faraday. Soc., 14, 1, 17 (1922).
[2] Dhar: loc. cit.

In the reaction between nitric acid and mercury, formic acid acts as an accelerator. In the case of oxalic acid, precipitates of cupric oxalate and mercurous oxalate are formed which cover the metals and protect them from further action. That is why oxalic acid is such a great retarder. The yield of mercurous nitrite was very small in these cases, though the amount of mercury dissolved was fairly large in several cases. It seems probable that the organic substances like tartaric acid, citric acid, glycerine, etc., combine and form complex ions with mercurous nitrite and mercuric nitrite. Many complex ions containing mercury are well known. The retarding action of these substances is probably associated with their reaction on the active substance, viz. nitrous acid. The nitrous acid which is formed by the action of copper or mercury on nitric acid is possibly partially destroyed by its reaction on the reducing agents like tartaric acid, citric acid, glycerol etc.

It is well known that sulphur compounds retard the slow oxidation of phosphorus. Recently Moureu and Dufraisse[1] have shown that many sulphur compounds retard several oxidation reactions. Now in order to find out whether the sulphur compounds retard the oxidation of copper and mercury by nitric acid, we have investigated the influence of various sulphur compounds on this reaction. The experimental results are given in Table IV.

TABLE IV

i) volume of $HNO_3$ = 20 c.c.
ii) " " = 15 c.c.
} of 26%

i) volume of sulphur compd = 5 c.c.
ii) " " " = 10 c.c.
} of 1%.

Total volume = 25 c.c.
Reaction = 4 hours.

| No. of experiment | Name of Sulphur compound used | Strength of sulphur compound | Amount of copper dissolved in grm. in presence of sulphur compound taken | | Amount of mercury dissolved in grm. in presence of sulphur compound taken | | Amount of mercurous nitrite formed in grm. in presence of sulphur compound taken. | |
|---|---|---|---|---|---|---|---|---|
| | | | 5 c.c. | 10 c.c. | 5 c.c. | 10 c.c. | 10 c.c. | 10c. |
| 1 | Blank | —— | 0.6430 | 0.0908 | 6.0616 | 3.6834 | 0.12 | 0.09 |
| 2 | Sodium-β-naphthalene sulphonate | 1.0% | 0.6948 | 0.0844 | 3.4578 | 0.0994 | 0.00 | 0.00 |
| 3 | Sulphonal | do | 0.6894 | 0.0722 | 5.3394 | 3.1960 | do | do |
| 4 | Sodium-anthraquinone sulphonate | do | 0.6880 | 0.0852 | 6.4320 | 0.8694 | do | do |
| 5 | Sodium-benzene sulphonate | do | 0.6620 | 0.0772 | 6.5534 | 3.3126 | 0.25 | do |
| 6 | Thio-urea | do | 0.6570 | 0.0476 | 0.0036 | 0.0012 | 0.00 | do |
| 7 | Sodium-β-naphthalene sulphonate | do | 0.5954 | 0.0712 | 6.7012 | 3.5060 | 0.24 | do |
| 8 | Sulphanilic Acid | do | 0.0196 | 0.0136 | 3.1306 | 0.0056 | 0.00 | do |

In each of the above experiments, 20 c.c. of nitric acid of 26% concentration and 5 c.c. of the solution of the sulphur compound were used in one set

[1] Compt. rend., 178, 824, 1397, 1862; 179, 237 (1924).

and 15 c.c. of nitric acid of the same concentration and 10 c.c. of the sulphur compound were used in the other set so that the total volume in each case being 25 c.c. In the blank experiment, only 5 c.c. or 10 c.c. of distilled water were added to 20 c.c. or 15 c.c. of nitric acid to make the total volume 25 c.c. The duration of reaction was 4 hours at 24°C.

The experimental results on the reaction of nitric acid on copper show that small quantities of sodium-$\beta$-naphthalene sulphonate, sulphonal, sodium-anthraquinone sulphonate, sodium benzene sulphonate and thiourea appreciably accelerate the reaction whilst sodium-$\alpha$-naphthalene sulphonate is a weak and sulphanilic acid a powerful retarder. When the concentration of the sulphur compounds is doubled, all of them are retarders. With mercury and nitric acid, small quantities of sodium-$\alpha$-naphthalene sulphonate, sodium-benzene sulphonate, and sodium-anthraquinone sulphonate are accelerators whilst sulphonal, sodium-$\beta$-naphthalene sulphonate, sulphanilic acid and thiourea are retarders. When the quantity of sulphur compounds is doubled, all of them in this case as well are retarders. The yield of mercurous nitrite by the action of mercury and nitric acid in presence of these sulphur compounds is in many cases nil and in others very small. It seems very probable that this is due to the fact that complex substances are formed between mercuric and mercurous ions and the sulphur compounds. It is well known that sulphur compounds have a great affinity for mercury compounds and many stable complex ions containing sulphur and mercury are known. The retarding effect of these sulphur compounds, when stronger solutions are used, is most probably caused by their action on the active substance namely the nitrous acid which is partly destroyed by its reaction on the sulphur compounds. Now some of the sulphur compounds in small quantities act as a feeble accelerator in the action of copper or mercury on nitric acid. It is quite probable that small quantities of these substances would act on the nitric acid and generate nitrous acid which would accelerate the chemical change. Consequently it is probable that two opposing reactions are taking place in the solution, viz. (1) the formation of nitrous acid by the reducing action of the sulphur compounds on nitric acid and (2) the removal of nitrous acid by their reaction on the sulphur compounds. Now at such concentrations of the sulphur compounds, when the first action predominates over the second, we are likely to get acceleration whilst when the second reaction counter-balances the first we get retardation. There is another factor which might lead to retardation and that is the adsorption of the sulphur compounds on the surface of the metals. Copper and mercury have a great affinity for sulphur compounds and it is probable that some of the sulphur compounds would be adsorbed and be deposited on the surface of the metals and would partilly prevent or retard the reaction between the metals and nitric acid. Moreover the amount of adsorption will be greater, the greater the concentration of the sulphur compounds.

Conroy[1] found that arsenious acid retards the action of iron and hydrochloric acid but we have found that the action of copper and nitric acid is accelerated by arsenious acid. The accelerating effect is caused by the reduction of nitric acid to nitrous acid by the presence of arsenious acid. In this investigation we have studied the influence of ten alkaloids on the reaction between nitric acid and copper or mercury. The experimental results are given in Table V.

TABLE V

i) volume of $HNO_3$ = 20 c.c.
ii) " " = 15 c.c. } of 26%

i) volume of alkaloid = 5 c.c.
ii) " " = 10 c.c. } of 1%

Total volume = 25 c.c. Reaction = 4 hours

| No. of experiment | Name of substance (alkaloid) used | Strength of the substance (alkaloid) | Amount of copper dissolved in grm. in presence of alkaloid taken | | Amount of mercury dissolved in grm. in presence of alkaloid taken | | Amount of mercurous nitrite formed in presence taken | |
|---|---|---|---|---|---|---|---|---|
| | | | 5 c.c. | 10 c.c. | 5 c.c. | 10 c.c. | 5 c.c. | 10 c.c. |
| 1 | Blank | —— | 0.5280 | 0.1078 | 4.6976 | 2.4190 | 0.48 | Nil |
| 2 | Narcoline | 1.0% | 0.6524 | 0.1172 | 6.0714 | 2.5744 | Nil | do |
| 3 | Strychnine | do | 0.6252 | 0.2152 | 6.0020 | 2.7200 | do | do |
| 4 | Quinidine Sulphate | do | 0.6156 | 0.1216 | 5.6986 | 1.9698 | 0.46 | do |
| 5 | Quinine Sulphate | do | 0.6070 | 0.1114 | 6.0644 | 1.9014 | 0.07 | do |
| 6 | Cinchonine | do | 0.6050 | 0.0664 | 5.8850 | 2.4174 | 0.15 | do |
| 7 | Morphine Hydrochlor. | do | 0.5704 | 0.1184 | 5.8356 | 2.7612 | Nil | do |
| 8 | Brucine | do | 0.5682 | 0.1115 | 5.7656 | 2.9720 | 0.05 | do |
| 9 | Caffeine | do | 0.5592 | 0.0568 | 6.7682 | 2.3772 | 0.10 | do |
| 10 | Cocaine Hydrochlor. | do | 0.2366 | 0.0616 | 5.8698 | 0.0538 | Nil | do |

In case of the above experiments, 20 c.c. of nitric acid of 26% concentration and 5 c.c. of the solution of alkaloid were used in one set and 15 c.c. of nitric acid of the same concentration and 10 c.c. of the solution of the alkaloid were used in the other set, so that the total volume in each case being 25 c.c. In making the solutions of the alkaloids, each of them was dissolved in 5 c.c. of nitric acid of 20% concentration and the solution was made up to 100 c.c. Also 5 c.c. of the same nitric acid of 20% were made up to 100 c.c. with distilled water and this solution was used in the case of the blank experiment. In the blank experiment only 5 c.c. or 10 c.c. of the above dilute nitric acid were added to 20 c.c. or 15 c.c. of nitric acid of 26% concentration to make the total volume 25 c.c. The duration of reaction was 4 hours at 21°C.

From the above experimental results it will be observed that in the reaction between nitric acid and copper, narcotine, strychnine, quinidine sulphate, quinine sulphate, cinchonine, morphine hydrochloride, brucine, and caffeine act as feeble accelerators whilst cocaine hydrochloride is the only retarder, when small quantities of these substances are added. When the concentration of these alkaloids is doubled, cinchonine, cocaine hydrochloride,

[1] J. Soc. Chem. Ind., 20, 316 (1901).

and caffeine are retarders whilst the others are accelerators. In presence of small quantities of all the above alkaloids, the reaction between mercury and nitric acid is accelerated, whilst the concentration of the alkaloids is doubled, cinchonine, caffeine, quinidine sulphate and quinine sulphate act as feeble retarders whilst cocaine hydrochloride acts as a marked retarder, the other alkaloids remaining accelerators. In the case of cocaine hydrochloride copious precipitate was obtained due to the reaction between cocaine and mercuric and mercurous salts in the solution. The explanation of the accelerating and the retarding effects of these alkaloids is probably the same as that advanced in the case of sulphur compounds. In a recent paper, Rane and Mata Prasad[1] have shown that alkaloids retard the reaction between iron and hydrochloric acid.

We have also investigated the influence of sunlight on the reaction between nitric acid and copper and mercury. In a previous paper[2] it has been shown that most chemical reactions are accelerated by sunlight and the data in Table VI show that the action of nitric acid on copper or mercury is highly accelerated by sunlight:—

TABLE VI

i) Temperature inside the room = 20°C Reaction = 4 hours
ii) " in sunlight = 31°C Strength of $HNO_3$ = 26%

| No. of experiment | Substance used in the experiment | Volume of nitric acid added in c.c. of 26% concentration | Volume of distilled water added in c.c. | Total volume in c.c. | Amount of substance dissolved in grm. in 4 hours inside the room in diffused light at a temperature of | | Amount of substance dissolved in grm. in 4 hours in sunlight, the temperature of which being 31°c | Amount of mercurous nitrite formed in grm. | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | in diffused light inside the room at a temperature of | | in sunlight at a temperature of 31°c |
| | | | | | 20°C | 31°C | | 20°c | 31°c | |
| 1 | Copper | 20 | 5 | 25 | 0.3146 | 0.6802 | 0.8158 | —— | —— | —— |
| 2 | Mercury | do | do | do | 4.6924 | 6.5242 | 7.3674 | 0.52 | 0.65 | 0.63 |

## Summary

1. Maximum yield of mercurous nitrite is obtained with nitric acid of 26% concentration at a temperature of 30°C.

2. When approximately equivalent solutions of various nitrates are added in the reaction between nitric acid and mercury, the amount of mercurous nitrite is greatly influenced by their presence. The order of their efficiency is the following:—

Mercurous nitrate > ferric nitrate > manganous nitrate > nickel nitrate > uranium nitrate > chromium nitrate > cobalt nitrate > copper nitrate.

[1] J. Phys. Chem. 29, 249 (1925).
[2] Proc. Akad. Wet. Amsterdam, 24, 1324 (1916).

3. When nitric acid reacts with an element, nitrous acid is the primary product of the reaction. No nitrous acid is formed when no reaction takes place between the element and the nitric acid.

4. In the reaction between nitric acid and copper, reducing agents like tartaric acid, citric acid, formic acid, oxalic acid, glycerine, glucose, or cane sugar act as marked retarders whilst in the reaction between nitric acid and mercury, all the above reducing agents except formic acid act as marked retarders, formic acid being in this case an accelerator. Also the yield of mercurous nitrite in these cases is very small although the amount of mercury dissolved is fairly large in several cases.

5. Organic sulphur compounds in small concentration act in some cases as accelerators and in others as retarders in the reaction between nitric acid and copper or mercury, whilst in greater concentration, all of them act as retarders. Similar results are obtained when several alkaloids are used instead of the organic sulphur compounds.

6. The reaction between nitric acid and copper or mercury is greatly accelerated in sunlight.

*Chemical Laboratory,*
*Allahabad University,*
*Allahabad.*
*March 30, 1926.*

# A POSSIBLE MECHANISM FOR THE LOWERING OF THE HEAT OF ACTIVATION OF A REACTION BY A CATALYTIC SURFACE

BY ROBERT E. BURK

## Heat of Activation and Reaction Velocity

Much evidence has accumulated in recent years to show that the velocities of homogeneous chemical reactions at different temperatures are in accord with the empirical equation $d \ln k/dT = Q/RT^2$, brought forward by Arrhenius[1] in 1889. 'Q' is the 'heat of activation', which is found to be the amount of energy molecules must possess, in excess of their average energy, in order to react.

Kinetic analyses of several homogeneous bimolecular gas reactions,[2, 3, 4] have greatly clarified the mechanisms of these reactions, and have shown that their rates can be interpreted on the basis of simple thermal activation by collision. This work indicates that for bimolecular reactions, the mechanism of activation cannot depend upon the specific nature of the reactants, and that the rates of bimolecular reactions are governed simply by the availability of their heat of activation, i. e. by the magnitude of 'Q'.

There seems to be considerable justification, therefore, for the view that the rates of chemical reactions are determined by the magnitude of their heats of activation. It would seem to follow then that in order for a catalyst to accelerate a chemical reaction it must in general lower its heat of activation. This view, which would not rule out special effects, such as the assistance of the walls in dissipating the excess energy of the newly formed molecules in reactions of the type $A+B=AB$, nor the effect of the change in the order of the reaction on the surface,[5] appears to be held by various workers[6]. Nevertheless, nothing very definite has been advanced to explain the exact way in which the surface could be expected to lower the heat of activation. Thus H. S. Taylor[7] in the "Fourth Report of the Committee on Contact Catalysis" says that "our knowledge is almost negligible on the nature of the activation process induced in the reactant by its association with the catalyst."

The consensus of opinion seems to be that the attractive force between molecules varies inversely as the eighth or ninth power of their distance apart, as calculated by Debye[8] and others. On this basis Langmuir[9] has calculated that the attractive force of a surface, which enables molecules to be adsorbed, will decrease to half its value in $0.3 \times 10^{-8}$ cms. This is about one seventh

---

[1] Arrhenius: Z. physik. Chem., 4, 226 (1889).
[2] W. C. McC. Lewis: J. Chem. Soc., 113, 471 (1918).
[3] Hinshelwood and Burk: Proc. Roy. Soc., 106 A 284 (1924).
[4] Hinshelwood and Hughes: J. Chem. Soc., 125, 1841 (1924).
[5] Hinshelwood and Prichard: J. Chem. Soc., 127, 1552 (1925).
[6] Constable: Proc. Roy. Soc, 108, 355 (1925).
[7] Taylor: J. Phys. Chem., 30, 145 (1926).
[8] Debye: Physik. Z., 21, 178 (1920).
[9] Langmuir: Trans. Faraday Soc., 17, 610 (1922).

the diameter of the monatomic neon molecule,[1] and therefore probably not much more than this fraction of the diameter of any atom in the molecule adsorbed. The only possible exception would be the hydrogen atom, but it's minimum diameter[2] is $1.0 \times 10^{-8}$. This would mean that adsorption is a very localized matter indeed, and that the attractive force of the surface cannot be very strong at distances greater than the diameter of the atom actually attached in the adsorbed molecule. Therefore, the possibility that the adsorbed *molecule as a whole* may be in a field of force which, acting directly and not through the chain would distort it in virtue of differences in 'polarity' or 'unsaturation' of different parts of the molecule would be ruled out.

Let us consider the thermal decomposition of a molecule A-B. For the decomposition to take place, A and B must be torn apart. If the decomposition is homogeneous and monomolecular the energy necessary to separate A from B is directly the heat of activation, whatever the nature of the bond between A and B. If the decomposition is bimolecular, there must still be a partial separation of A and B at the moment of collision against some sort of attractive forces. The heat of activation per molecule is, however, less in this case. (The writer is aware that one cannot be dogmatic as to just what happens at the moment of collision, but it is difficult to see how something like this can be avoided). Whatever the source of the energy of activation then, the net result is that which would be obtained if A and B were separated by a force sufficiently strong to overcome their mutual attraction. It seems inevitable, therefore, that if one actually does apply a large enough force, the separation of A and B will be accomplished, and if the force is not sufficient to effect the separation completely, it will nevertheless partially separate them and thus diminish the heat of activation.

It is the purpose of the present paper to offer a possible explanation of the mechanism by which the heats of activation can be lowered by catalytic surfaces.

## Outline of the Theory

In view of the extremely short range of molecular attraction, emphasized above, it would seem that a surface could accomplish this partial separation of the atoms A and B in the molecule A-B only if *both atoms* are attached to the surface, and the adsorbing atoms are so spaced that the distance between the points of maximum intensity in their attractive forces is not quite the same as the corresponding distance in the molecule A-B. Adsorption at two or more points under these conditions is the essential feature of the proposed mechanism, and the suggested condition necessary for a surface to lower the heat of activation.

The diagram, Fig. 1., is supposed to represent the spacing in the atoms in the surface of a solid which catalyzes the decomposition of the molecule A-B. An adsorbed atom is represented as connected with the adsorbing surface by a dotted line. According to the theory, both A and B must be attached in

[1] Rankine: Proc. Roy. Soc., 83 A, 516 (1910).
[2] Sommerfeld: "Atomic Structure and Spectral Lines," translated by H. L. Brose. p. 213.

order for the decomposition of A-B to be catalyzed. The figure represents a momentary condition of the surface. There are three effective pairs i. e. 1-6, 3-8 and 5-10. The surface atoms 2, 4, 7, 9, and 11 are 'out of action' through single adsorption. 12 is bare. A short time later, the doubly adsorbed molecules may have decomposed and the products partly evaporated as atoms, or, by combining with others of their kind from adjacent spaces, as molecules. Also, some of the single adsorbed molecules will have evaporated as such, thus offering new surface atom pairs with the proper spacing for effective double adsorption eg. 7-4.

The effectiveness of the surface atom pair in diminishing the heat of activation would depend upon the attractive force of each adsorbing atom for the respective atoms of the adsorbed molecule, and therefore upon the nature of each of the four atoms concerned, and upon the orientation of the surface atoms. The distance apart of the pair of adsorbing surface atoms which would result in the maximum catalytic effectiveness would depend upon the strengths of the adsorbing forces and their rate of decrease with distance, upon the distance apart of the centres of the attractive forces concerned in the adsorbed molecule, and upon the rate of decrease in the heat of activation as the two atoms of the adsorbed molecule are moved relative to each other. In view of the very short range of molecular forces, pairs of surface atoms would be expected to be catalytically active only when their distances apart are very close to the distance of maximum effectiveness. This point is strongly emphasized as it accounts for the extreme variability of some catalytic surfaces. The arguments are equally valid for molecules attached to surfaces at more than two points.

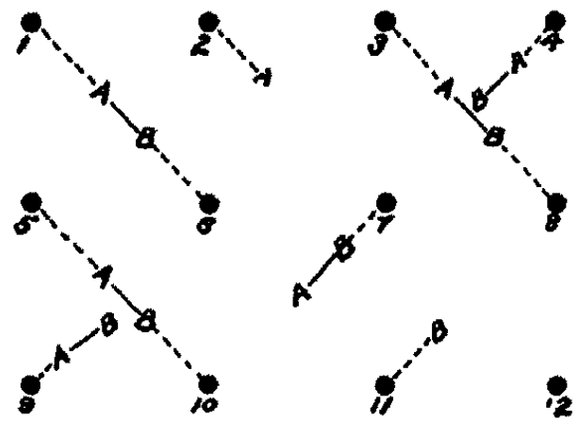


FIG. 1

The remarks of W. C. McC. Lewis[1] at the Faraday Society discussion on catalysis, while they are less definite and are framed in the language of the radiation hypothesis, embody some of the features of the proposed theory.

### Evidence in Favour of the Theory

It is very difficult to subject this theory to a conclusive test. However, *a priori* theoretical considerations as outlined above render it very probable. It is also worthy of note that the multiple adsorption theory is capable of explaining the numerous diverse phenomena of catalytic behaviour in more definite terms than others which have been suggested. Some of these will be briefly discussed.

That a molecule can be attached to a surface by more than one point was suggested by Hinshelwood[2] in connection with experiments on the thermal de-

[1] W. C. McC. Lewis: Trans. Faraday Soc., 17, 662 (1922).
[2] Hinshelwood and Burk: J. Chem. Soc., 127, 1114 (1925).

composition of ammonia, where it was found that the quartz surface as different temperatures showed capricious variability. It was also found in these experiments that added hydrogen sometimes retarded the reaction and sometimes failed to do so.

Adkins[1,2,3,4] has been led by numerous experiments to the conclusion that the spacing of the surface affects the reactivity of the adsorbed molecule, but is not definite as to the exact mechanism by which this is brought about.

Langmuir[5] has also considered the spacing of surface atoms to be capable of affecting the velocities of chemical reactions taking place upon them, but his apparent conception is quite different from that advanced in this paper, and supplements it.

The observation of Gauger and Taylor[6] that the adsorptive capacity of nickel for hydrogen is different at 25° from the value at 305° can be interpreted as evidence for multiple adsorption. The adsorptive capacity of copper for carbon monoxide[7] also varies with temperature. This evidence would be conclusive if the same effects were observed on single faces of crystals composed of one kind of atom only. On whole crystals (crystal powders), a certain number of saturation limits would be expected corresponding to the number of types (strengths) of force fields offered by the individual atoms of the crystal. A definite number of saturation limits would also be expected from the various possible types of multiple and single adsorption. An investigation of the number of saturation limits on crystal powders at different temperatures should therefore furnish convincing data as regards multiple adsorption.

## Promoter Action

Promoter action, which has been one of the least understood of catalytic phenomena, receives a ready interpretation on the basis of multiple adsorption. The proposed mechanism of promoter action will be illustrated by the decomposition of hydrogen peroxide by glass wool,[8] promoted by $CuSO_4$ and $MnSO_4$. On the glass surface alone, one can imagine $H_2O_2$ to be doubly adsorbed and the attraction of the surface for the oxygen atoms of the $H_2O_2$ to be strong, but that for the hydrogen atoms weak (or vice-versa). When the copper or manganese salts are added they are adsorbed on the surface, and offer points of strong attraction for whichever atom of the $H_2O_2$ that is weakly adsorbed on the glass, thus offering, in conjunction with the glass, effective pairs for the catalysis of the $H_2O_2$ decomposition. The action of the promoter was quite marked as the following table shows.

---

[1] Adkins and Nisson: J. Am. Chem. Soc., 45, 809 (1923).
[2] Adkins and Nisson: J. Am. Chem. Soc., 46, 130 (1924).
[3] Adkins and Lazier: J. Am. Chem. Soc., 46, 2291 (1924).
[4] See also Adkins' remarks in the Fourth Report of the Committee on Contact Catalysis, (Loc. Cit.).
[5] Langmuir: (Loc. Cit. p. 618).
[6] Gauger and Taylor: J. Am. Chem. Soc., 45, 920 (1923).
[7] Taylor: "Fourth Report . . . ." (Loc. Cit.).
[8] Elissaloff: Z. Elektrochem., 21, 352 (1915).

| Conc. of $CuSO_4$ millimols/litre. | Amount of glass wool (grams). | Relative rate. |
|---|---|---|
| 0 | 0.5 | 0.06 |
| 1.54 | 0.5 | 0.67 |
| 3.10 | 0.5 | 0.68 |
| 1.54 | 0 | 0.10 |
| Conc. of $MnSO_4$ | | |
| 0 | 2.3 | 0.0085 |
| 0.2 | 2.3 | 0.0860 |
| 0.2 | 0 | 0.0052 |

The glass wool in these experiments was digested in order to remove the alkali. Also even more marked promoter action was obtained when Jena glass wool was used, so that it could scarcely be a question of the formation of a third compound with marked catalytic properties.

The catalytic action should have dropped off from a maximum as the glass wool became saturated with $CuSO_4$, on the basis of a multiple adsorption mechanism. Elissafoff did not investigate this point thoroughly but 3.1 millimols of $CuSO_4$ per litre (see the table above), produced no added promoting effect over 1.54 millimols per litre of soft glass wool. In separate adsorption experiments with Jena glass wool, saturation was reached at a concentration of 50 millimols of $CuSO_4$ per litre.

The reaction appeared to be monomolecular on the surface.

Again this evidence is not absolute proof, but the explanation of promoted reactions of this type along the lines of that described above is quite definite and plausible, and the alternatives vague.

## Poisons and Active Centres

There has been abundant evidence to demonstrate the following phenomena, among others, with regard to catalytic poisons.

(a) There are cases where a poison will stop catalytic action without stopping adsorption to a proportionate degree. For example Pease[1] has found that mercury poisons a copper catalyst for the hydrogenation of ethylene, with a marked reduction in the adsorption of hydrogen, but only a slight reduction in the adsorption of ethylene.

The rate of this reaction on a copper catalyst was cut down 88% by 0.5 c.c. of CO, whereas this catalyst was capable of adsorbing 5 c.c. of CO, 1 c.c. of $H_2$ and 2 c.c. of ethylene.[2]

(b) Some catalysts can be poisoned with respect to one reaction but not with respect to another.

Thus Vavon and Husson[3] found that with 3 gms. of platinum black and 5 gms. of diethyl ketone in 50 c.c. of acetic acid, 25 c.c. of hydrogen were 'fixed' in four minutes. On addition of 2.3 milligrams of $CS_2$ the action stopped.

[1] Pease: J. Am. Chem. Soc., **45**, 2296 (1923).

[2] Pease and Stewart: J. Am. Chem. Soc. **47**, 1235 (1925).

[3] Vavon and Husson: Compt. rend., **175**, 277 (1922).

On adding 2 gms. of piperonal 25 c.c. of hydrogen were fixed in four minutes. This action was stopped by the addition of 1.4 mgs. more of $CS_2$. The catalyst was still able to reduce nitrobenzene, but the addition of more $CS_2$ stopped even this action.

Hydrogen exerts a strong retarding effect upon the thermal decomposition of ammonia on platinum,[1] and but a slight retarding effect upon the thermal decomposition of formic acid on platinum[2] and hydriodic acid on platinum.[3]

The rate of interaction of $H_2$ and $CO_2$ on platinum is proportional to the pressure of $H_2$ up to high pressures,[4] whereas the rate of the reaction passes through a sharp maximum as the pressure of $CO_2$ is increased to the same value.

These phenomena, together with certain other evidence, have led various investigators to the conclusion that catalytic reactions take place on 'active centres' of the surface which have been considered to be 'small areas' of unusually high activity.[5] Taylor has considered them to be 'peaks' of highly unsaturated surface atoms.[6]

While it seems certain that some of this evidence points to the existence of active centres, e.g. that of Pease and Stewart and of Hinshelwood and Prichard, some of it can be interpreted in other ways. In the case of the copper catalyst poisoned by mercury, the amount was sufficient to form a monomolecular layer. The surface is now really mercury, which can be imagined to adsorb both ethylene and hydrogen without necessarily offering effective atom pairs for the activation of either.

Poisoning data could be imagined, on the basis of multiple adsorption, which would give the same impression as some of those cited above, even on plane crystal surfaces. Thus consider the activation of a long molecule to be brought about by multiple adsorption of two points with several atoms intervening. The surface could now be completely blocked as regards this activation by the adsorption of relatively few molecules of say $CS_2$ if they are permanently held, and are distributed at random over the surface. The surface could then still adsorb considerable quantities of short molecules like hydrogen, or molecules which could be adsorbed in a vertical position, and have a small 'head', like nitrobenzene.

However, crystal lattices would not be expected to have very high catalytic activity, unless a frequent spacing of suitable atoms happened to be just that required for effective multiple adsorption. The metals used in the reactions on hot wires consist of minute crystals embedded in vitreous materials.[7] Therefore, it seems likely that when the evidence points definitely to reaction centres in these cases, that the reaction is taking place either on the vitreous

---

[1] Hinshelwood and Burk: J. Chem. Soc., 127, 1105 (1925).
[2] Tingey and Hinshelwood: J. Chem. Soc., 121, 1668 (1922).
[3] Hinshelwood and Burk: J. Chem. Soc., 127, 2896 (1925).
[4] Hinshelwood and Pritchard: J. Chem. Soc., 127, 806 (1925).
[5] Constable: Loc. Cit.
[6] Taylor: Loc. Cit.
[7] Beilby: "Aggregation and Flow of Solids" (1921).

portion, or at the borders of the crystals (one atom adsorbed on the crystal and the other on the vitreous portion), or both.

The other well known phenomena of catalytic behaviour have been interpreted in the light of molecules stretched through multiple adsorption, e.g. the variability of catalytic surfaces, change in catalytic activity with heat treatment, roughening of catalytic surfaces, the lack of correspondence between the amount of adsorption and activation, varying saturation capacity of the surface for different substances, specific activation of the case of reactions which can proceed in more than one way etc. Detailed applications of the theory in these cases will not be communicated at present, since the fact that this theory is capable of explaining them does not necessarily mean that the theory is the real cause of the effects. However, these phenomena would seem to follow necessarily from multiple adsorption under the specified conditions, whereas it is not clear why they should from the less definite theories of contact catalysis.

The writer will attempt some experiments which he hopes will yield more direct evidence for the assumptions of the theory.

*Physical Chemistry Laboratory,*
*Balliol and Trinity Colleges,*
*Oxford.*

## NEW BOOKS

**Corrosion:** *Causes and Prevention. By Frank N. Speller. 23×15 cm; pp. xiii+621. New York and London: McGraw-Hill Book Company, 1926. Price: $6.00.* In the preface the author says: "Interest in the corrosion problem has been increasing for many years. This has inspired investigators and writers to such an extent that it is now difficult to follow the voluminous technical literature relating to this subject and select that which is useful. One object of this work has been to take an inventory of the available information and classify it according to a simple and practical system to make it clearer and more readily available to those who have not studied the subject in detail. It will be seen from a study of the various controlling factors, that those which act external to the metal afford a natural and logical basis of classification of the various types of corrosion. Such a system has been followed in this book. In addition to the available information from the literature, data have been included from the experience of the author and those with whom he has been associated in the study of corrosion during the past twenty years," p. viii.

The book is divided into two parts: general principles and preventive measures. Under general principles the chapters are entitled: introductory outline of the corrosion problem; nature and mechanism of corrosion—theories of corrosion; influence of methods of manufacture and treatment; influence of factors internal to the metal—composition; influence of factors external to the metal—classification; principles and methods of corrosion testing; relative corrosion of ferrous metals. Under preventive measures the chapters are entitled: prevention of corrosion in the atmosphere; prevention of corrosion under water; prevention of corrosion in closed water systems by removal of dissolved oxygen; prevention of corrosion in high-pressure steam plants—boiler water treatment; prevention of corrosion in steam and hot water heating systems; chemical corrosion; prevention of corrosion underground; stray-current electrolysis; classified list of selected references on the corrosion of ferrous metals; appendix.

"It was thought for many years that wrought iron actually had a fibrous structure and, indeed, the number of persons still holding this view is suprisingly large. Many valuable properties were attributed to puddled iron on account of its "fibrous structure" which were denied to steel because of its "crystalline structure." The microscope has summarily disposed of this erroneous belief in showing that the ferrite constituting the bulk of wrought iron is in no way different from the ferrite forming the bulk of low carbon steel. Both are equally crystalline," p. 62.

"Cast-iron pipes are now being made by the de-Lavaud centrifugal process. The molten metal is poured synchronously from a moving trough into a rapidly revolving horizontal mold and is thus progressively fed throughout the length of the mold as it revolves. This metal has a dense fine-grained structure which must be annealed to give sufficient ductility. The texture is different from gray iron. While not so likely to suffer from graphitic corrosion, there is some question as to the effect this treatment will have on durability. This material, however, has not been used long enough to determine its standing compared with regular cast iron. A modification of the centrifugal process has recently been introduced using sand-lined molds; this avoids the necessity of an annealing operation," p. 71.

"A surface which has been highly polished is very much less attacked than a rough surface. Frequently it withstands exposure for a considerable length of time before showing any corrosion, while unpolished surfaces under the same conditions may be badly attacked in a relatively short period. Polished surfaces usually corrode more evenly. This is particularly true of high-chromium steels. The rougher, more strained, and less uniform a surface, the sooner corrosion will start and the more localized the action will be," p. 74.

"The analysis [of the Delhi pillar] might be taken for an ordinary sample of modern charcoal iron except that the carbon is a little high. The dry hot climate of Hindustan probably has had much to do with the durability of this particular sample of old iron. The

pillar was evidently hammer forged, during which process a considerable amount of the fusible slag formed was probably worked into intimate contact with the surface. Although positive proof has not been obtained so far, Rosenhain is inclined to explain the great durability of this pillar and similar cases by the presence of an excess of protective cinder found on the surface of the metal. Samples of such iron rusted freely when cut up so as to expose a fresh surface.

"In 1908, the author had the opportunity to make a close examination of some of the old French pipe left on the Isthmus of Panama about twenty years before. Much of the pipe was apparently unprotected by paint. Some pieces of this were almost as good as new, but others were almost entirely destroyed by rust. Apparently this was not due to any essential difference in the process of manufacture, for pieces of both wrought iron and steel pipe were found in the material which survived, as well as in that which was badly corroded. Analyses of many samples of these failed to indicate anything unusual in the composition. It is possible that the metal which did not corrode was first exposed during the hot dry season, at which time a dehydrated oxide coating was formed by the heat of the sun and protected the steel from later attack. It is interesting to note that several tests which the author made on old piping from this source showed that, on removing the surface coating, the old metal corroded in the atmosphere of the Isthmus at much the same rate as steel pipe made by modern processes," p. 85.

"In 1923 Buck reported the results of an extensive series of tests on bare sheet metal under actual service conditions in three different characters of atmosphere. The results of this research proved a very decided superiority for open-hearth and bessemer steel containing copper in amounts of 0.15 to 0.30 percent over similar steel without the copper content, and indicated that the life of such material is more than doubled by the introduction of copper. Later investigation proved that this estimate is very conservative," p. 103.

"Many investigators have noted and commented upon the remarkable difference between the dense, dark-colored, and closely adherent rust film on copper steel, and the loose, spongy, and light-red film on non-copper steels. It is apparent that the dense rust film which forms on copper steel becomes a real and fairly efficient protector to the underlying metal, and experiments have shown that the corrosion rate on copper steels becomes less after several months' exposure. . . .

"From the data at hand it seems there is a strong indication that the well-known, harmful influence of sulphur on corrosion [*in atmosphere*] is in some manner controlled by the addition of copper, and also that the structure of the rust film formed is a function of the increased resistance peculiar to copper steel. This difference in structure may be due to the slower corrosion rate, and it also seems probable that, at a later period, it acts mechanically as a protector of the underlying metal. It also seems probable that the theory of sulphur control, above mentioned, does not completely explain the phenomenon, for the reason that Burgess and Aston find that by adding copper to pure electrolytic iron (presumably sulphurless), beneficial results are obtained from a corrosion standpoint," p. 110.

"The addition of from 0.10 to 0.25 percent copper to normal open-hearth or bessemer steel is decidedly beneficial when the metal is exposed without protection to wet and dry weather conditions. The same is probably true in a large measure when the metal is painted or coated. The maximum effect is obtained at about 0.15 percent with 0.05 percent sulphur contents. As a rule, the addition of copper to steel appears to have no decided influence one way or the other when the metal is exposed under water, in the soil, or in places where the air does not have free access. It should be pointed out, however, that there are many varieties of soil and water, and that relatively few tests have as yet been made in such media, compared with the more complete experience with copper steel in the atmosphere. Under atmospheric conditions, the effect of copper is much more marked than is the purity of iron or steel.

"More thorough investigation and study is required before the variable influence of copper in subaqueous and atmospheric corrosion can be explained satisfactorily. The advantage of copper-bearing steel, however, has been satisfactorily demonstrated under atmospheric conditions and in certain kinds of salt water and a considerable amount of this

material is now being used for construction which is exposed to such conditions. It has been estimated that in 1923, approximately 500,000 tons of copper-bearing steel were made in the United States," p. 119.

"Hydrochloric, sulphuric, or sulphurous acids attack stainless steel or iron rapidly. Nitric acid of all strengths has practically no action on such metal and is, therefore, a good criterion for distinguishing stainless from ordinary iron or steel. Chromium steel which has been immersed in 1.20 specific gravity nitric acid for 24 hours will resist sulphuric acid for several hours, due to the passivifying effect of the nitric acid.

"While stainless steel is attacked by pure dilute sulphuric acid, Hatfield has shown that in the hardened condition, it is not attacked in mine water, which contains sulphuric acid and ferric sulphate, unless the ratio of sulphuric acid to ferric sulphate exceeds 5 to 1. Ferric sulphate in acids has the opposite tendency on ordinary steel, where it acts as a depolarizer and increases the rate of corrosion. The retarding action on chromium alloys is probably due to the increased tendency for the metal to become passive in the presence of oxidizing compounds," p. 126.

"At high temperatures, chromium steels are oxidized less than are carbon steels, and form the characteristic colored tempering films at a higher temperature. Considerably higher temperatures are required to give the same thickness of oxide on the stainless steels which do not actually begin to scale below 1500° to 1800°F (816° to 982°C) depending upon the amount of chromium present," p. 131.

"Turbulent flow in pipe lines and agitation of solutions in open vessels by aeration usually bring about a marked increase in the rate of corrosion. This is to be expected as the amount of dissolved oxygen reaching the metal surface is usually a maximum under these conditions. *In the absence of oxygen*, if the motion of the solution in contact with the surface is not uniform, the area subject to the higher velocity becomes anodic with local solution of the metal. When dissolved oxygen is present, the polarity will usually be the reverse as the area which is in contact with solution at the higher velocities received a greater amount of oxygen and therefore tends to become cathodic," p. 149.

"The humidity of air above the corroding solution influences the rate of solution of gaseous oxygen by quiet water. The rate is greater for dry than for humid air. This is due to the increase in the rate of evaporation from the liquid surface as the air above it becomes dryer. Evaporation cools the surface layer of liquid so that it becomes more dense and sinks, thus distributing the dissolved oxygen (which was adsorbed at the surface) through the solution, and bringing fresh unsaturated liquid to the surface.

"This phenomenon causes even more rapid oxygen absorption in salt solutions where, because of the evaporation taking place, the surface of the solution is concentrated. Thus, in addition to the cooling effect, the concentration effect still further increases the density of the liquid at the surface and aids the formation of convection currents. This effect reaches a maximum at a concentration of about one percent in sodium chloride solutions," p. 152.

"High temperature oxidation appears to be due mainly to the direct chemical combination of oxygen with the metal; whereas the action may always be considered to be electrochemical at lower temperatures in the presence of moisture," p. 193. Pilling and Beckworth "divide the metals into two groups:(*a*) those which form oxides having a cellular or porous non-protective structure; and (*b*) others which form a continuous protective oxide. The former include most of the light metals with low-melting points, such as magnesium and calcium, while the latter include copper, nickel, chromium, aluminum, and iron. They have shown experimentally, especially in the case of copper, nickel, and some of the copper-nickel alloys, that the rate of oxidation at any temperature is dependent upon the rate at which oxygen is transferred through the oxide layer. In the case of copper, this is thought to be dependent upon the rate of solution and diffusion of oxygen through this layer. The rate of oxidation decreases with the time of exposure (at a constant temperature) in the form of a simple quadratic parabola, the amount of oxidation being proportional to the square root of the time. This is analogous to the retarding influence of natural protective coatings deposited from water which may follow a similar law," p. 194.

"The system of classification which has been developed and used throughout this book includes five separate classes: (1) atmospheric corrosion; (2) underwater corrosion; (3) underground corrosion; (4) chemical corrosion; (5) electrolysis (due to a superimposed current). Each is distinguished by the controlling influence of different, well-recognized, external factors. The outstanding characteristics of each class or type of corrosion will be taken up briefly.

"Atmospheric corrosion is characterized by the presence of oxygen in excess, moisture being present only part of the time. The metal is wetted and dried and is subjected to the action of sunlight and variable weather. Metal roofing, fence wire, bridges, rails, steel tanks, and cars, are examples of material used under such conditions. At least eighty percent of the steel in use is subject to this class of corrosion," p. 195.

"Underwater corrosion in practice includes water conduits of all kinds, heating systems, steam boilers, submerged iron and steel works, and other such materials. It probably applies to ten percent of the ferrous metals in use. The dissolved oxygen usually necessary for corrosion to continue is obtained originally from the air and is limited in amount. Thus the conditions are the reverse of those in the atmosphere with respect to the ratio between the available supply of oxygen and water. That is to say, in the atmosphere, polarization by hydrogen is prevented by the large excess of oxygen, whereas in water the metal surface is always more or less polarized.

"It is not surprising, therefore, to find that underwater corrosion differs widely in nearly every respect from atmospheric corrosion. The products of corrosion usually contain about one-third ferrous hydroxide, as the metal is incompletely oxidized due to the lack of oxygen, and the rust is soft and more uniform in texture. Under similar conditions, neither the amount nor the structure of the rust formed is influenced to any appreciable degree by the ordinary changes in composition found in commercial iron and steel," p. 196.

"Underground corrosion, where electrolysis from stray currents does not enter into the problem, constitutes a class which combines some of the characteristics of each of the two foregoing classes, but which also exhibits certain characteristics peculiar to itself. Something of the importance of this class of corrosion may be judged from the fact that more than half of the pipe manufactured in this country, amounting to over a million tons annually, is used underground in the construction of water, oil, and gas lines. Besides pipe and other structures underground, this class may include the corrosion of ferrous metals in concrete, in cinders, or in any case where the metal is enclosed by a more or less solid mass capable of containing water," p. 197.

"Considering the relative influence of factors internal and external to the metal, it seems clear that, with few exceptions, external factors predominate and determine the rate of natural corrosion with ordinary iron and steel. Composition is of minor importance in corrosion underwater and, with the notable exception of the copper contents, the composition of ordinary rolled iron and steel is also relatively unimportant in the air.

"The mass of evidence which has been accumulated on the relative corrosion of wrought iron and steel, clearly points to this general conclusion which might have been predicted from the present knowledge of the influence of these factors. It is also true that the *relative* corrosion of metals varies greatly under different conditions. This is strikingly illustrated by the fact that in the air, copper-bearing steels corrode much slower than ordinary iron or steel, but in fresh water, there is no appreciable difference in the corrosion rate of the two. Generalizations should be avoided in considering relative corrosion," p. 267.

"American vermilion (basic chromate of lead) gave better results in the Atlantic City tests than any other single pigment tested, having a rating of practically 100 percent even after four years of exposure. Instances have, moreover, been cited where this pigment used upon iron surfaces has given protection from rust for periods greatly exceeding ten years. In subsequent tests at Atlantic City and in Washington, this pigment gave very remarkable results, showing greater resistance to wear than any other paint tested. Unlike red lead, it does not weather to a whitish surface, being apparently unaffected by the carbon dioxide in the atmosphere. Due, however, to its relatively high cost as compared to red lead, its use has been restricted as the sole constituent of metallic primers. Nevertheless,

it is being used very satisfactorily in relatively small amounts, say from ten to fifteen per-cent, in many metal primers. A wider use for this very valuable pigment should follow. An attempt was made a few years ago by A. S. Cushman and H. A. Gardner to surface-coat the particles of certain pigments by a chromatizing process. By this process, there was formed around the pigment particles a coating of basic chromate of lead. While the pigment thus formed is not as durable as 100 percent chromate of lead, it has, in various experiments, given excellent protection to metal over a long period," p. 292.

"Zinc oxide is a strongly rust-inhibitive pigment, due to its basic nature. This influence asserts itself when used in combination with lead pigments in light-tinted paints which are to some extent used for finishing coats. One of the best metal paints for general use can be made with a mixture of iron oxide and zinc oxide, the zinc oxide greatly increasing the rust-preventing properties of the paint. This type of paint is finding quite a wide application in railroad work and is giving generally good service. Zinc dust, because of its position in the electrochemical series, is an excellent protective of iron and steel surfaces, to some extent acting like galvanizing. In fact, a so-called "liquid galvanizing" has been prepared from a finely divided zinc dust composition in boiled linseed oil. Paints made with equal amounts by weight of zinc dust and zinc oxide are remarkably efficient as primers for metal surfaces," p. 293.

"An aluminum paint film has a number of unique properties. Its bright metallic surface is highly reflecting. The metallic aluminum flakes are entirely opaque and hence protect the underlying vehicle from the sunlight, which is a most important factor in causing deterioration of paints. Aluminum powder has been shown to considerably increase the water-resisting qualities of the paint film. Before applying aluminum paint to steel, it is desirable to paint the metal with a priming coat of a good basic pigment, utilizing the protective property of the aluminum in the finishing coats," p. 295.

"The phosphate coatings are somewhat similar to oxide coatings. They are produced by the action of several combinations of chemicals, all of which produce iron phosphates on the surface of the metal. In general, these coatings are slightly less cathodic to iron than the oxide coatings, and, therefore, are more protective. This fact, coupled with their better adherence to the iron surface and their pleasing appearance, has given them a rather extensive application. Like oxide coatings, they are made more protective by treatment with a suitable oil. As in other coatings of this nature, however, they are not sufficiently resistant to be used under exposed conditions," p. 302.

"Steel embedded in concrete exposed to salt air near the sea is more subject to attack than in concrete completely submerged in the sea water. This is due to the fact that moist air will penetrate through porous concrete to the metal, while salt water may not. Corrosion of the reinforcing metal, covered with two to four inches of good concrete, has occurred above the high-water level of concrete piers in the sea. The volume of the rust formed is about three times that of the metal, so that its expansive power is usually sufficient to cause spalling of the concrete. In the same locations, no trouble has been experienced with the concrete under the sea water. Under most atmospheric conditions, however, two to four inches of *well-mixed* concrete is sufficient to give permanent protection. When not directly exposed to the weather, as in the protection of structural members in buildings, a covering two inches thick will usually suffice. Where reinforcement is necessary, in concrete exposed to sea air, the metal used for this purpose should be painted with two thin coats of a red oxide of iron paint made up with China-wood oil and spar varnish, or dipped in a bituminous coating, and then dusted with sand. After all the best protection will be obtained by using a dense concrete of proper proportions, thoroughly mixed and well tamped around the bars to a sufficient thickness," p. 304.

"A petroleum grease mixture carrying about 65 percent by weight of zinc dust, fine enough to pass a 200-mesh sieve, has been developed in the Research Laboratory of the National Tube Company and is used to protect pipe threads against galling and corrosion. A little sodium chromate is desirable unless all water is eliminated from the grease," p. 307.

The process of calorizing was developed "as the result of research in the General Electric Company Laboratories in 1911, in an attempt to protect iron from oxidation at high tem-

peratures when the metal was heated under oxidizing conditions. Aluminum oxide is formed on the calorized surface and, to a large extent, protects the metal from further oxidation as long as the temperature does not exceed 1700°F (927°C). At this temperature the protective film of oxide begins to break down. Figure 66 indicates the rate of oxidation on pieces of calorized steel tubing compared with untreated tubing at 1830 and 1475 °F (989 and 802°C). Calorizing has been found useful in preventing the deterioration of superheater tubes, pyrometer tubes, and certain oil refinery equipment exposed to high temperatures and corrosive sulphur compounds such as are found in pressure stills," p. 320.

"Large steel water mains have been successfully cement lined without reinforcement by placing a concrete wooden mold in the pipe and pouring the cement mixture through temporary holes made in the top of the pipe. Steel sections of the New York Catskill Aqueduct were lined in this way with a 1 to 2 sand-portland cement mixture two inches in thickness, It is most important in all cases, of course, to protect the cement from loss of water by evaporation until it is thoroughly set. These large pipes were protected and reinforced on the outside by a jacket of portland cement concrete. Where organic matter did not form on the interior surface of the pipe, the cement-lined conduits showed relatively little reduction in flow capacity when tested after five years service. Under these conditions, the inside diameter of cement-lined pipe may be figured considerably smaller than ordinary asphalt-coated pipe to secure the same rate of flow without cleansing over a long period," p. 336.

"Although sodium silicate usually gives satisfactory protection in very pure waters, yet it has been found that the presence of calcium and magnesium salts, particularly the carbonates, greatly aids in the formation of such coatings. While these coatings are, no doubt, more or less porous in character, they are usually sufficiently dense, adherent, and evenly distributed to retain a high ferrous-hydroxide concentration near the metal, and to interfere with the diffusion of oxygen to the metal surface," p. 349.

"Several years experience in the design and installation of nearly 200 plants in the United States for the removal of oxygen from water has demonstrated that the same type of apparatus cannot be used for all purposes. The choice of the best system for any existing set of conditions depends, among other things, upon the maximum hourly rate of flow of water, the number of high peak loads at which water is required for use, the steam supply and pressure available, how much residual oxygen is permissible, and whether or not an engineer is always on duty. For the hot-water supply of buildings of moderate size, using up to about 1,000 gallons per hour, the deactivator, with or without a filter, is usually the most convenient and economical appliance to use. In larger buildings and in large steam power plants, a mechanical deaerator of suitable design will take up less space and is usually more economical and efficient.

"Where water conditions are such that the protection of both the cold and hot water piping of a building is necessary, it may be most economical to reduce the free oxygen in all the water entering the building to one cubic centimeter per liter or less by a vacuum deaerator operating at normal temperature and, after heating the water for the hot-water supply system, to remove the balance with a deactivator or another mechanical deaerator. By properly proportioning the plant, it should be possible to regulate the residual oxygen in the cold and hot water so that the life of these systems would be about equal and would be commensurate with the expected life of the building," p. 396.

"In comparatively small buildings, where the length of the piping system is not over 100 or 200 feet or where very large quantities of water are used, oxygen removal apparatus may be too costly to install. In such cases, considerable protection and clear rust-free water may often be obtained by the addition of lime or sodium silicate," p. 397.

"Large savings in reduced depreciation of heating systems could undoubtedly be realized and expensive repairs avoided, if building owners would occasionally employ an industrial water chemist to test the quality of the water and steam and to advise on the conditions of the system and the water treatment required. A limited amount of such service should cost approximately little. Such tests involve the determination of free oxygen, carbon dioxide, and pH value of the steam entering the system and of the condensate from the returns, in addition to the usual analyses of the feed water and the water in the boilers," p. 456.

"Most of the corrosion in steam-heating systems occurs inside the short pieces of pipe (nipples) leading from the radiators. These should preferably be made of extra strong pipe. In such systems threaded joints are numerous and may permit the infiltration of air, so that great care should be taken to see that all joints and valves are made and maintained air tight. Pipe threads should be clean-cut with good dies so as to make a tight joint. Too little attention is paid to this matter.

"A suitable thread lubricant is a necessity, as the ordinary threading die does not cut a thread which is gas tight unless some sort of thread filler is used when the pipe is installed. The ordinary well-known red lead-glycerine mixture is good, but it has been found that any of the thread lubricants can be made to produce a tighter and more durable joint by the addition of about 60 percent zinc dust, fine enough to pass a 200-mesh sieve. This provides a metallic lubricant which fills up irregularities in the thread, and thus assists in making a tight joint. The use of zinc dust for this purpose was developed in the Research Laboratory of the National Tube Company, and applied successfully as a thread lubricant for use on tubular goods for the oil fields where the service is particularly severe," p. 461

"It would be well for all owners of large buildings to occasionally examine the inside of some of their steam return lines so that if corrosion is found, it may be stopped before serious damage is done. Most central-heating companies are glad to cooperate and advise in conserving the property of their customers when notified that such damage is going on and should, for the benefit of all concerned, make daily tests of the quality of the steam which they sell. The time is probably coming when steam will be sold on a specification for quality, as are steel, coal, and other commodities. On the other hand, it would seem that building owners and architects should pay more attention to the construction of steam systems, so that all connections will be made as tight as possible, with sufficient grade to carry off condensate, and with proper protection of the exterior of the piping against corrosion," p. 462.

"Cast iron is corroded very little by fuming sulphuric acids; but a number of cases have been recorded where the metal has cracked in practice with almost explosive violence. While this was formerly attributed to the pressure produced by sulphur dioxide and hydrogen formed by corrosion between the crystalline grains of the metal, more recent work by Banigan, has indicated that free sulphur trioxide reacts readily with silicon in the metal, forming silicon dioxide, which owing to the consequent increase in volume causes rupture. Hamlin and Turner state that in order to resist acids, cast iron should have a high combined and low graphitic carbon content," p. 479.

"The major portion of corrosion underground takes place on iron and steel tubular products, so that much of the discussion of soil corrosion will necessarily be based upon records and experiences with gas, water, and oil lines. On the whole, experience indicates that the life of iron and steel pipe, underground, has been considerably underestimated. The actual replacement records of several iron and steel oil lines more than a hundred miles long, traversing what might be classed as unusually corrosive soil, show an average annual replacement of only 0.43 of 1 percent of the line over a period of 25 to 30 years. Nearly all of these replacements occurred in the latter half of this period. Under more favorable conditions in many parts of the United States, cases are known where hundreds of miles of steel pipe used for transporting oil and gas shows practically no corrosion in that length of time, and some instances are on record where wrought iron and steel pipe lines have been in use for forty years with practically no action on the metal due to the soil," p. 495.

"In some kinds of soil, cast iron is subject to a peculiar form of disintegration known as "graphitization" or "graphitic softening." This action is the result of the selective corrosion of the ferrite (pure iron grains) of the metal. The skeleton structure which remains consists mainly of the products of corrosion and the non-corrodible matter in the cast iron, i.e., the graphite, carbide, silicide, and oxides of iron, and what remains of the uncorroded metallic iron. This structure retains the form of the original metal, but is soft enough to be easily cut with a knife. If left undisturbed, it is often strong enough to carry water or gas under low pressure, but is likely to fail under shock. Stray electric currents sometimes

produce this effect, but it seems to occur more commonly in certain corrosive soils where electric currents are absent, particularly in those soils which carry calcium sulphate or similar salts. Graphitization also occurs in sea water," p. 505.

"The rapid deterioration of the conduit carrying hydrogen sulphide water has been explained as the result of the contact effect set up by the layer of elementary sulphur and iron sulphide which collected on the surface of the metal, since these substances are strongly cathodic to iron. Laboratory experiments, in this investigation, indicated that the rate of corrosion was increased as much as 500 percent when cast iron was placed in contact with the deposit from the inside of the pipe (iron sulphide and elementary sulphur) and immersed in the Mondorf water. The mechanism of the action has also been explained as due to the fact that the hydrogen sulphide precipitates iron sulphide, and in this way decreases the metal-ion concentration sufficiently to accelerate the corrosion. The increased acidity of the unaerated solution, due to the hydrogen sulphide and carbon dioxide contents, may also have been a factor of importance. Whatever the mechanism of the action, the important point is that it was much more rapid in the presence of dissolved hydrogen sulphide, presumably in the absence of oxygen. This may have a bearing upon the severe corrosion sometimes found in oil wells which usually carry saline water often with more or less dissolved hydrogen sulphide and carbon dioxide," p. 510.

These extracts show how good the book is. There are some points—not many—which do not seem up to standard. Ferrous oxide or hydroxide in alkaline solution is one of the most powerful reducing agents we have and it is therefore improbable that a film of this substance plays any appreciable part in preventing the corrosion of iron in alkali, pp. 39, 171, 485. It seems a pity to ascribe to Walker, p. 19, the addition of acid to the cathode compartment in order to cause corrosion of the anode, when Ostwald had cleared up this point more than fifteen years earlier. The author evidently has not read any of the better work on passivity, pp. 190, 354, and his views on the subject are quite primitive.

The reviewer does not agree with the statement, p. 275, that "if the electrochemical theory is the correct explanation for corrosion in water, it naturally follows that it is also true for corrosion in the air. The only difference is the relative importance of the various controlling factors." This does not follow at all and it makes one wonder whether the electrochemical theory is really much more than a form of words to the author.

One cannot criticize the book on the ground that it is merely a compilation of data, because the author admits quite frankly that that was all he could do; but the fact that it is apparently quite impossible to do much more than chronicle tests is a damning commentary on the way in which the technical people have wasted their time in the study of corrosion.

*Wilder D. Bancroft*

**Recent Advances in Physical and Inorganic Chemistry.** *By Alfred W. Stewart. Fifth edition. 14×22 cm; pp. 312. London: Longmans, Green and Co., 1926. Price: 18 shillings.* Any fresh issue of such a volume as the one under review, if it is to be worthy of its title must of necessity differ from its predecessors. The author's present revision has been so thoroughgoing that this fifth edition is really almost a new book, only three chapters of the previous issue remaining intact. Prof. Stewart's main theme is the stupendous change in the fundamental conceptions of chemical science which the last quarter of a century has witnessed, and in a complete and highly skilful exposition he traces the manner in which the various tributary streams have gone to swell the present main current of chemical thought. In a series of interesting chapters the significance, in this connexion, of radioactivity, the electron, the structure and disintegration of the atom, X-ray spectra, positive ray analysis, isotopes, atomic numbers and similar topics is fully discussed.

Introductory and final chapters review the gap between the older and the newer chemistry, as well as the problems still outstanding in connexion with the chemical elements and their relationships. In emphasizing the dramatic change of view regarding the chemical elements which has occurred in recent times, the author is almost contemptuous of the ingenuity and technique devoted earlier to the exact determination of atomic weights: "the case of the determiners of atomic weights in the nineties and later is one of the most pathetic

in the whole history of science: for out of that ungrudging effort towards accuracy nothing has resulted so far as real advance in knowledge is concerned." The terms of this comment appear to the reviewer far too sweeping: they smack rather of journalism than of sober scientific judgment. Further, in stating that the "chemical atomic weights" correspond to nothing real, and that, being merely averages, they are purely mathematical figments, the author is oblivious of the very real basis, statistical though it may be, on which all chemical practice still rests.

Among the other topics selected by the author for consideration are such as active hydrogen, active nitrogen, hydrides, some effects of intense drying, and Telsa-luminescence spectra. Considerable space is devoted to the hydrides, to their preparation and to their properties, more especially in relation to the periodic system; the difference between the hydrides of elements in Groups I & II, and those of elements in later groups is emphasised. So far as the hydrides of elements in the earlier groups is concerned, the hydrogen appears to behave like a halogen: this is shown, for example, by the results of electrolysing lithium and calcium hydrides.

Some of the problems which have recently been in the forefront of physico-chemical investigation and discussion, such for example as the nature of gaseous reactions in relation to radiation and molecular collision, and the measurement of ionisation and activity in solutions have not been considered in this volume. After all, every one would probably choose different subjects for discussion, and the author will no doubt keep in view for treatment on a future occasion such topics as those mentioned. It seems certain that another edition should be called for at no very distant date. *J. C. Philip*

**Practical Photomicrography.** *By J. E. Barnard and Frank V. Welch. Second Edition 21×14 cm. pp. xii + 316. New York and London; Longmans, Greene & Co.; Edward Arnold Co., 1925. Price: $6.00.* The microscopist whose work leads him into photomicrography starts at a considerable advantage, "since the difficulties encountered are chiefly those of the proper use and adjustment of the microscope, rather than the mastering of the technical difficulties of the purely photographic portion."

"On the other hand, the photographer who wishes to enter upon a new field will find that in order to attain any degree of success he has to master the use of the microscope as an optical instrument and also to acquire a general knowledge of the objects which he wishes to photograph."

"*Practical Photomicrography*" is written for both classes of workers; considerable space is devoted to the optical equipment most suited for photomicrographic work and to the manipulation of the microscope and its various accessories. The treatment of the photographic side is concise and definite and is supplemented by a chapter devoted to brief discussions of ultra-violet photomicrography, metallography, stereoscopic and color photographs. The present edition of the book is essentially similar to the earlier one in scope and point of view; the changes are of a minor character and do hardly enough justice to the great bulk of recent work on special apparatus and methods. Apparently the authors (like most writers on microscopy) have written primarily for workers in the biological sciences and the problems of the chemist, the physicist, the metallurgist, the petrographer, and the engineer, who are using photomicrography quite as much, receive little more than passing mention. To fill this gap and to direct the reader to some of the more theoretical aspects of the subject, as an aid in the solution of his own special problems, a more extensive bibliography than that contained in the appendix should be available.

Although the books on microscopy proper commonly give considerable space to methods of preparation and mounting of the specimen for examination, a chapter might well have been included covering the methods which are best suited to photomicrographic objects, particularly since there are numerous difficulties peculiar to this field which are not very serious in visual work. The authors are so well qualified to give invaluable advice on problems of this sort, and on questions of illumination and interpretation, that it seems unfortunate that they have not seen fit to emphasize this eminently "practical" aspect of the work. After all, one can learn about microscopes and photography from any of a large number of

books; workers in the different branches of science are probably familiar with the technique of preparation and interpretation before they approach the subject of photomicrography, but it is highly desirable that the accumulated experience with various types of objects should be assembled for the guidance of other workers in similar fields, and as a source of suggestions applicable to quite unrelated lines of investigation. *C. W. Mason*

**Lehrbuch der Physik.** *By Arnold Berliner. Third edition. 25 × 18 cm, pp. x+645. Berlin: Julius Springer, 1924. Price: 18.60 gold marks.* This book is intended primarily for medical and chemical students and is therefore kept fairly elementary. The general subdivisions are mechanics, liquids, gases, heat, sound, electricity, and light.

There is an interesting account on p. 204 of Mayer's discovery of the mechanical equivalent of heat. "The equivalence of heat and work was first postulated by the physician Julius Robert Mayer in 1842. The clue came from an observation in Java, when letting blood, that the venous blood there is surprisingly bright red while in Europe it is dark red owing to the considerable content of carbon dioxide. It was known at the time that animal heat is due to the oxidation of the food and that carbon dioxide is formed during the slow combustion. With this as a starting point Mayer explained his observation from the fact that the human body—in order to keep its temperature at the same point—needs to develop less heat in a hot climate because the loss of heat by radiation is less; and that consequently it develops less carbon dioxide. We owe to Mayer the conception that the heat of oxidation of the food is converted into mechanical energy according to the first law of thermodynamics."

On pp. 213-215 there is a detailed discussion of Nernst's third law of thermodynamics. No explanation is offered, p. 223, why water should have a maximum density at 4°. There is an implication that water has a minimum density at 0°; but what is really meant is that that is the lowest temperature at which liquid is stable in presence of water vapor.

On p. 593 is the erroneous statement that the colors on the wings of some butterflies and beetles are chiefly diffraction colors. While there are many lines in some cases, they are scarcely parallel enough to make a satisfactory grating. Pfund has shown that only a portion of the color of mother-of-pearl is due to a grating structure. On p. 594 is the statement that the scattering of light by turbid media is a diffraction phenomenon; but it is not shown that this view is consistent with the fact that the short wave-lengths are the ones that are scattered chiefly.

The reviewer was interested in a paragraph on p. 614. "Fluorescence and phosphorescence interest us also because they make the substances sources of light (luminescent paint for instance.) Such luminescent sources differ from the ordinary sources of light in that the temperature is relatively low; they emit light almost without heat. Other luminescence phenomena are, for instance, the light of the firefly, the electrical discharges in dilute gases (Geissler tubes), the light obtained on heating certain crystals (fluorspar), etc. The waves sent out by these substances are almost exclusively light-waves in the popular sense; these sources of light are therefore very efficient." The author does not include salt flames in the Bunsen burner under chemiluminescence, as he really should.

On p. 619 one would have liked a little more definite statement as to the emission of light by a colored solution at ordinary temperatures. It seems to be that they emit no visible light because a black body emits no appreciable light at ordinary temperature; but it is not stated definitely or clearly. Since a black body does emit infra-red rays at ordinary temperatures, it seems as though it should be possible to photograph the spectrum of a potassium chromate solution in the dark if one gave a sufficiently long exposure. If not, one would like to know whether the trouble is in the photographic plate or in the theory.
*Wilder D. Bancroft*

**Kristalle und Röntgenstrahlen.** *By P. P. Ewald. 24 × 16 cm; pp. ix+327. Berlin; Julius Springer, 1923. Price: $6.35.* This book is based on a course of lectures given at Munich a number of years ago. The chapters are entitled: atomic theory; fundamental crystallographic conceptions; crystallographic structure theory; interference; Röntgen rays;

outline of experimental methods; the Bragg process—spectroscopy; interference in lattices and the base numbers—determination of structure from the Bragg photographs; Laue's method and the interpretation of the Laue photographs; the formation of the Laue images and the control of structure; the Debye-Scherrer process; complete diagrams, structure of fibres, constitution of metals; representation of the structures; geometry of the lattices; ion lattices, isomorphism, solid solutions; chemical bearing of the interpretation of the crystal structures; lattice forces and the properties of substances.

The mean distance apart of molecules or atoms in a crystal is only a few tenths of a micromillimeter, p. 34. The mean wave-length of visible light is therefore at least a thousand times greater than the distance between the atoms in a solid. From the description in the text, p. 99, it seems difficult to believe that molecules of calcium fluoride do not exist in the crystal. It is very surprising that standing for eighteen days at ordinary temperature should change the crystalline structure of rolled tin as much as it appears to, p. 144.

On p. 186 there is a paragraph as to how one can tell an ion lattice from an atom lattice where atom is used to signify the absence of an electrical charge. According to Ewald one has an ion lattice if the crystal shows residual rays, pyroelectricity, or piezoelectricity. Under certain favorable circumstances one can also demonstrate the presence of ions from the X-ray photographs alone—because the amplitutde of the waves going from the single atoms is proportional to the number of electrons.

*Wilder D. Bancroft*

**Mikroanalyse nach der Mikro-Dennstedt-Methode.** *By Casimir Funk. 22 × 15 cm; Munich: J. F. Bergmann, 1925.* That the method of the Microanalysis of Organic Compounds still awaits the advent of its Liebig is a fact appreciated by the many who have failed to achieve success in their attempts to follow the methods of Dubsky, Pregl, and other pioneers in this field. The Author of this pamphlet had the privilege of seeing the process carried out in Pregl's laboratory; but, after a series of failures extending over a year, was led to abandon this method of effecting the combustion in favor of that of Dennstedt, and in some fifteen pages he gives an admirably clear description of his Micro-Dennstedt method which he claims to be superior to the Macro-method.

Time only will show if other, and less experienced, workers can use this method with equal success, or whether the year's apprenticeship in the older methods is a necessary prelude.

*M. A. Whiteley*

**L'Hydrogène et les Gaz nobles.** *By J. J. Van Laar. 23 × 15 cm; pp. 79. Leiden: A. W. Sijthoff. Price: 3 florins.* The publishers of the Recueil des Travaux chimiques des Pays-Bas are planning to issue a series of Theoretical and Practical Monographs in French or English four times a year. The monographs will be about eighty pages in length and will include important researches by well-known authors. The first in the series is this one by van Laar. This is a compilation of data, including atomic weight, molecular volume, molecular and atomic weights, boiling-point and triple point, critical data, vapor pressures, densities of co-existent phases, dissociation, molecular attraction, etc.

*Wilder D. Bancroft*

**Fortschritte der Kolloidchemie.** *By Herbert Freundlich. 22 × 14 cm; pp. 109. Dresden and Leipzig: Theodor Steinkopff, 1926. Price: 5.50 marks.* Freundlich considers that the time has come when we must make more definite our conception of adsorption, electrical potentials at surfaces, coagulation, state and shape of colliodal particles, etc. With this in view, the eight chapters are entitled: adsorption; electrokinetic potential; adsorption, valence, and coagulation; rate of coagulation; the stability of hydrophile sols; the state and shape of colloid particles; the absolute value and changes of the surface forces in colloids; photodichroism and related phenomena.

Traube pointed out that the lowering of the surface tension of water by organic substances is greater the longer the carbon chain. Freundlich claims that this can only be true

in case the organic chain lies flat in the surface of the liquid. It seems to the reviewer that one could get a similar result, at least qualitatively, if the molecules stood vertically and the longer ones had to be sucked in farther. To explain the adsorption from these solutions by charcoal, Freundlich postulates that the affinity between water and the organic compound is the important factor and not any special affinity between the organic compound and charcoal. In view of the very specific adsorption of gases by charcoal, this conclusion is not convincing.

There is a very interesting account of Warburg's synthesis of blood charcoal, pp. 4-8. The addition of a silicate to sugar charcoal gives a material which adsorbs amino acids without accelerating their oxidation. The addition of iron causes increased oxidation of the amino acids and this reaction is poisoned by prussic acid.

Freundlich defines as the electrokinetic potential the potential difference which plays a part in cataphoresis and electrical endosmose experiments. This is not to be confused with the thermodynamic potential with which Nernst's theory deals. Freundlich considers the electrokinetic potential as due to an adsorbed film of finite thickness and varying concentration. The properties of this film may vary considerably with the nature and concentration of electrolytes in the mass of the solution.

Freundlich breaks a lance in favor of the view that a trivalent ion is not necessarily adsorbed more strongly than a univalent ion even though it causes coagulation at lower concentrations. This is a pleasing half-truth. It may be true if the concentrations are expressed in molecular weights; but it cannot be true if the concentrations are expressed in equivalent weights. Actually the variations are usually far outside these limits. Freundlich still clings to the belief that the amounts of the coagulating ions which are carried down are equivalent. This is not true experimentally, as Weiser has shown, and is only true theoretically in case the coagulum has no adsorbing action of its own.

Freundlich considers that the stability of hydrophile sols is due chiefly to hydration and he ascribed this explanation to Kruyt. He does not explain what he means by hydration. If he means the formation of definite chemical compounds, he is unquestionably wrong. If he means water peptization, there is nothing especially new about it. At that he does not give us anything very definite as to why tannin and gelatine precipitate each other. It is very doubtful also whether hydration is the important factor in determining the viscosity of hydrophile sols. An agglomeration to chains or threads is the essential thing.

Freundlich ascribes to Haber, p. 67, the statement that precipitates are more nearly amorphous, the more rapidly they are formed. Von Weimarn did not say exactly that because he believes everything to be crystalline; but he certainly showed that one gets a gelatinous mass with very rapid precipitation.

Weigert has shown that in the production of photohalides, there is not only a color adaptation but a polarization adaptation, p. 95. Glass plates were covered with a thin film of silver chloride in gelatine. This was dried and exposed to light until it was bluish red. When this photochloride layer was exposed to polarized red light, there was formed a red spot which was dichroic and doubly refracting.

One cannot get enthusiastic over this book. Theory has never been Freundlich's strong point and he has ignored consistently and apparently deliberately all non-European work.

Colloid chemistry is not now, and is not likely to be, a German science.

*Wilder D. Bancroft*

# THE INFLUENCE OF THE IONIC CHARGE ON THE OSMOTIC BEHAVIOUR OF ALCOHOLIC SOLUTIONS

BY O. E. FRIVOLD

## Introduction

In a previous note[1] the electric properties of the solvent on the osmotic condition of solutions were the object of further investigation on the basis of boiling point measurements in alcoholic solutions, and with a uni-univalent salt (LiCl) as an electrolyte. These measurements plainly show that the dielectric properties of the solvent play a prominent part in explaining the divergencies of the osmotic pressure, the increase of the boiling point, and so forth, from the values that might be expected in an ideal solution.[2] From the graphical representation in the work mentioned it is evident that the divergences diminish with the increase of the dielectric constant. This corresponds to the circumstance that the effect of the mutual electric forces between the ions diminishes with the increase of the dielectric constant of the solvent. According to Debye-Hückel's interionic theory of the electrolytes, the relative divergencies shown by the increase of the boiling point from the classic values are inversely proportional to the dielectric constant magnified in the power 3/2. In spite of the possibility of determining a temperature difference with an accuracy of ca. 0.0005°C at ca. 60-70°C by means of a differential thermometer constructed by Menzies, this prediction of the theory could only be tested approximately. At all events, it may be stated as regards the measurements in methyl and ethyl alcohol, that the curves drawn through the points measured go into origo with tangents coinciding with those predicted by the theory. Recently the theory on this point has been further confirmed by cryoscopic measurements of very diluted solutions with cyclohexanol as a solvent which are at present being carried out in collaboration with Professor E. Schreiner[3] and by measurements of electrode potentials.[4]

## The Aim of this Investigation and the Interionic Theory of Debye-Hückel.

In this note we shall account for the results of some ebullioscopic measurements in alcoholic solvents in order, if possible, to determine the significance of the ionic charge in the osmotic behaviour of alcoholic solutions.

It is evident that the valency of the ions in a solution and thereby their charges is of great importance in an endeavour to explain the divergencies of

---

[1] O. E. Frivold: "Die Naturwissenschaften", Jahrg. 12, 413-414 (1924); Physik. Z., 25, 465-473 (1924).

[2] By later mentioning will be called "classical values".

[3] E. Schreiner and O. E. Frivold: "Die Naturwissenschaften", Jahrg. 13, Heft 41 (1925).

[4] A. A. Noyes and W. P. Baxter: J. Am. Chem. Soc., 47, 2122 (1925). Further indications of literature will be found in this publication.

osmotic pressure, etc., observed from the classical values, when the electric forces between the ions are to be made responsible for the divergencies mentioned. For, the greater the ionic charge, the stronger will be the interionic forces and thus the mutual obstruction.

*In the first place, the problem was to test the divergencies mentioned quite empirically in very small concentrations by the help of boiling-point measurements.*

For these measurements were used three different salts, LiCl, $CoCl_2$ and $La(NO_3)_3$, that is, salts which contain uni-univalent, bi-univalent and tri-univalent ions. Two solvents were applied which have dielectric constants very different from the dielectric constant of water viz. methyl- and ethyl-alcohol. At the boiling-points the dielectric constants for these alcohols as stated according to measurements by R. Abegg, W. Seitz and F. Ratz[1] are 22.7 and 18.7 respectively.

*Secondly, this investigation aims at studying the influence of the ionic charge on the osmotic behaviour of alcoholic solutions in order to ascertain whether there is correspondence between the divergencies mentioned and the results proceeding from Debye's interionic attraction theory.*

The following three results are predicted by this theory: That the relative divergencies from the classical value of the increase of the boiling-point, the decrease of the freezing-point, etc., observed are proportional to the square root of the ionic concentration, inversely proportional to the product of the dielectric constant of the solvent and the temperature magnified in the power 3/2, and lastly proportional to a valency factor of $w = \left(\frac{\Sigma \nu_i F_i^2}{\Sigma \nu_i}\right)^{3/2}$ where $\nu_i$ is the number of ions of the quality $i$ into which a molecule of the salt is divided and $F_i$ is the valency which the ions $i$ possesses. The three salts that were applied have the valency factors of respectively $w = 1, 2.\sqrt{2}$ and $3.\sqrt{3}$. The proportional factor is determined entirely by known quantities, viz., by the elementary quantity $\epsilon = 4.77.10^{10}$ E. S. U. and Boltzmann's constant $k = 1.37.10^{16}$ erg.

According to Debye, the relative divergencies of the increase of the boiling-point (or the decrease of the freezing-point) from the classical value at infinite dilution can be expressed by the following simple formula:—

$$(1) \quad \frac{\bar{\Delta}-\Delta}{\bar{\Delta}} = 1 - g = \alpha \frac{w}{(DT)^{3/2}} \sqrt{\nu\gamma}$$

where $\bar{\Delta}$ and $\Delta_1$, respectively, represent increase of the boiling point according to the classic theory, and the increase of the boiling point observed, g the osmotic coefficient, $\alpha = 9{,}82.10^5$, $w = \left(\frac{\Sigma \nu_i F_i^2}{\Sigma \nu_i}\right)^{3/2}$, D the dielectric constant,

[1] R. Abegg and W. Seitz: Z. physik. Chem., **29**, 246 (1899); F. Ratz: **19**, 94 (1896).

T the temperature, w the valency factor, $\nu = \Sigma\nu_i$ the entire number of ions into which a molecule of the diluted electrolyte is divided and $\gamma$ the concentration expressed in mole per litre solution.

If the concentration becomes so great that the dimensions of the ions are not small in comparison with the dimensions of the ionic atmosphere, the theory predicts a divergence from the proportionality mentioned. But if the empirical values determined are followed towards constantly smaller concentrations the curve empirically determined may according to the theory be expected to go into the origo with a tangent which the theory predicts. The inclination of this tangent is determined only by the valency factor $w$, the dielectric properties of the solvent and the temperature (see formula 1).

## The Experimental Operation

The measurements were carried out with the same instruments as were employed in the previous work (loc. cit.), namely, a differential thermometer constructed by Menzies[1] and a boiling-point apparatus indicated by Menzies and Wright[2]. The thermometer mentioned allows the measurement of temperature differences with an accuracy of ca. 0.0003°C at a temperature of 100°C, and has proved to be very suitable for this purpose. An endeavour was made to counteract overheating, first with a thin platina wire smelted into the bottom of the vessel and, secondly, by adding suitable quantities of garnets while the measurements were in progress.

### Solvents and Salts employed

The following solvents and salts were employed for the measurements whose results are given in Tables I, II and III. The methyl-alcohol was partly a very pure preparation from Kahlbaum. For some measurements I also used methyl-alcohol absolute, kindly placed at my disposal by Professor E. Schreiner. The ethyl alcohol partly contained ca. 0.1 per cent water, partly an absolute alcohol, kindly provided by Professor H. Goldschmidt. No difference was noticeable in either case, whether absolute alcohol or the other preparation was used.

The cobalt cloride employed was a preparation from Kahlbaum (pro analysi). It was twice recrystalized, then pulverized, and for a long time heated at 200°C until the weight was constant. The expulsion of the six crystal water could also be determined by comparing the loss of weight calculated with the loss of weight really observed. There was an agreement under 1 per cent. The lanthanum nitrate was a preparation from Kahlbaum (pro analysi) which was exhausted by letting the salt stand for a long time in a vacuum desiccator over $P_2O_5$, next by heating the salt pulverized for a long time in a desiccating vessel until the weight was constant. It was ascertained that a basic nitrate was not formed through this heating process, by a nitrogen determination of the exhausted salt according to the method of Kjeldhl. This

[1] J. Am. Chem. Soc., 43, 2309 (1921).

[2] J. Am. Chem. Soc., 43, 2314 (1921).

analysis was performed by Mr. F. Ender and gave the following result. The percentage quantity calculated according to the formula $La(NO_3)_3$ is 12.92. Two analyses experimentally gave 12.77 and 12.70. From this statement it must be admitted that the salt was entirely free from water and not partly passed into a basic nitrate.

It should be noted that the salts employed are very hygroscopic. Before small quantities of the salt were passed into small glass tubes provided with corks the salt as well as the glass tubes were heated to a temperature of between 120 and 150°C.

## Results of the Measurements

In Tables I, II and III, under $\gamma'$ will be found the concentration expressed in mole salt diluted in 1000 gr. solvent, $\sqrt{\nu\gamma'}$ indicates the square root of the ionic concentration, $\bar{\Delta}$ the increase of the boiling point calculated from the classical theory (edial solution) $\Delta$ the same quantity observed and $1-g = \frac{\bar{\Delta}-\Delta}{\bar{\Delta}}$ cates the relative divergences of the boiling point from the classical values. As the measurements with LiCl have previously been published (loc. cit.) the results found for LiCl in $CH_3OH$ and in $C_2H_5OH$ are only represented in the following graphical representation.

### Table I

$CoCl_2$ in $CH_3OH$

$$D = 22.7\,,\ 1 - g = \frac{\bar{\Delta}-\Delta}{\bar{\Delta}}$$

$$\bar{\Delta} = 0.86\,.\,3\gamma'^{1}$$

Boiling point of solvent at 760 mm Hg = 64.7°C.

Density of solvent at boiling point $\rho$ = 0.7468.

| $\gamma'$ | $\sqrt{3\gamma'}$ | $\bar{\Delta}$ | $\Delta$ | $1-g$ |
|---|---|---|---|---|
| 0.00709 | 0.146 | 0.0183 | 0.0132 | 0.279 |
| 0.02105 | 0.251 | 0.0544 | 0.0291 | 0.464 |
| 0.0557 | 0.409 | 0.1437 | 0.0670 | 0.533 |
| 0.0933 | 0.529 | 0.2408 | 0.1013 | 0.580 |
| | | Second Series | | |
| 0.01428 | 0.207 | 0.0369 | 0.0244 | 0.340 |
| 0.03215 | 0.310 | 0.0829 | 0.0453 | 0.454 |
| 0.0525 | 0.397 | 0.1354 | 0.0661 | 0.511 |
| 0.0916 | 0.524 | 0.2364 | 0.1106 | 0.533 |

[1] The ebullioscopic constants were taken from P. Walden: "Molekulargrössen von Elektrolyten".

## Table II

$CoCl_2$ in $C_2H_5OH$

$$D = 18.7\ ,\ 1 - g = \frac{\bar{\Delta} - \Delta}{\bar{\Delta}}$$

$$\bar{\Delta} = 1.15.\ 3\gamma'$$

Boiling point of solvent at 760 mm Hg. = 78.5°C.

Density of solvent at boiling point $p$ = 0.7389.

| $\gamma'$ | $\sqrt{4\gamma'}$ | $\bar{\Delta}$ | $\Delta$ | $1-g$ |
|---|---|---|---|---|
| 0.0681 | 0.452 | 0.2348 | 0.0794 | 0.662 |
| 0.1358 | 0.638 | 0.469 | 0.1478 | 0.684 |
| 0.2080 | 0.790 | 0.717 | 0.1982 | 0.724 |
| 0.2695 | 0.899 | 0.930 | 0.2685 | 0.711 |
| **Second Series** | | | | |
| 0.00584 | 0.132 | 0.0202 | 0.0100 | 0.506 |
| 0.01743 | 0.229 | 0.0602 | 0.0220 | 0.635 |
| 0.03465 | 0.322 | 0.1195 | 0.0368 | 0.692 |
| 0.0676 | 0.450 | 0.2335 | 0.0641 | 0.726 |
| 0.1103 | 0.575 | 0.3808 | 0.1083 | 0.716 |
| **Third Series** | | | | |
| 0.00661 | 0.141 | 0.0228 | 0.0112 | 0.508 |
| 0.0138 | 0.204 | 0.0476 | 0.0216 | 0.547 |
| 0.0229 | 0.262 | 0.0790 | 0.0341 | 0.568 |
| **Fourth Series** | | | | |
| 0.00606 | 0.135 | 0.0209 | 0.0091 | 0.565 |
| 0.01538 | 0.215 | 0.0531 | 0.0179 | 0.662 |
| 0.0234 | 0.265 | 0.0806 | 0.0333 | 0.588 |

TABLE III

$La(NO_3)_3$ in $C_2H_5OH$

$$D = 18.7,\ 1 - g = \frac{\bar{\Delta} - \Delta}{\bar{\Delta}}$$

$$\bar{\Delta} = 1.15.\ 4\gamma'$$

| $\gamma'$ | $\sqrt{4\gamma'}$ | $\bar{\Delta}$ | $\Delta$ | $1-g$ |
|---|---|---|---|---|
| 0.01624 | 0.255 | 0.0746 | 0.0224 | 0.700 |
| 0.03204 | 0.358 | 0.1473 | 0.0399 | 0.730 |
| 0.0580 | 0.482 | 0.2665 | 0.0676 | 0.746 |
| 0.0999 | 0.632 | 0.4595 | 0.1186 | 0.742 |
| | | Second Series | | |
| 0.01668 | 0.258 | 0.0767 | 0.0139 | 0.818 |
| 0.0358 | 0.378 | 0.1646 | 0.0352 | 0.786 |
| 0.0564 | 0.476 | 0.2592 | 0.0587 | 0.772 |
| 0.0769 | 0.555 | 0.3535 | 0.0838 | 0.763 |
| 0.1197 | 0.692 | 0.5500 | 0.1370 | 0.750 |
| | | Third Series | | |
| 0.00277 | 0.105 | 0.0127 | 0.0066 | 0.481 |
| 0.00570 | 0.151 | 0.0262 | 0.0116 | 0.557 |
| 0.00951 | 0.195 | 0.0437 | 0.0169 | 0.614 |
| | | Fourth Series | | |
| 0.00282 | 0.106 | 0.0130 | 0.0053 | 0.592 |
| 0.00596 | 0.154 | 0.0274 | 0.0090 | 0.672 |
| 0.00885 | 0.193 | 0.0430 | 0.0140 | 0.675 |

## Discussion of the Results obtained

In Figs. 1, 2 and 3 the results are represented graphically. The square root of the ionic concentration has been put down as an abscissa and the relative divergences of the increase of the boiling point from the classical values put down as an ordinate. In Fig. 1 the results of the measurements in methyl alcohol, whose dielectric constant at the boiling point is $D = 22.7$, are indicated. In the measurements the two salts LiCl and $CoCl_2$ were employed. The valency factors of these two salts are respectively 1 and 2.83. In Figs. 2 and 3 the results of the measurements in ethyl alcohol, whose dielectric constant at the boiling point is $D = 18.7$ are represented. LiCl, $CoCl_2$ and $La(NO_3)_3$, which have the valency factors 1, 2.83 and 5.20 were used as electrolytes. The graphical statement plainly shows what part the ionic charge plays, the divergencies growing along with the increase of the valency factor.

According to Debye's theory, the curves drawn through the points experimentally fixed may be expected to go into origo with the tangents, which are represented in the figure and which are calculated by the formula 1. In Table IV the values which decide the inclination of the tangents calculated from the formula 1 are indicated.

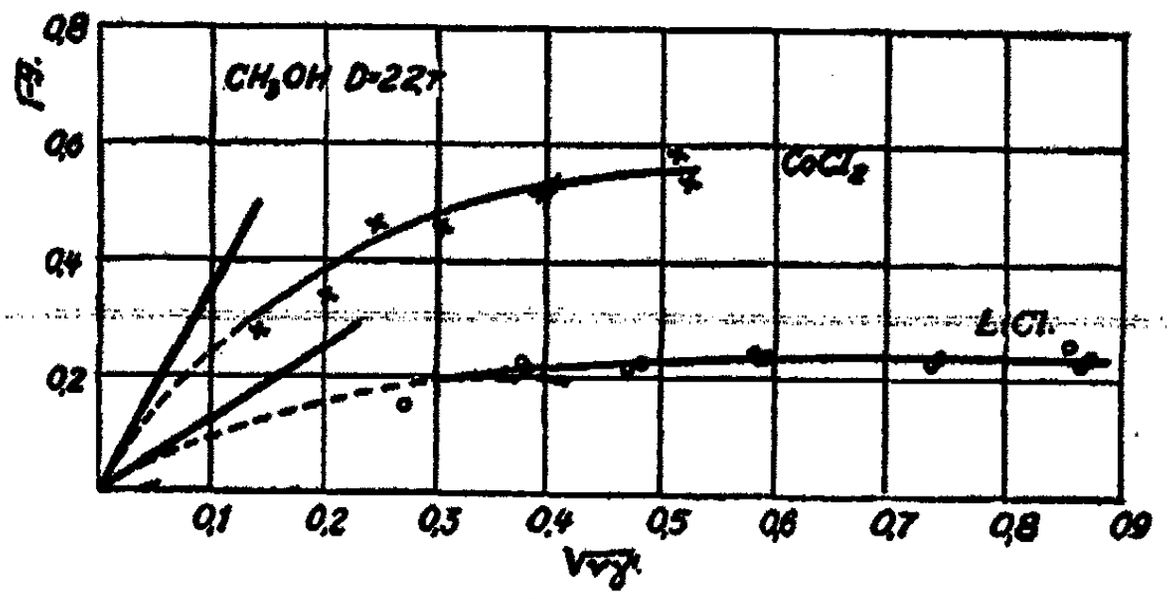



FIG. 1

These calculations were performed with the concentration expressed in mole pro 1000 gr. solvent ($\gamma'$). With the small concentrations it is permissible to put down $\gamma = \rho\gamma'$ where $\rho$ is the density of the solvent and $\gamma$ the concentration expressed in mole per liter solution.

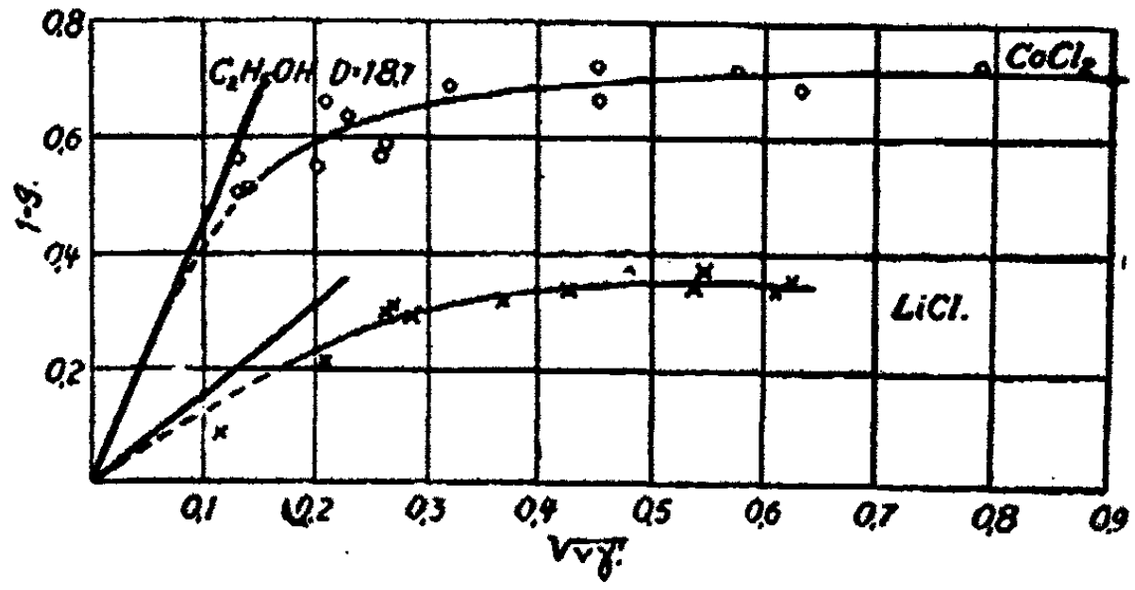



FIG. 2

TABLE IV

| | $CH_3OH$ | $C_2H_5OH$ |
|---|---|---|
| 1 − g LiCl | $1.32.\sqrt{2\gamma'}$ | $1.65.\sqrt{2\gamma'}$ |
| 1 − g $CoCl_2$ | $3.60.\sqrt{3\gamma'}$ | $4.49.\sqrt{3\gamma'}$ |
| 1 − g $La(NO_3)_3$ | | $8.25.\sqrt{4\gamma'}$ |

Although it was not possible to perform measurements with sufficiently small concentrations in order to ascertain whether there is quantitative agreement with the theory on this point, *it is at any rate possible to state that curves plotted through the points experimentally found and origo in small concentrations coincide with the tangents theoretically calculated.*

In greater concentrations, according to the theory, the proportionality between the divergencies measured and the square root of the ionic concentration may be expected not to hold good any longer. The reason for this being so,

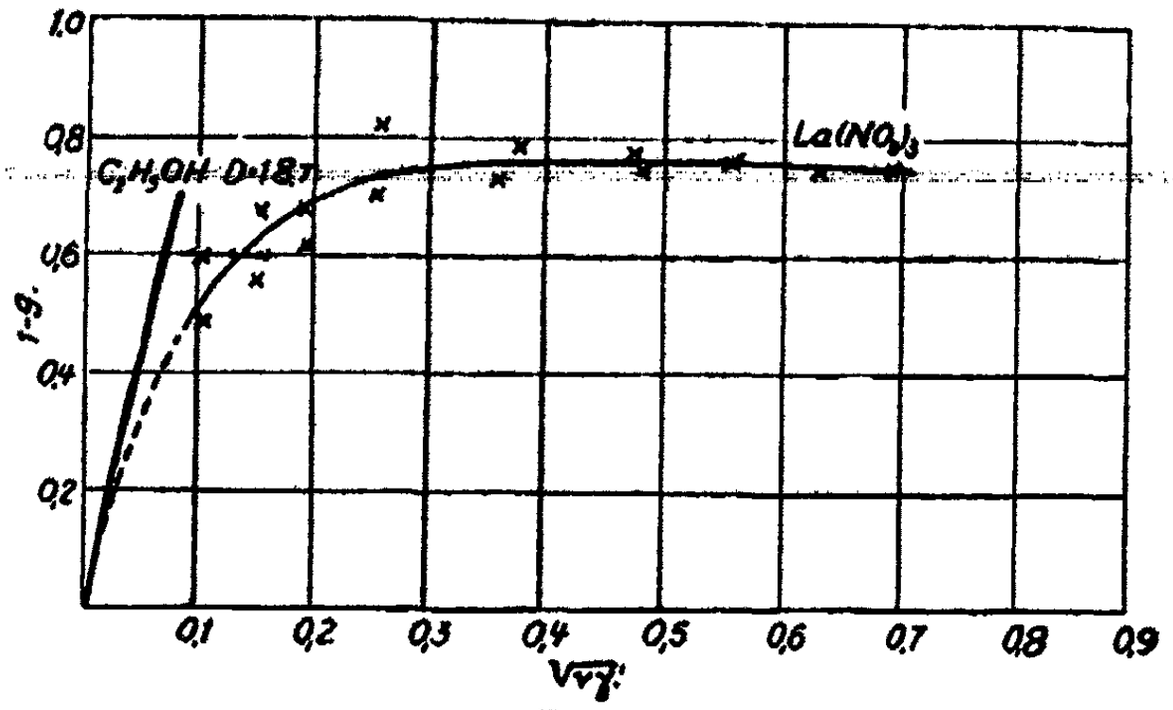



FIG. 3

is that the dimensions of the ions in comparison with the dimensions of the ionic atmosphere will be the more evident, the greater the concentration is. The theory of Debye indicates how it is possible by the aid of the divergencies from the proportionality between $1 - g$ and $\sqrt{\nu\gamma'}$ in greater concentrations to calculate the dimensions of the mean diameter of the ions. How this calculation is performed has been pointed out in the first publication of Debye and Hückel[1]. Reference is also made to the previous publication by the author (loc. cit.). I shall therefore merely indicate in Table V and VI which values of $1 - g$ and $\sqrt{\nu\gamma'}$ were employed for calculating the mean diameters of the ions and their values calculated (a).

TABLE V

$CH_3OH$

| | 1 − g | $\sqrt{\nu\gamma'}$ | a. $10^8$ cm. |
|---|---|---|---|
| LiCl | 0.24 | 0.59 | 5.4 |
| $CoCl_2$ | 0.52 | 0.40 | 4.7 |

[1] Debye and Hückel: Physik. Z., 24, 185 (1923).

TABLE VI
$C_2H_5OH$

| | 1−g | $\sqrt{\mu\gamma^1}$ | a. $10^8$ cm. |
|---|---|---|---|
| LiCl | 0.35 | 0.63 | 3.96 |
| $CoCl_2$ | 0.71 | 0.90 | 4.17 |
| $La(NO_3)_3$ | 0.75 | 0.69 | 5.78 |

Excepting the remarkably great value of the mean diameter of the ions in LiCl in methyl alcohol, the values are otherwise of the same quantity order as those found for the ionic diameters in aqueous solutions. Thus Debye and Hückel have calculated for $La(NO_3)_3$ in aqueous solution a ionic diameter equal to $4.97.10^{-8}$ cm.

All in all, one may say that these investigations contribute to verify the inter-ionic theory of Debye. As far as it has been possible by these measurements to test this theory, this also is the case when it is a question of the influence of the dielectric properties of the solvent.

## Summary

The aim of this investigation was by the help of ebullioscopic measurements to study the influence of the ionic charge on the osmotic behavior of alcoholic solutions. For the measurements were employed LiCl, $CoCl_2$ and $La(NO_3)_3$, that is to say salts consisting of resp. uni-uni, bi-uni and tri-uni valent ions. Methyl-alcohol and aethyl-alcohol (dielectric constants resp. D = 22.7 and 18.7 by the boiling points) were used as solvents. The results are compared with the interionic attraction theory of Debye-Hückel.

I wish to express my heartiest thanks to the directors of the "Jubilæumsfond" who have granted the funds necessary to carry out this work.

*The Physical Laboratory*
*University,*
*Oslo (Christiania),*
*February, 1926.*

# ADSORPTION FROM SOLUTION BY ASH-FREE ADSORBENT CHARCOALS II. PROPERTIES OF PURIFIED ADSORBENT CHARCOALS[1]

BY ELROY J. MILLER

It has generally been considered that charcoals of different origin have different and characteristic properties as far as their ability to adsorb substances from solution is concerned. In previous papers,[2],[3] from work on ash-free activated sugar charcoal, it has been pointed out that many of the properties of charcoal can be explained on the basis of adsorbed substances on their surfaces and mechanically held or occluded inorganic matter. From the results obtained with pure sugar charcoal it seemed certain that adsorbed acids and occluded or admixed inorganic matter were really responsible for the specific action of the various charcoals on solutions of acids, bases, and salts and for the contradictory data and conclusions reported in the literature concerning the existence of hydrolytic adsorption.

If the properties of these charcoals are largely dependent upon the ash and adsorbed substances then it should logically follow that all the charcoals would show the same behavior in adsorption from solution of acids, bases, and salts, provided they could be freed from the ash and adsorbed substances. The charcoals when freed from impurities might also be reasonably expected to show the same selectivity toward solutions of electrolytes as pure activated sugar charcoal and all of them should differ among themselves only in degree of activity since it is possible to prepare sugar charcoal in all degrees of activity varying from practically inert to activity of the higher order. Likewise, the charcoals of low adsorptive power may be activated until they are highly active.

Hitherto it has not been possible to test these hypotheses experimentally since no method has been known whereby the impurities may be removed from the charcoals. The method developed in this laboratory[4] for the purification of adsorbent charcoals now enables us to put these hypotheses to experimental test. This has been done with representative adsorbent charcoals and the data amply substantiate the validity of the foregoing hypotheses. All the charcoals when freed from impurities show the same selective adsorption from solutions of acids, bases, salts, acid dyes, and basic dyes. Their adsorptive properties are identical with those exhibited by pure activated sugar charcoal. The results obtained in a study of the adsorbent properties of ash-free charcoals of animal, vegetable, and carbohydrate origin prepared by the previously mentioned method are presented in this paper.

[1] Published as Journal article No. 37 from the chemical laboratory of the Michigan Agricultural Experiment Station. Published by permission of the Director.

[2] Bartell and Miller: J. Am. Chem. Soc., **44**, 1866 (1922); **45**, 1106 (1923).

[3] Miller: J. Am. Chem. Soc., **46**, 1150 (1924); **47**, 1270 (1925).

[4] J. Phys. Chem., **30**,

## Experimental

### Adsorption of Acid and Base by Purified Charcoals.

One of the outstanding characteristics of pure activated sugar charcoal is its capacity for adsorbing relatively large quantities of acids and its inability to adsorb even the slightest traces of the strong inorganic bases.[1] The behavior of the purified charcoals toward acids and bases was, therefore, determined first. It was found that the purified charcoals, like the pure sugar charcoal, adsorbed acids very strongly but did not adsorb the bases. Data

TABLE I

Adsorption of Benzoic Acid and Sodium Hydroxide by Ash-free Charcoals

| Weight and kind of charcoal used | Solution used | Amount of acid or alkali adsorbed equivalent to cc 0.02 N |
|---|---|---|
| 0.25 g Blood Charcoal | 100.0 cc 0.02 N Benzoic Acid | 50.8 |
| 0.25 " " " | 100.0 cc 0.02 N Benzoic Acid | 50.8 |
| 10.00 " " " | 100.0 cc 0.02 N NaOH | 0.0 |
| 10.00 " " " | " " " | 0.0 |
| 0.25 " Norit | 100.0 cc 0.02 N Benzoic Acid | 33.6 |
| 0.25 " " | 100.0 cc 0.02 N Benzoic Acid | 33.9 |
| 10.00 " " | 100.0 cc 0.02 N NaOH | 0.0 |
| 10.00 " " | " " " " | 0.0 |
| 0.25 " Activated Sugar Charcoal (a) | 100.0 cc 0.02 N Benzoic Acid | 57.4 |
| 0.25 " " " Charcoal (b) | 100.0 cc 0.02 N Benzoic Acid | 26.4 |
| 10.00 " " " Charcoal (a) | 100.0 cc 0.02 N NaOH | 0.0 |
| 10.00 " " " Charcoal (b) | " " " " | 0.0 |

are presented in Table I illustrating the relative adsorption of acids and bases by Merck's blood charcoal, a charcoal of animal origin, Norit, a charcoal of vegetable origin, and activated sugar charcoal, a charcoal of carbohydrate origin. The charcoals had been purified until the ash content was reduced to 0.05% or less. Benzoic acid was chosen for use because it is one of the most highly adsorbable acids and is frequently used to test the activity of adsorbent charcoals. The adsorbability of other acids was determined also and it was found that the order of their relative adsorbability by the various charcoals was the same as that reported for activated sugar charcoal[2]. That is, all the charcoals adsorbed benzoic acid most and the strong inorganic acids such as hydrochloric and sulfuric least.

[1] Bartell and Miller: J. Am. Chem. Soc., 45, 1106 (1925).
[2] Bartell and Miller: J. Am. Chem. Soc., 45, 1109 (1923).

The data in Table I show the preferential adsorption of acid and the total lack of any attraction for base. Thirty to fifty per cent. or more of the acid was adsorbed from 100 cc. of 0.02N benzoic acid by 0.25 g of the charcoals while ten grams of the charcoals did not adsorb a measurable quantity of sodium hydroxide from 100 cc. of a sodium hydroxide solution of the same concentration.

### Hydrolytic Adsorption of Methylene Blue by Purified Charcoals

When it had been established that the purified charcoals manifested the same selectivity of adsorption for acids and non-adsorption of bases as that

TABLE II

*Hydrolytic Adsorption of Methylene Blue by Purified Charcoals*

| | cc of 0.02 N NaOH required to neutralize filtrate from successive additions of 20 cc of 0.0025 M methylene blue solution to 0.25 g purified charcoal. | |
|---|---|---|
| Number of Addition | Blood Charcoal | Norit |
| 1 | 0.00 | 0.00 |
| 2 | 0.10 | 0.20 |
| 3 | 0.50 | 0.85 |
| 4 | 1.00 | —— |
| 5 | 1.10 | —— |
| 6 | 0.90 | —— |
| | (Duplicate Experiment) | |
| 1 | 0.00 | 0.00 |
| 2 | 0.10 | 0.20 |
| 3 | 0.50 | 0.90 |
| 4 | 1.00 | —— |
| 5 | 1.20 | —— |
| 6 | 0.90 | —— |

exhibited by pure sugar charcoal it seemed quite likely that the same would hold true for adsorption from solutions of basic dyes, acid dyes, and neutral salts. Adsorption of the basic dye, methylene blue, was first studied. Experiments similar to the ones[1] made with pure sugar charcoal were carried out. It was found as in the case of pure sugar charcoal that the purified charcoals adsorbed definite quantities of methylene blue completely, leaving the solution neutral in reaction. The adsorption of larger amounts of methylene blue left larger and larger amounts of acid in solution. Data showing this to be the case are presented in Table II. The experiment was carried out as follows: To 0.25 g. of charcoal in a 50 cc. Erlenmeyer flask was added 20 cc. of a 0.0025M methylene blue solution. The flask was evacuated to remove as

[1] Bartell and Miller: J. Am. Chem. Soc., 44, 1873 (1924).

much of the adsorbed air as possible. After standing for 24 hours with occasional shaking the charcoal was filtered off and the amount of acid in the filtrate was determined by titration with 0.02N NaOH using methyl red as indicator. The charcoal was then returned to the flask and a second addition of methylene blue solution made. This was repeated until too much dye remained in solution and prevented titration.

TABLE III

Hydrolytic Adsorption of Ammonium Eosin by Purified Charcoals

| Number of Addition | Blood Charcoal | Norit |
|---|---|---|
| | cc of 0.02 N HCl required to neutralize filtrate from successive additions of 20 cc of 0.0025 M ammonium eosin solution to 0.25 g of purified charcoal. | |
| 1 | 1.40 | 1.40 |
| 2 | 0.50 | 0.40 |
| 3 | 0.30 | —— |
| 4 | 0.30 | —— |
| 5 | 0.15 | —— |
| 6 | 0.10 | —— |
| | (Duplicate Experiment) | |
| 1 | 1.40 | 1.35 |
| 2 | 0.50 | 0.40 |
| 3 | 0.30 | —— |
| 4 | 0.30 | —— |
| 5 | 0.15 | —— |
| 6 | 0.10 | —— |

**Hydrolytic Adsorption of Ammonium Eosin by Purified Charcoals**

Experiments similar to the ones[1] carried out with pure sugar charcoal and acid dyes were repeated with the purified charcoals and ammonium eosin, an acid dye. Again the results were identical with those obtained with the sugar charcoal. To 0.25 g. of charcoal were added successive 20 cc quantities of 0.0025M ammonium eosin solution. After each addition the charcoal was filtered off and the amount of alkali in the filtrate determined by titration with 0.02N hydrochloric acid and phenol red indicator. A glance at Table III reveals the fact that the larger amounts of ammonium hydroxide appeared in solution after adsorption of the first 20 cc of ammonium eosin solution and that less and less alkali was set free as the adsorption of the dye decreased. This is, as previously pointed out, what would be expected from the fact that the charcoals adsorb acids and especially the organic acids very strongly but do not adsorb the inorganic bases at all. Hydrolysis is increased and acid is adsorbed, leaving free base in solution.

[1] Bartell and Miller: J. Am. Chem. Soc., 45, 1107 (1923).

## Hydrolytic Adsorption of Neutral Salts by Purified Charcoals

In a previous paper[1] it has been shown that adsorbed inorganic acids can be quantitatively removed from pure activated sugar charcoal by boiling with a slight excess of sodium or potassium hydroxide. In the same place and in a subsequent paper[2] it was shown that the sugar charcoal adsorbed from solution of the neutral inorganic salts, such as potassium chloride, potassium nitrite, and potassium sulfate only the acid arising from hydrolysis and that none of the salt as such (molecular) was adsorbed. The same has been shown to be true of the purified ash-free charcoals. When known amounts of acid have been adsorbed by the charcoals they can be quantitatively removed by boiling with a slight excess of standard alkali. As a matter of fact this procedure is part of a test for the purity of the charcoal that is applied to each lot of charcoal before use in adsorption studies in this laboratory. (The details of this test will be described later). It is unnecessary to repeat all of these experiments in detail. The following data in Table IV on the hydrolytic adsorption of potassium chloride by purified Norit and purified blood charcoal are illustrative of the results obtained with numerous salts and many samples of purified charcoals from various sources.

TABLE IV

Hydrolytic Adsorption of Potassium Chloride by Purified Charcoals

2.0 gm charcoal plus 100 cc 4 N KCl solution

| Adsorbent | Alkali set free during adsorption Equivalent to cc of 0.02 N | Acid extracted from charcoal after adsorption Equivalent to cc of 0.02 N | Amount of chloride found in extract from charcoal after adsorption. Equivalent to cc 0.02 N |
|---|---|---|---|
| Blood Charcoal | 12.10 | 12.23 | 11.83 |
| " | 10.10 | 10.30 | 10.50 |
| " | 14.50 | 14.39 | 14.66 |
| Norit | 15.80 | 15.39 | 15.57 |
| " | 12.40 | 11.56 | 12.48 |
| " | 14.46 | 14.72 | —— |

Two grams each of the charcoals were shaken with 100 cc of 4N potassium chloride solution. They were then filtered and the amount of alkali set free, the amount of adsorbed acid on the charcoal, and the amount of chloride on the charcoal were determined in the manner originally described[3]. The results are conclusive. Adsorption from neutral inorganic salt solutions by the purified charcoals, like that by the pure sugar charcoal, is hydrolytic and results in the setting free of alkali and the adsorption of an equivalent quantity of acid.

[1] Miller: J. Am. Chem. Soc., 46, 1150 (1924).
[2] Miller: J. Am. Chem. Soc., 47, 1270 (1925).
[3] Miller: J. Am. Chem. Soc., 46, 1150 (1924).

## Effect of Purification on Adsorbent Power of Charcoals

The activity of the charcoals was tested before and after purification in order to determine whether the purification process had any effect on their adsorptive capacities since this would be an indication of whether or not the process of removal of the ash alters in any way the fundamental nature or form of the active carbon. From numerous observations it seemed certain that the fundamental nature of the adsorbents is not changed by the treatment. The charcoals seemed to have approximately the same adsorptive capacity for various substances such as acids and dyes, before and after treatment. A test was made, however, in order to have more exact information on the point. A sample of blood charcoal was dried at 120°C. Its ash content was found to be 8.4%. It was then purified and its ash content reduced to 0.06%. The activity before and after purification was determined by adsorption of benzoic acid with the following results:

0.25 g of charcoal before purification adsorbed the equivalent of 48.8 cc of 0.02N benzoic acid from 100 cc of 0.02N benzoic acid solution.

0.25 g of charcoal after purification adsorbed the equivalent of 52.26 cc of 0.02N benzoic acid under the same conditions. Based on weight of adsorbent before and after purification the activity was considerably greater after purification. When allowance is made, however, for the removal of the inert ash it is seen that the activity of the adsorbent is practically unchanged. A loss of 8.4% ash was balanced by an increase of 7.1% in activity.

Further evidence that the purification process does not effect the fundamental nature of the adsorbent carbon is found in the fact that a pure activated sugar charcoal that has been subjected to the treatment has the same properties after treatment that it had before.

## Tests for the Activity and Purity of Adsorbent Charcoals

From the results obtained in the studies with the pure activated sugar charcoal tests have been developed by means of which the activity and purity of adsorbent charcoals may be determined. Numerous tests have been used heretofore to determine the activity of charcoals. Adsorption of dyes such as malachite green and methylene blue, adsorption of phenol, and adsorption of iodine are examples of tests frequently advocated in the literature. While all of these are of value they, nevertheless, have obvious disadvantages. A test, at once simple and giving parallel results with the others, has been found convenient and reliable and without necessitating the use of expensive apparatus and complex reagents of uncertain purity. The test, adsorption capacity for benzoic acid, is carried out as follows:

To 0.25 g of charcoal (dried at 120°C. or above) in a 200-300 cc pyrex Erlenmeyer flask is added 100 cc of 0.02N benzoic acid solution. The flask is shaken to insure thorough wetting of the charcoal. Evacuating the flask with a good water pump facilitates the wetting of the charcoal and also removes adsorbed air. The mixture is allowed to stand for 18-24 hours with an occa-

sional shaking by hand[1] after which it is filtered with the aid of slight suction through a disk of hardened ash-free filter paper in a Gooch crucible. The amount of acid adsorbed is determined by titration of aliquots of the filtrate with 0.02N sodium or potassium hydroxide. A good grade of charcoal will adsorb in the neighborhood of 50% of the acid but by further activation it is possible to increase the adsorption capacity somewhat.

The presence or absence of adsorbed acids and alkaline inorganic matter in the charcoals may be determined by two tests based on the fact that inorganic acids adsorbed on charcoal may be quantitatively removed and estimated by treatment with alkali and on the fact that charcoal free from adsorbed acids does not have any effect on the strong inorganic bases: (a) A known amount of hydrochloric acid is added to a sample of charcoal. The acid is then quantitatively removed and determined. If the amount removed is the same as the amount added it is evident that there are neither adsorbed acids nor alkaline impurities present. (b) The absence of adsorbed acids is further confirmed by shaking the charcoal with a known amount of sodium or potassium hydroxide. If none of the hydroxide is neutralized it is certain that there are no adsorbed acids on the charcoal. The tests are carried out as follows:

(1) Two grams of charcoal in an Erlenmeyer flask are shaken with twenty cc of 0.02N hydrochloric acid. After an hour or two thirty cc of 0.02N sodium hydroxide is added and the suspension is boiled for a few minutes. It is then filtered through a disk of hardened filter paper in a Gooch crucible and washed several times with conductivity water. The charcoal is then washed back into the flasks with conductivity water, 10 cc more of alkali added, boiled for a few minutes, and filtered as before. The charcoal is finally washed two or three times by boiling with conductivity water and filtering. The combined filtrates and washings are transferred to an Erlenmeyer flask and titrated with 0.02N hydrochloric acid, observing the usual precaution of boiling off carbon dioxide between the later additions of acid until the lemon yellow color of the indicator (phenol red) is permanent. The factor for the alkali is obtained by standardizing against the hydrochloric acid in the same manner. If the amount of alkali used is exactly equivalent to the acid originally added to the charcoal plus that required in the titration of the filtrate and washings it is obvious that there are no alkaline impurities on the charcoal. If the amount of alkali is greater than this sum it indicates, of course, that there are adsorbed acids on the charcoal. If the amount is less than this sum it indicates the presence of soluble alkaline impurities.

(2) Two grams of charcoal are suspended in approximately 100 cc of conductivity water in an Erlenmeyer flask and 20 cc of 0.02N sodium hydroxide is added. The suspension is boiled for a few minutes and filtered in the usual manner. The charcoal is washed as before by boiling two or three times with conductivity water and filtering. The combined filtrates are titrated

[1] Equilibrium would be reached much sooner, of course, if the shaking were done in a mechanical shaker but practically the same results are obtained in the longer period with occasional shaking by hand.

with 0.02N. hydrochloric acid as in (1). If the amount of alkali in the filtrates is the same as that originally added the absence of adsorbed acid is assured; if less, the presence of acid on the charcoal is indicated.

As started earlier in this paper, these tests have been regularly applied to each new lot of charcoal used in adsorption work and consistent results have always been obtained with charcoals conforming to these standards of purity.

The method for purification of adsorbent charcoals described in the previous paper together with these tests for activity and purity make it possible to clear up many contradictory statements and reports existing in the literature on adsorption from solution by charcoal and should insure consistent and reproducible results in the future in this field of investigation. In another paper the results so far obtained with the pure ash-free charcoals will be compared with the data reported in recent years for unpurified materials.

## Summary and Conclusions

(1) The properties of adsorbent charcoals of representative types and origins which have been freed from ash and adsorbed substances have been studied.

(2) All adsorbent charcoals after purification have the same properties of selective adsorption from solutions of electrolytes.

(3) The adsorbent properties of these purified charcoals are identical with those of pure ash-free activated sugar charcoal.

(4) All pure ash-free adsorbent charcoals adsorb acids but do not adsorb the inorganic hydroxides. All adsorb salts hydrolytically.

(5) The data in this paper afford further evidence that the prevailing idea that charcoals adsorb acids and bases equally is erroneous.

(6) Methods are described by means of which the activity and purity of adsorbent charcoals may be determined. These tests enable the investigator to determine whether or not his charcoal contains adsorbed acids or alkaline impurities and whether it is of high or low order of activity.

*East Lansing,*
*Michigan.*

# COLLOIDAL SYSTEMS IN NITROMETHANE*

BY JOHN WARREN WILLIAMS AND J. A. SKOGSTROM

In the course of a series of experiments concerning the physical properties of nitromethane it was noted and reported[1] that the effect of various drying agents on that liquid presented an interesting study. It was shown at that time that when phosphorus pentoxide is used to dry nitromethane a colloidal suspension is obtained which does not settle provided slight amounts of water are present. When the water content is reduced to within certain limits a gel is formed on standing, and there is a relation between the amount of water present and the time required for the formation of the gel. It was also stated that the gel formation might again be stopped by reducing the water concentration still further. Apparently there are, therefore, rather definite concentrations of water corresponding to the most rapid and positive formation of the gel and concentrations above and below which gels do not form.

A possible explanation of these effects was given[1] as follows: "The phosphorus pentoxide is present in a finely divided condition and is surrounded by a protecting film of phosphoric acid which has been formed in the reaction with the water which is present in small amounts. Perhaps in this case the phosphoric acid-phosphorus pentoxide agglomerates are held in a definite and regular structure, with the nitromethane occupying the spaces within the gel structure."

This explanation suggested that other substances which are reactive with phosphorus pentoxide in a manner similar to that of water might be effective as peptizing agents in nitromethane systems. Also further experiments using water as the peptizing agent were carried out. The purpose of this paper is, then, to present the results of these studies.

The results are of particular interest in the light of results published by Brown and Bury[2] on "Colloid Systems in Nitrobenzene." This paper and the previous paper of this series[1] appeared almost simultaneously.

## Purification of Materials

The nitromethane used in the experiments was obtained from two sources, the Eastman Kodak Company, and this laboratory. The liquid prepared here was made by the method described by Auger.[3] In all cases the nitromethane was dried with calcium chloride, after which it was dried with phosphorus pentoxide and allowed to stand for a week. It was distilled directly from the drying agent into carefully dried flasks, the boiling points of the fractions used were constant to within 0.05°C.

* Contribution from the Laboratory of Physical Chemistry, University of Wisconsin.

[1] Williams: J. Am. Chem. Soc., 47, 2644 (1925).

[2] Brown and Bury: J. Phys. Chem., 29, 1312 (1925).

[3] Auger: Bull. (3) 23, 333 (1900).

The various organic acids, aldehydes, ketones and alcohols were purified and dried according to the usual methods, after which they were carefully fractionated. The phosphorus pentoxide, of "C. P." grade, was obtained from the Mallinckrodt Chemical Company, and was used in most cases without further purification since it was impossible in several trials to detect any difference in the colloidal properties of the nitromethane, other things being equal, when re-sublimed phosphorus pentoxide was used.

## Experimental Results

The experimental work is described in two sections:

A. Experiments with water as peptizing agent.
B. Experiments with other peptizing agents.

Section A. The object of this series of experiments was to prove that the concentration of water present in nitromethane may be reduced to such an extent that colloidal systems of phosphorus pentoxide cannot be formed in nitromethane. The method used is detailed below.

Nitromethane (about 15cc) was distilled directly from phosphorus pentoxide into each of several glass tubes which had been thoroughly cleaned and dried. To each tube was added approximately one gram of phosphorus pentoxide. The open ends of the tubes were passed rapidly through a fine jet of escaping steam to introduce an amount of water sufficient to cause rapid gel formation. The tubes were then sealed off. The material in the tubes was not shaken. The time required for the gel to form was approximately one week. The tubes were allowed to stand fifteen months, after which a considerable portion of the nitromethane had synerized. This nitromethane must have been intensively dried. When it was shaken with a fresh portion of phosphorus pentoxide it was impossible to prepare a gel or even a permanent suspension. The fact that the phosphorus pentoxide settles out completely on standing seems to demonstrate that when water is absent or reduced to a very low concentration, nitromethane no longer shows colloidal properties with phosphorus pentoxide.

In this connection it may be mentioned that the addition of small amounts of water to nitrobenzene make possible the preparation of colloidal solutions of phosphorus pentoxide which show similar properties to the systems in nitromethane, a fact which Brown and Bury do not mention.

Section B. With organic acids, aldehydes, ketones, and alcohols it has been found possible to prepare colloidal solutions of phosphorus pentoxide in nitromethane. The phenomenon seems to be exactly similar to that reported when water is used as the peptizing agent. For certain concentrations of the peptizing agent the solutions become more and more viscous and finally set to a firm gel. There is in all cases a definite concentration of agent which corresponds to the most rapid and positive formation of the gel, and concentrations above and below which gels do not form.

A series of experiments was carried out using the lower members of the aliphatic acid homologs as peptizing agents. A typical experiment consists of

treating ten grams of nitromethane (distilled directly from phosphorus pentoxide into a small flask) with 0.05 gr. formic acid. To this solution approximately 0.5 gram of phosphorus pentoxide is added and the time required for the gel to set is noted. A summary of the results of this series is given in Table I.

An exactly similar series of experiments, shown in Table II, was carried out using the lower members of the aliphatic alcohol homologs, the effects of methyl, ethyl, propyl, iso-propyl, butyl, iso-butyl and amyl alcohols being studied. These systems showed similar properties.

TABLE I

Gel Formation in Nitromethane with Aliphatic Acids.

10 grams $CH_3NO_2$ and 0.5 gram $P_2O_5$ used in all cases.

| Peptizing Agent | Molecular Amt. Used | Time of Setting of Gel | Color of Gel. |
|---|---|---|---|
| Formic Acid | 0.00264 | 14 days | |
| | .00528 | | White |
| Acetic Acid | 0.00174 | 30 min. | |
| | .00348 | 90 min. | Dark Brown |
| | .00522 | 30 min. | |
| Propionic Acid | 0.00137 | 120 min. | |
| | .00274 | 10 min. | Brown |
| n-Butyric Acid | 0.00108 | 1 min. | |
| | .00217 | 5 min. | Yellow |

TABLE II

Gel Formation in Nitromethane with Alcohols.

10 grams $CH_3NO_2$ and 0.5 gram $P_2O_5$ used in all cases.

| Peptizing Agent | Molecular Amt. Used | Time of Setting of Gel | Color of Gel. |
|---|---|---|---|
| Methyl Alcohol | 0.0022 | 21 days | White |
| Ethyl Alcohol | 0.00173 | 21 days | White |
| | .00346 | | |
| Propyl Alcohol | 0.00133 | 14 days | White |
| | .00266 | | |
| Iso-propyl Alcohol | 0.00133 | 65 min. | Cream |
| | .00266 | 10 min. | |
| Butyl Alcohol | 0.00109 | 40 min. | Yellow |
| | .00218 | 15 min. | |
| Iso-butyl Alcohol | 0.00109 | 60 min. | |
| | .00218 | 30 min. | White |

From these tables it will be noted that for equimolecular amounts of peptizing agent the time required for the formation of the gel tends to decrease with an increase in the length of the hydrocarbon chain, at least as far as the experiments have been carried out. In some instances the gel formation is exceedingly rapid. The time of gel formation for the lower members seems to approach that of the water system.

The aldehydes and ketones showed similar behavior. The gels formed were in all cases highly colored.

## Theoretical

The explanation of these effects would seem to be exactly analogous to that given for the water systems. The phosphorus pentoxide present in a finely divided condition reacts chemically with the peptizing agent to form a protecting film about each particle. These agglomerates are then held in a definite, regular gel structure. There are several reasons which indicate that the gels are formed as a result of a chemical reaction between the phosphorus pentoxide and the drying agent.

First, the fact that the gels are of different colors is an indication of chemical reaction. These colors correspond to those obtained when $P_2O_5$ is allowed to react with the peptizing agent in the pure state. The cause of these reactions may be considered to be the great affinity of the phosphorus pentoxide for molecules containing an hydroxyl group. These reactions are in general very complicated leading in many cases to polymerization.

Second, when traces of benzene and other substances which do not react chemically with phosphoric anhydride are added to the pure nitromethane-phosphorus pentoxide system there seems to be no tendency toward gel formation. The solution becomes slightly milky, but not at all to the extent which is obtained when the more active peptizing agents are used.

Third, heat is evolved when the peptizing agent is added to the mixture of nitromethane and phosphorus pentoxide. In several cases this evolution is accompanied by a violent reaction. When formic acid was added an evolution of carbon monoxide gas took place showing that it was decomposed by the phosphorus pentoxide according to the reaction

$$HCOOH \rightarrow CO + H_2O$$

Table I shows that the time required for this gel to set is of the same order as that reported[1] for the water systems.

It is difficult to account for these colloidal systems in nitromethane in any other manner. It is true that in nitromethane itself there is the possibility of reaction with phosphorus pentoxide, since it has been shown[2] that an equilibrium exists between tautomeric forms which may be represented as follows:

$$CH_3N \begin{matrix} =O \\ =O \end{matrix} \underset{\text{acid}}{\overset{\text{alkali}}{\rightleftharpoons}} CH_2N \begin{matrix} =O \\ -OH \end{matrix}$$

[1] Williams: J. Am. Chem. Soc., 47, 2644 (1925).

[2] Hantzsch and Schultze: Ber., 29, 699, 2251 (1896).

It does not seem probable, however, that the colloidal systems can be explained on the basis of this tautomerism, since similar colloidal systems are found in nitrobenzene, a substance which does not show tautomerism.

In addition, the results of experiments described under Part A indicate that colloidal systems are not formed when pure, dry nitromethane is treated with phosphorus pentoxide.

## Conclusions

Although the colloidal systems which have been described are in many respects similar to those reported for the nitrobenzene systems their explanation appears to differ. Referring to the formation of colloidal systems in nitrobenzene, Brown and Bury state that "chemical reaction between the constituents can hardly explain this behavior". The evidence here presented seems to indicate that colloidal systems in nitromethane are formed as a result of a chemical reaction.

From the results of experiments which have already been reported it would seem as if it might be possible to prepare colloidal systems in many of the more common non-reactive organic liquids, such as benzene, toluene, pentane, hexane, carbon tetrachloride, chloroform, etc., with phosphorus pentoxide provided the correct amount of peptizing agent could be introduced. Systems of this sort should be comparatively simple ones from which definite conclusions regarding the structure of gels could be drawn.

## Summary

1. The formation of colloidal systems of phosphorus pentoxide in nitromethane with water as a peptizing agent is described. There is a definite concentration of water above and below which a gel will not form, also there is a definite concentration of water which corresponds to the most rapid and positive formation of the gel.

2. Colloidal systems of phosphorus pentoxide in nitromethane are formed with organic acids, aldehydes, ketones and alcohols as peptizing agents. Within definite concentration limits of peptizing agent gels are obtained in comparatively short intervals of time.

3. Evidence is presented which indicates that the formation of these colloidal systems results from a chemical reaction between the phosphorus pentoxide and the drying agent.

*Madison,*
*Wisconsin.*

# THE HEAT CAPACITY OF CALCIUM SILICATE

BY GEORGE S. PARKS AND KENNETH K. KELLEY

In an extremely careful and accurate investigation White[1] has determined the specific heats of silica and of a number of silicates between room temperature and an upper limit of 1100° to 1400° C. Except for the case of silica itself, it appears that none of these compounds have hitherto been studied at lower temperatures. In view of this situation, we have recently made measurements upon one of Dr. White's samples, $CaSiO_3$ in the form of pseudo-wollastonite, from liquid air temperatures up to that of the room. Thus the heat capacity curve for this substance is now known from 88° to 1573° K.

## Material, Method and Results

The pseudo-wollastonite was a synthetic material, which Dr. White had used previously in his determinations at higher temperatures and which he very kindly loaned to us for the present investigation. Concerning it he says, in his article, "the solid impurities are undoubtedly negligible in their effect on the specific heat. Probably this is also true of the gaseous impurities. . . ." From this statement and the degree of accuracy of White's work, we may safely conclude that impurities in this sample will not cause an error as great as 0.1%.

In principle, the method of Nernst was employed with an aneroid calorimeter for measuring the "true" or instantaneous heat capacity at constant pressure. The apparatus and details of experimental procedure were exactly the same as those described in an earlier paper.[2] In view of the accuracy of the various measurements involved, we believe that the error in the specific heats thus obtained is in no case greater than 1%.

TABLE I

The Heat Capacities of Pseudo-Wollastonite at Constant Pressure

| Temp. °K | Cp per gram | Cp per gram atom |
|---|---|---|
| 88.2 | 0.0653 | 1.52 |
| 91.1 | 0.0678 | 1.57 |
| 92.3 | 0.0684 | 1.59 |
| 95.7 | 0.0725 | 1.68 |
| 151.5 | 0.1133 | 2.63 |
| 194.7 | 0.1396 | 3.24 |
| 199.4 | 0.1416 | 3.29 |
| 275.4 | 0.1735 | 4.03 |
| 278.2 | 0.1754 | 4.07 |
| 295.8 | 0.1829 | 4.25 |
| 298.3 | 0.1832 | 4.25 |

[1] White: Am. J. Sci., 47, 1 (1919).

[2] Parks and Kelley: J. Phys. Chem., 30, 47 (1926).

Our experimental values, expressed in terms of the 15° calorie and with all weights reduced to a vacuum basis, appear in Table I. In Table II we have also recorded White's data for the true mean atomic heats of pseudo-wollastonite. In the neighborhood of 273° K. where the two sets of data overlap, the value taken from our curve is 1.1% above that of White, who estimates a possible uncertainty of 0.6% in his result. Thus this difference is

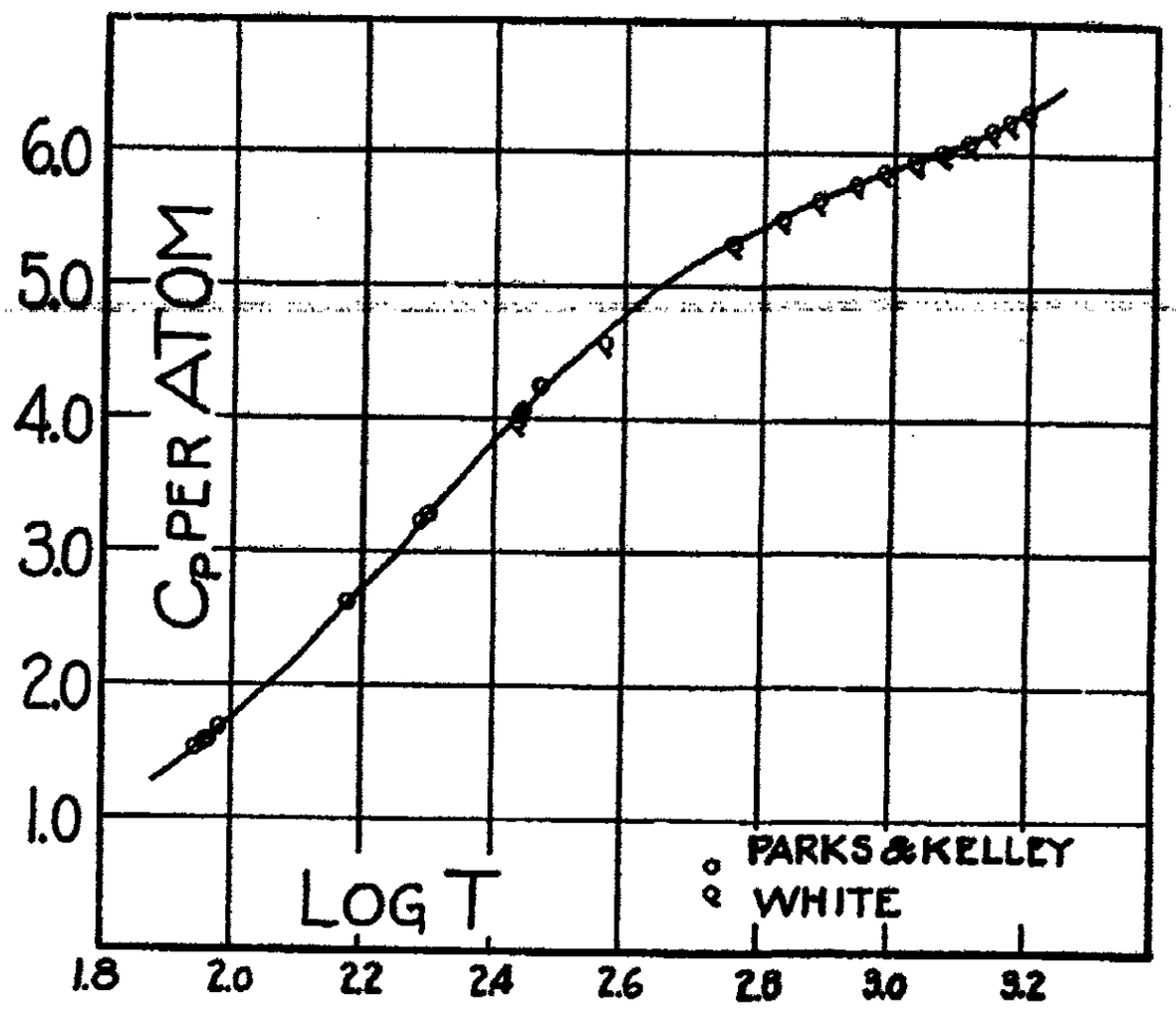



FIG. 1

well within the maximum possible discrepancy (1.6%), based upon the estimated possible errors of 1.0% and 0.6%, respectively, in the two separate investigations. The two sets of results are shown graphically in Fig. 1 where Cp per gram atom is plotted against the logarithm of the absolute temperature.

TABLE II

White's Results for Pseudo-Wollastonite

| Temp. °K. | Cp per gram atom | Temp. °K. | Cp per gram atom |
|---|---|---|---|
| 273.1 | 3.98 | 1073.1 | 5.95 |
| 373.1 | 4.58 | 1173.1 | 6.02 |
| 573.1 | 5.32 | 1273.1 | 6.10 |
| 673.1 | 5.50 | 1373.1 | 6.18 |
| 773.1 | 5.65 | 1473.1 | 6.26 |
| 873.1 | 5.77 | 1573.1 | 6.33 |
| 973.1 | 5.87 | | |

## Discussion

Calcium metasilicate might well be considered as a product of the reaction, $CaO+SiO_2=CaSiO_3$, and according to Kopp's law its molecular heat capacity should be the sum of the heat capacities of calcium oxide and silicon dioxide. Using our own data[1] for calcium oxide at the lower temperatures together with those of Magnus[2] above 300°K. and the results of Simon[3] and of White for silica glass, we have constructed curves for these two compounds and have thereby obtained the molecular heat capacities which appear in Columns 2 and 3 of Table III. The fourth column contains the experimental

TABLE III

Molecular Heat Capacities of $CaSiO_3$ and its Components

| Temp., °K. | Cp of CaO experimental | Cp of $SiO_2$ experimental | Cp of $CaSiO_3$ experimental | Cp of $CaSiO_3$ calculated |
|---|---|---|---|---|
| 100 | 3.78 | 3.84 | 8.8 | 7.6 |
| 150 | 6.52 | 5.90 | 13.0 | 12.4 |
| 200 | 8.38 | 7.74 | 16.5 | 16.1 |
| 250 | 9.52 | 9.35 | 19.0 | 18.9 |
| 300 | 10.24 | 10.74 | 21.2 | 21.0 |
| 350 | 10.74 | 11.75 | 22.5 | 22.5 |
| 400 | 11.14 | 12.60 | 23.6 | 23.7 |
| 450 | 11.42 | 13.40 | 24.7 | 24.8 |
| 500 | 11.62 | 14.10 | 25.6 | 25.7 |
| 550 | 11.82 | 14.67 | 26.3 | 26.5 |
| 600 | 11.96 | 15.03 | 26.8 | 27.0 |
| 650 | 12.08 | 15.36 | 27.3 | 27.4 |

values for the molecular heat of pseudo-wollastonite, while in the last column appear the corresponding results calculated by adding the heat capacities of the component oxides. As the data clearly show, the agreement between the calculated and the experimental values is excellent above 200° K., altho there is considerable discrepancy below this point.

By a similar procedure we have been able to estimate successfully the heat capacity of magnesium silicate above 300° K., as the following data in Table IV indicates. In this particular case we have used White's experimental results for magnesium silicate and the values of Magnus for magnesium oxide.

---

[1] Parks and Kelley: loc. cit.

[2] Magnus: Physik. Z., 14, 5 (1913). In calculating his results, Magnus takes the interval specific heat as equal to the true specific heat at the middle temperature of the interval. As White has shown, this procedure causes progressively larger errors in the heat capacity of silica as we go to higher temperatures, the error being 2 to 3% for the interval 17-550° C. In preparing the data for the oxides of calcium and magnesium in the present paper, we have therefore increased somewhat the values obtained by Magnus at these higher temperatures. Our corrections are respectively 0.8% and 2.5% at 450° and 650° K. and vary proportionately in the intervening range.

[3] Simon: Ann. Physik, (4) 68, 255 (1922).

TABLE IV

Molecular Heat Capacities of $MgSiO_3$ and its Components

| Temp., ° K. | Cp of MgO experimental | Cp of $SiO_2$ experimental | Cp of $MgSiO_3$ experimental | Cp of MgSiO calculated |
|---|---|---|---|---|
| 300 | 8.92 | 10.74 | 19.8 | 19.7 |
| 350 | 9.62 | 11.75 | 21.4 | 21.4 |
| 400 | 10.13 | 12.60 | 22.9 | 22.7 |
| 450 | 10.41 | 13.40 | 24.2 | 23.8 |
| 500 | 10.68 | 14.10 | 25.2 | 24.8 |
| 550 | 10.94 | 14.67 | 26.0 | 25.6 |
| 600 | 11.18 | 15.03 | 26.6 | 26.2 |
| 650 | 11.38 | 15.36 | 27.0 | 26.7 |

In view of these two examples, it seems reasonable to conclude that the heat capacity of a simple silicate can be accurately estimated, except at the very lowest temperatures, from the known heat capacities of its component oxides.

*Department of Chemistry,*
*Stanford University,*
*April 28, 1926.*

# SOLUBILITY OF SILVER OXIDE
## (in mixtures of water and alcohol at 25° C.)

BY SIMON KLOSKY AND LEO WOO[1]

### Introduction

The solubility of silver oxide in water has been determined by several workers using different methods,[2] but no data seem to be available on the solubility of silver oxide in mixtures of water and alcohol.

### Experimental

Silver oxide was prepared by treating a concentrated solution of analyzed silver nitrate with an excess of sodium hydroxide solution, made by dissolving sticks of C. P. sodium hydroxide. The precipitate was allowed to settle and washed by decantation until the wash water gave no sodium flame test. The silver oxide was then dried in a desiccator over concentrated sulphuric acid.

The ethyl alcohol was prepared by carefully redistilling twice with a long column still a constant boiling fraction of 95% C. P. ethyl alcohol. No attempt was made to dry the alcohol—its composition having been determined by measuring the density with a pyknometer.

The dried silver oxide was placed in mixtures of water and alcohol contained in bottles which were equipped with mercury seals to prevent evaporation of alcohol. The bottles were put in a thermostat at 25° C. and stirring was continued for about ten hours. The solutions were filtered after being allowed to settle for about an hour. A small amount of 0.1N KCl was added to the filtrate and the turbidity was compared with that of a standard solution prepared by precipitating silver nitrate of known concentration under identical conditions including the same percentage of alcohol. Two determinations were made in each case. The mean values are given below:

| % of alcohol by weight. | Solubility of silver oxide, mgms. per liter. |
|---|---|
| 0 | 26.2 |
| 10.95 | 19.7 |
| 22.92 | 18.1 |
| 34.30 | 17.6 |
| 45.70 | 17.4 |
| 64.00 | 14.5 |
| 77.00 | 12.0 |
| 91.50 | 9.1 |

[1] Contribution from the Martin Maloney Chemical Laboratory of The Catholic University of America. Extract from Master's Thesis, 1926.

[2] Noyes and Kohr: J. Am. Chem. Soc., 24 1144 (1902).—Gravimetric. Abegg and Cox: Z. physik. Chem., 46 1 (1903).—E. M. F. Rebière: Bull. (4) 17, 309 (1915).—Gravimetric. Whitby: Z. anorg. Chem., 67 62 (1910).—Colorimetric. Bottger: Z. physik. Chem., 46, 521 (1903)—Conductivity.

The results can be represented by a curve whose shape is similar to that of silver nitrate in mixtures of water and alcohol.

An attempt was made to determine the solubility of silver oxide in mixtures of water and alcohol by precipitating as AgI.[1] The results were much higher, which was due to the adsorption of barium ion used as a precipitating agent. The amount of barium adsorbed was determined and when calculated as barium iodide yielded values in agreement with those found nephelometrically.

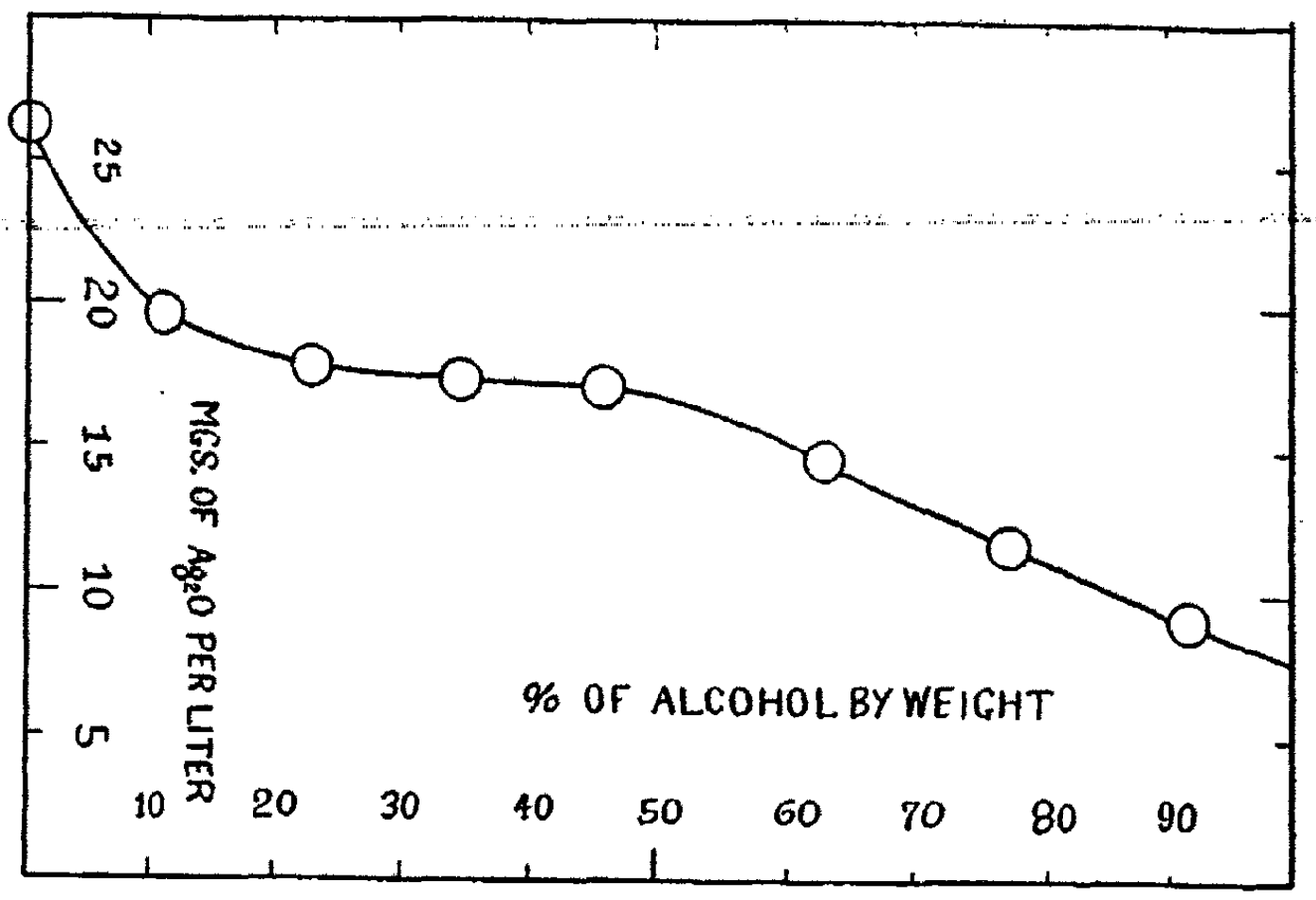



FIG. 1

## Summary

The solubility of silver oxide in mixtures of alcohol and water has been determined at 25° C. by a nephelometric method.

[1] Flynn: Unpublished work, Martin Maloney Chemical Laboratory, 1925.

# ADSORPTION AND REACTION. II*

## The Setting of Litharge-Glycerine Cement.

BY HARVEY A. NEVILLE

A mixture of lead monoxide and glycerine is the answer to many requirements for a practical cement. The set product has considerable strength, is waterproof, and makes a tight joint, since it expands slightly in hardening. There is, however, almost no information available concerning either the type of reaction involved in its setting or the product formed.

The reaction between litharge and glycerine, resulting in a cement, was found to be highly exothermic. This suggested that the process could be followed by the method employed to study the setting of plaster of Paris, described in the previous article[1]. The results when the method is applied to mixtures of litharge and glycerine seem of particular interest because of their complete analogy to those obtained for plaster of Paris. The processes of setting in the two cases are obviously not similar in respect to the type of chemical action which obtains, but they are alike in that they both involve two stages: (1) a preliminary adsorption of the liquid phase by the solid; followed by (2) a chemical reaction between the adsorbed liquid and the adsorbent.

### Experimental Part

The procedure was quite as in the study of plaster of Paris. Small cardboard boxes (about one cu. in.) were used as molds for the cement. The mixture of litharge and glycerine was stirred vigorously in a small beaker for either one or three minutes and then poured into the mold. A thermometer was introduced and the mold was placed in an insulated receptacle. The rise in temperature with time was noted and the curves, as illustrated in Fig. 1, closely resemble those for plaster of Paris. The point -S- on the curves indicates the end of the first stage in the setting. At this time the mass is quite stiff and has a dry appearance. The volume change of the mixture in setting was also determined and, as in the case of plaster of Paris, consists in a contraction corresponding to the first stage, followed by a slight expansion as the chemical reaction occurs.

The existence of two distinct forms of lead monoxide, yellow rhombic and red tetragonal, has finally been definitely established[2]. Commercial litharge is usually a buff colored powder, and this form was used in these experiments except where otherwise stated. The litharge was in all cases sifted through a 120-mesh sieve. Some commercial litharge consists of scales or flakes and has a red color. This is the red tetragonal form, produced by crystallization from

* Contribution from the Department of Chemistry of the University of Illinois.

[1] Neville: J. Phys. Chem., 30, 1037 (1926).

[2] Applebey and Reid: J. Chem. Soc., 121, 2129 (1922).

the molten stage. If any form of lead monoxide is heated to dull redness, it changes to a canary yellow powder. These forms have different rates of setting with glycerine, as noted in Table I. The commercial buff powder sets most rapidly. It is probably amorphous or incompletely crystalline—somewhat as is plaster of Paris—and hence its adsorptive ability is great. The yellow powder, made by heating litharge just below its melting point, probably has a more complete crystal structure and it sets less readily. The red

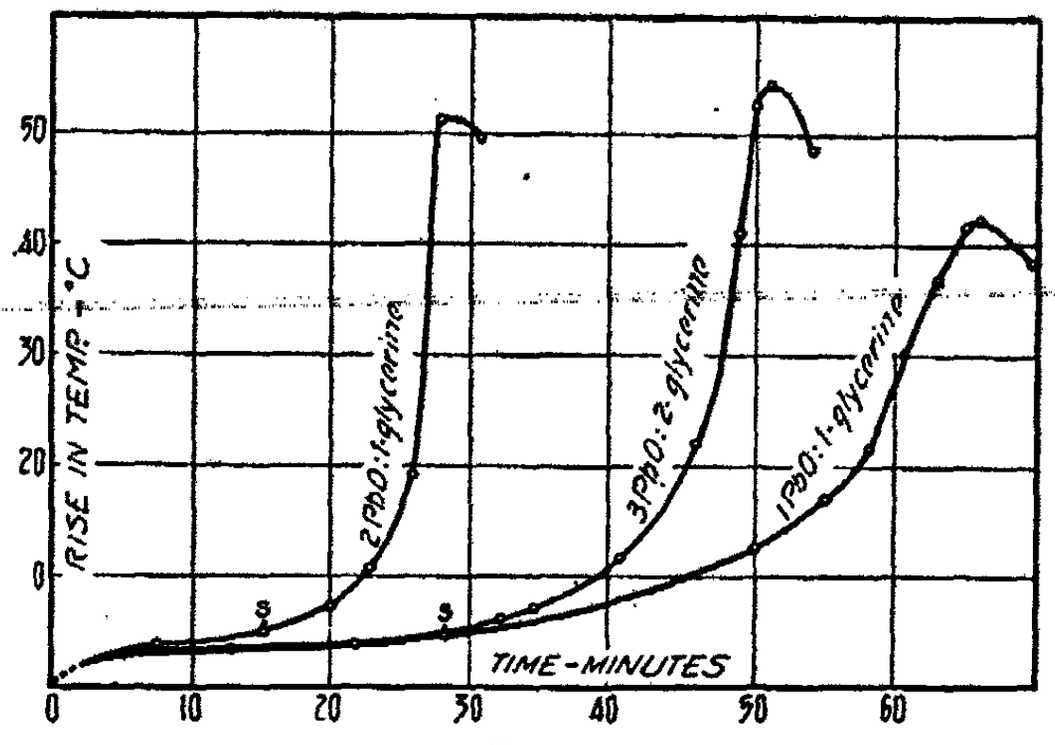



FIG. 1

The Setting of Litharge and Glycerine—Thermal Effect

crystalline form, even when finely powdered, tends to settle out from the mixture with glycerine, showing lack of adsorptive capacity. Its setting is slow; very little chemical action occurs as is shown by the relatively slight rise in temperature. This flaky red form of litharge is hence not satisfactory for use in the cement.

TABLE I

| Description of Materials | | | | Stirred 1 min. | Stirred 3 min. |
|---|---|---|---|---|---|
| *Equimolecular:* | | | | | |
| 1. Litharge and glycerine, | | | | *4 hours | 66 min. |
| 2. " | " | " | both dried at 106°C. | *1 day | *3 hours |
| 3. " | " | " | with 10% water added | 30 min. | 20 min. |
| 4. " | " | " | " " " " to litharge instead | 20 " | 13 " |
| 5. " | " | " | with 10% dil. HCl added | —does not set— | |
| 6. " | " | " | " 10% dil. KOH " | 13 min. | |
| 7. " | " | " | " 10% sat. $Pb(NO_3)_2$ | —very slow—crumbly | |
| 8. PbO (yel) | " | " | " 10% water | 36 min. | |
| 9. PbO (red) | " | " | " 10% " | †56 " | |

* Approximately.

† Rise in temperature only 8°C. Product crumbly.

| *Proportions* | *Rise in Temperature* | |
|---|---|---|
| 1 mol. PbO : 1 mol. glycerine | 44 degrees C. | 66 min. |
| 3 mol. PbO : 2 mol. " | 57 " | 51 " |
| 2 mol. PbO : 1 mol. " | 54 " | 28 " |

*Acceleration.*—The results set forth in Table I show that the dried materials set very slowly, hence water is a catalyst for the reaction. Furthermore, the catalytic effect of water is more pronounced if the water is used to moisten the litharge rather than added to the glycerine. The setting is also hastened if the mixture is stirred for a longer time at the start. Acids and salts with neutral or acid reaction, dissolved in water and added to the glycerine, prevent or retard the setting. Alkalies and salts with basic reaction ($Na_2CO_3$) accelerate the setting. The $OH^-$ ion apparently aids the adsorption of the liquid phase by the solid, while the $H^+$ ion prevents it—probably being preferentially adsorbed.

*Products of the Reaction.*—The large amount of heat evolved in the setting of litharge-glycerine cement indicates that a definite chemical reaction occurs. Merwin[1] states that well-defined crystals are formed when litharge is suspended in hot glycerine and the mixture agitated. He assigns to the product the formula $PbO.C_3H_6O_2$. This would mean that the substances reacted in equimolar proportions and that a molecule of water was eliminated. This may be true when, as in this case, a large excess of glycerine is present. It can be shown that water is actually a product of the reaction; for, if carefully dried materials are allowed to react and the set product is ground and placed in an oven at 106°C., the loss in weight can be determined. If an excess of litharge is used, corresponding at least to the ratio 3 litharge: 2 glycerine, the loss in weight of the product at 106° is greater by one-fourth than is to be expected from Merwin's formula. It corresponds more nearly to one and one-half molecules of water from a molecule of glycerine. This would indicate that the reaction is:

$$3\ PbO + 2\ C_3H_5(OH)_3 = Pb_3(C_3H_5O_3)_2 + 3\ H_2O + \text{Heat.}$$

Also leading to this conclusion is the fact that mixtures of litharge and glycerine in the proportion of the equation give the greatest evolution of heat, as illustrated in Fig. 1 and noted in Table I. This then is the optimum proportion for complete utilization of both litharge and glycerine.

The product of the reaction between litharge and glycerine is a very light buff color, sometimes almost white. The material is practically waterproof, a little surface action to produce lead hydroxide apparently occurring. However, if the set material is finely ground and boiled with water, it is completely hydrolyzed to lead oxide and glycerine.

If the set product is heated, decomposition occurs to form oxidation products of glycerine and a carbonaceous residue mixed with lead. If the heating is conducted in absence of air and below the melting point of lead, pyrophoric lead is obtained. The carbonaceous matter present aids in keeping the lead in a finely divided form.

[1] Merwin: J. Ind. Eng. Chem., 9, 390 (1917).

## Summary

1. The setting of litharge-glycerine cement, like the setting of plaster of Paris, is a two-stage process: (a) Adsorption of liquid phase by solid, accompanied by contraction in volume. (b) Exothermal chemical reaction between adsorbed liquid and adsorbent.

2. The rate of setting is shown to depend upon the form of PbO used and upon the dryness of the glycerine. Water, $OH^-$ ions, and stirring accelerate the setting; $H^+$ ions prevent setting.

3. Water is shown to be a product of the reaction and a definite formula is assigned to the other product.

4. The product is completely hydrolyzed by boiling with water. It produces pyrophoric lead if heated in absence of air.


*Urbana, Illinois.*

# STUDIES IN ADSORPTION. PART XV

## Adsorption of Ions by Aluminium Hydroxide and by a Mixture of Barium Sulphate and Aluminium Hydroxide.

BY M. R. MEHROTRA AND N. R. DHAR

In a previous paper[1] published from this laboratory the adsorption of several anions by barium sulphate in the course of its precipitation has been determined. The barium sulphate was obtained by the interaction of a concentrated solution of barium hydroxide and an equivalent amount of sulphuric acid solution. The following order of adsorption of different anions was obtained:

$$Cr_2O_7'' > S_2O_3'' > BrO_3' > AsO_4''' > C_2O_4'' > IO_4' > IO_3' > MnO_4' > NO_2' > Fe(CN)_6^{IV} > Fe(CNO_6''' > Cl' > CNS' > Br' > I'$$

whilst Weiser and Sherrick[2] working with different barium salts and potassium sulphate obtained the following order

$$NO_3' > NO_2' > ClO_3' > Fe(CN)_6^{IV} > MnO_4' > Cl' > Fe(CN)_6''' > Br' > CN' > CNS' > I'$$

the results are expressed in millimoles.

It will be observed from the above results that, in general, monovalent and bivalent anions are more adsorbed than trivalent and tetravalent anions.

As no experiments on the adsorption of ions by a mixture of adsorbents have yet been made, it was thought desirable to determine the adsorption of anions by a mixture of barium sulphate and aluminium hydroxide.

In the present paper we have determined the adsorption of different anions by a mixture of barium sulphate and aluminium hydroxide in equivalent proportions generated by the reaction of barium hydroxide on aluminium sulphate according to the following equation:—

$$6Ba(OH)_2 + 2Al_2(SO_4)_3 = 6BaSO_4 + 4Al(OH)_3$$

### Experimental

Standard solutions of concentrated barium hydroxide and of aluminium sulphate were prepared. 25 c.c. of aluminium sulphate was taken in a 100 c.c. flask to which the solution of the electrolyte which is to be adsorbed was added and after adding the calculated quantity of water the precipitates were formed by adding 25 c.c. of barium hydroxide solution making up the total volume of the mixture to 100 c.c. The mixture was set apart for 24 hours and the clear supernatant liquid was used in determining the amount of adsorption. The method of estimation of the anions was the same as that adopted in the paper already referred to. The results are given in Table I.

---

[1] Kolloid-Z., 35, 144 (1924).
[2] J. Phys. Chem., 23, 205 (1919).

TABLE I

Adsorptions of anions by a mixture of barium sulphate and aluminium hydroxide.

$BaSO_4$ = 0.7091 grm.

$Al(OH)_3$ = 0.1580 grm.

Total volume = 100 c.c.

| Electrolyte used | Original concentration in moles | End concentration in moles | Amount adsorbed in millimoles | Percentage of adsorption |
|---|---|---|---|---|
| $K_2Cr_2O_7$ | 0.05066 | 0.04010 | 1.0562 | 20.85 |
| | 0.04053 | 0.03178 | 0.8753 | 21.59 |
| | 0.03040 | 0.02319 | 0.7218 | 23.74 |
| | 0.02026 | 0.01369 | 0.6572 | 32.43 |
| | 0.01013 | 0.00606 | 0.4069 | 40.15 |
| $K_2C_2O_4$ | 0.06313 | 0.05734 | 0.5785 | 9.16 |
| | 0.05050 | 0.04540 | 0.5205 | 10.31 |
| | 0.03788 | 0.03345 | 0.4426 | 11.68 |
| | 0.02525 | 0.02138 | 0.3873 | 15.33 |
| | 0.01263 | 0.00981 | 0.2817 | 22.31 |
| $KMnO_4$ | 0.005197 | 0.004757 | 0.04405 | 8.47 |
| | 0.004158 | 0.003911 | 0.02467 | 5.93 |
| | 0.003118 | 0.002801 | 0.03171 | 10.16 |
| | 0.002080 | 0.001868 | 0.02114 | 10.16 |
| | 0.001040 | 0.000810 | 0.00229 | 22.03 |
| $KBrO_3$ | 0.05766 | 0.05450 | 0.3160 | 5.49 |
| | 0.04613 | 0.04317 | 0.2960 | 6.43 |
| | 0.03460 | 0.03217 | 0.2430 | 7.03 |
| | 0.02306 | 0.02067 | 0.2390 | 10.40 |
| | 0.01153 | 0.00967 | 0.1860 | 16.18 |
| $Na_2S_2O_3$ | 0.12433 | 0.11933 | 0.4993 | 4.01 |
| | 0.09946 | 0.09527 | 0.4194 | 4.61 |
| | 0.07460 | 0.07040 | 0.4194 | 5.62 |
| | 0.04973 | 0.04494 | 0.4793 | 9.63 |
| | 0.03730 | 0.03345 | 0.3844 | 10.30 |
| | 0.02487 | 0.02122 | 0.3645 | 14.65 |
| | 0.01243 | 0.01148 | 0.0946 | 23.69 |

TABLE I (Continued)

| Electrolyte used | Original concentration in moles | End concentration in moles | Amount adsorbed in millimoles | Percentage of adsorption |
|---|---|---|---|---|
| $KIO_3$ | 0.0310 | 0.0268 | 0.4200 | 13.44 |
| | 0.0248 | 0.0213 | 0.3500 | 13.97 |
| | 0.0186 | 0.0155 | 0.3100 | 16.66 |
| | 0.0124 | 0.0095 | 0.2900 | 23.38 |
| | 0.0062 | 0.0040 | 0.2200 | 35.48 |
| $KNO_2$ | 0.06341 | 0.06240 | 0.1014 | 1.57 |
| | 0.05073 | 0.04932 | 0.1412 | 2.86 |
| | 0.03805 | 0.03674 | 0.1308 | 3.43 |
| | 0.02537 | 0.02416 | 0.1205 | 4.75 |
| | 0.01268 | 0.01068 | 0.2001 | 15.77 |
| $K_4Fe(CN)_6$ | 0.03323 | 0.03188 | 0.1342 | 4.04 |
| | 0.02658 | 0.02534 | 0.1241 | 4.67 |
| | 0.01994 | 0.01897 | 0.0972 | 4.88 |
| | 0.01329 | 0.01259 | 0.0705 | 5.30 |
| | 0.00665 | 0.00633 | 0.0319 | 4.79 |
| $K_3Fe(CN)_6$ | 0.0590 | 0.0560 | 0.3000 | 5.08 |
| | 0.0472 | 0.0450 | 0.2200 | 4.66 |
| | 0.0354 | 0.0340 | 0.1400 | 3.95 |
| | 0.0236 | 0.0226 | 0.1000 | 4.23 |
| | 0.0118 | 0.0110 | 0.0800 | 6.94 |
| KCNS | 0.08803 | 0.08719 | 0.0841 | 0.94 |
| | 0.07042 | 0.06975 | 0.0673 | 0.92 |
| | 0.05282 | 0.05231 | 0.0505 | 0.92 |
| | 0.03521 | 0.03447 | 0.0742 | 2.07 |
| | 0.01761 | 0.01703 | 0.0574 | 3.22 |
| KCl | 0.12860 | 0.12220 | 0.6405 | 1.86 |
| | 0.10288 | 0.10088 | 0.2001 | 1.94 |
| | 0.07716 | 0.07516 | 0.2001 | 2.59 |
| | 0.05144 | 0.04984 | 0.1602 | 3.11 |
| | 0.02572 | 0.02462 | 0.1101 | 4.41 |
| KBr | 0.12860 | 0.12220 | 0.6405 | 1.86 |

From the experimental results it will be observed that the order of adsorption of the different anions is the following:—

$$Cr_2O_7'' > C_2O_4'' > IO_3' > BrO_3' > Cl' > S_2O_3'' > NO_2' > Fe(CN)_6''' > MnO_4' > Fe(CN)_6^{IV} > CNS'$$

In this case also it will be observed that in general a univalent ion is more adsorbed than the polyvalent ions.

In order to make these results quite comparable with the results obtained with barium sulphate alone we undertook a series of experiments on the ad-

sorption of anions by aluminium hydroxide in the course of formation by the reaction between aluminium sulphate and sodium hydroxide.

25 c.c. of standard aluminium sulphate solution was taken in a 100 c.c. flask to which the solution of the electrolyte to be adsorbed was added and finally 25 c.c. of sodium hydroxide solution was added. The total volume was always made up to 100 c.c. The results are given in Table II.

TABLE II

Adsorption of anions by aluminium hydroxide.
$Al(OH)_3$ = .1540 grm.
Total volume = 100 c.c.

| Electrolyte used | Original concentration in moles | End concentration in moles | Anount adsorbed in millimoles | Percentage of adsorption |
|---|---|---|---|---|
| $K_2Cr_2O_7$ | 0.04983 | 0.04850 | 0.1333 | 2.67 |
| | 0.03987 | 0.03867 | 0.1200 | 3.01 |
| | 0.02990 | 0.02883 | 0.1067 | 3.56 |
| | 0.01993 | 0.01883 | 0.1100 | 5.51 |
| | 0.00997 | 0.00933 | 0.0633 | 6.35 |
| $K_2C_2O_4$ | 0.06313 | 0.05862 | 0.4510 | 7.14 |
| | 0.05050 | 0.04660 | 0.2908 | 7.73 |
| | 0.03788 | 0.03446 | 0.3414 | 9.01 |
| | 0.02525 | 0.02201 | 0.3243 | 12.83 |
| | 0.01263 | 0.01020 | 0.2429 | 19.21 |
| $KMnO_4$ | 0.00508 | 0.00504 | 0.0036 | 0.78 |
| | 0.00406 | 0.00403 | 0.0036 | 0.87 |
| | 0.00305 | 0.00302 | 0.0031 | 0.99 |
| | 0.00203 | 0.00200 | 0.0031 | 1.25 |
| | 0.00106 | 0.00100 | 0.0015 | 1.50 |
| $KBrO_3$ | 0.05766 | 0.05680 | 0.083 | 1.44 |
| | 0.04613 | 0.04533 | 0.080 | 1.73 |
| | 0.03460 | 0.03383 | 0.077 | 2.21 |
| | 0.02306 | 0.02250 | 0.056 | 2.44 |
| | 0.01153 | 0.01117 | 0.036 | 3.18 |
| $Na_2S_2O_3$ | 0.11580 | 0.11444 | 0.1363 | 1.17 |
| | 0.09264 | 0.09155 | 0.1090 | 1.17 |
| | 0.06948 | 0.06857 | 0.0908 | 1.31 |
| | 0.04632 | 0.04569 | 0.0637 | 1.37 |
| | 0.02316 | 0.02266 | 0.0500 | 1.96 |
| $KIO_3$ | 0.03100 | 0.03000 | 0.1000 | 3.22 |
| | 0.02480 | 0.02400 | 0.0800 | 3.22 |
| | 0.01860 | 0.01800 | 0.0600 | 3.04 |
| | 0.01240 | 0.01200 | 0.0400 | 3.44 |
| | 0.00620 | 0.00600 | 0.0200 | 3.22 |

TABLE II (Continued)

| Electrolyte used | Original concentration in moles | End concentration in moles | Amount adsorbed in millimoles | Percentage of adsorption |
|---|---|---|---|---|
| $KNO_2$ | 0.06099 | 0.06099 | ——— | ——— |
| | 0.04879 | 0.04853 | 0.0259 | 0.49 |
| | 0.03659 | 0.03596 | 0.0635 | 1.60 |
| | 0.02440 | 0.02397 | 0.0424 | 1.58 |
| | 0.01220 | 0.01199 | 0.0211 | 1.54 |
| $K_4Fe(CN)_6$ | 0.03343 | 0.03257 | 0.0857 | 2.56 |
| | 0.02674 | 0.02586 | 0.0885 | 3.30 |
| | 0.02006 | 0.01921 | 0.0843 | 4.21 |
| | 0.01337 | 0.01271 | 0.0657 | 4.91 |
| | 0.00669 | 0.00614 | 0.0544 | 8.11 |
| $K_3Fe(CN)_6$ | 0.05975 | 0.05975 | ——— | ——— |
| | 0.04780 | 0.04750 | 0.030 | 0.62 |
| | 0.03585 | 0.03525 | 0.060 | 1.67 |
| | 0.02390 | 0.02350 | 0.040 | 1.67 |
| | 0.01195 | 0.01175 | 0.020 | 1.67 |
| KCNS | 0.07984 | 0.07956 | 0.0279 | 0.38 |
| | 0.06387 | 0.06363 | 0.0246 | 0.38 |
| | 0.04791 | 0.04772 | 0.0184 | 0.38 |
| | 0.03194 | 0.03178 | 0.0156 | 0.38 |
| | 0.01597 | 0.01587 | 0.0095 | 0.38 |
| KCl | 0.12573 | 0.12573 | ——— | ——— |
| | 0.10058 | 0.10034 | 0.0245 | 0.24 |
| | 0.07544 | 0.07525 | 0.0184 | 0.24 |
| | 0.05029 | 0.05017 | 0.0122 | 0.24 |
| | 0.02515 | 0.02508 | 0.0061 | 0.24 |

The order of the adsorption of the anions is the following:—

$C_2O_4'' > Cr_2O_7'' > Fe(CN)_6^{IV} > IO_3' > BrO_3' > S_2O_3'' > NO_2' > Fe(CN)_6''' > CNS' > MnO_4' > Cl'$.

Gann[1] working with a sol of aluminium hydroxide obtained the following order:—

Salicylate > picrate, Oxalate > $Fe(CN)_6'''$ > $Fe(CN)_6^{IV}$

whilst Weiser and Middleton obtained a following order:—

$PO_4''' > C_2O_4'' > SO_4'' > CrO_4'' > S_2O_3'' > Fe(CN)_6'''$ > dithionate > $Fe(CN)_6^{IV} > Cr_2O_7''$

We are now in a position to find out whether the adsorption by a mixture of barium sulphate and aluminium hydroxide, obtained by the action of barium hydroxide and aluminium sulphate, is greater or less than the adsorption by

[1] Kolloidchem. Beihefte 8, 63 (1916).

barium sulphate and aluminium hydroxide taken separately. The results on the adsorption of ions by barium sulphate are taken from the paper of Ghosh and Dhar[1]. The total volume in their experiments was 30 c.c. whilst in our experiments it was 100 c.c. In a previous paper[2] it has been proved that when

TABLE III

The results are given in millimoles.

| Anion adsorbed | Adsorption by $BaSO_4$ = .7091 gr. | Adsorption by $Al(OH)_3$ = .1540 | Sum | Actual adsorption by a mixture of $BaSO_4 + Al(OH)_3$ |
|---|---|---|---|---|
| $Cr_2O_7''$ | 0.3959 | 0.1333 | 0.5292 | 1.0562 |
| | 0.3545 | 0.1218 | 0.4763 | 0.8753 |
| | 0.2999 | 0.1079 | 0.4078 | 0.7218 |
| | 0.2435 | 0.0893 | 0.3328 | 0.6572 |
| | 0.1673 | 0.0646 | 0.2319 | 0.4069 |
| $MnO_4'$ | 0.04605 | 0.00350 | 0.04955 | 0.04405 |
| | 0.03545 | 0.00347 | 0.03892 | 0.02467 |
| | 0.02833 | 0.00310 | 0.03143 | 0.03171 |
| | 0.01839 | 0.00310 | 0.02149 | 0.02114 |
| | 0.00514 | 0.00150 | 0.00664 | 0.00229 |
| $BrO_3'$ | 0.2975 | 0.0830 | 0.3805 | 0.3160 |
| | 0.2694 | 0.0800 | 0.3494 | 0.2960 |
| | 0.2384 | 0.0770 | 0.3154 | 0.2430 |
| | 0.2006 | 0.0560 | 0.2566 | 0.2390 |
| | 0.1508 | 0.0360 | 0.1868 | 0.1860 |
| $S_2O_3''$ | 0.3847 | 0.1159 | 0.5006 | 0.4993 |
| | 0.3761 | 0.1075 | 0.4836 | 0.4194 |
| | 0.3581 | 0.0930 | 0.4511 | 0.4194 |
| | 0.3220 | 0.0748 | 0.3968 | 0.4793 |
| | 0.2851 | 0.0635 | 0.3486 | 0.3844 |
| | 0.2385 | 0.0490 | 0.2875 | 0.3645 |
| | 0.1785 | 0.0280 | 0.2065 | 0.0946 |
| $IO_3'$ | 0.1218 | 0.1000 | 0.1218 | 0.4200 |
| | 0.1102 | 0.0800 | 0.1902 | 0.3500 |
| | 0.1006 | 0.0600 | 0.1606 | 0.3100 |
| | 0.0812 | 0.0400 | 0.1212 | 0.2900 |
| | 0.0576 | 0.0200 | 0.0776 | 0.2200 |
| $NO_2'$ | 0.1226 | —— | 0.1226 | 0.1014 |
| | 0.1164 | 0.0259 | 0.1423 | 0.1412 |
| | 0.1053 | 0.0643 | 0.1696 | 0.1308 |
| | 0.0911 | 0.0465 | 0.1376 | 0.1205 |
| | 0.0630 | 0.0260 | 0.0890 | 0.2001 |

[1] Loc. cit.

[2] Chatterji and Dhar: Kolloid-Z., 33, 18 (1923).

TABLE III (Continued)

| Anion adsorbed | Adsorption by $BaSO_4$=.7091 gr. | Adsorption by $Al(OH)_3$=.1540 | Sum | Actual adsorption by a mixture of $BaSO_4+Al(OH)_3$ |
|---|---|---|---|---|
| $Le(CN)_1''$ | 0.0550 | 0.0857 | 0.1407 | 0.1342 |
| | 0.0364 | 0.0885 | 0.1249 | 0.1241 |
| | 0.0391 | 0.0843 | 0.1234 | 0.0972 |
| | 0.0270 | 0.0657 | 0.0927 | 0.0705 |
| | 0.0151 | 0.0544 | 0.0695 | 0.0319 |
| $Fe(CN)_1'''$ | 0.0610 | 0 | 0.0610 | 0.3000 |
| | 0.0572 | 0.0300 | 0.0872 | 0.2200 |
| | 0.0497 | 0.0600 | 0.1097 | 0.1400 |
| | 0.0398 | 0.0400 | 0.0798 | 0.1000 |
| | 0.0219 | 0.0200 | 0.0419 | 0.0800 |
| $CNS'$ | 0.0416 | 0.0279 | 0.0695 | 0.0841 |
| | 0.0398 | 0.0250 | 0.0648 | 0.0673 |
| | 0.0356 | 0.0220 | 0.0576 | 0.0505 |
| | 0.0305 | 0.0180 | 0.0485 | 0.0742 |
| | 0.0202 | 0.0125 | 0.0327 | 0.0574 |
| $Cl'$ | 0.0659 | ——— | 0.0659 | 0.6405 |
| | 0.0638 | 0.0230 | 0.0868 | 0.2001 |
| | 0.0588 | 0.0189 | 0.0777 | 0.2001 |
| | 0.0530 | 0.0147 | 0.0677 | 0.1602 |
| | 0.0386 | 0.0089 | 0.0475 | 0.1101 |

the amount of adsorbent and the concentration of the electrolyte to be adsorbed are constant, the adsorption is greater the greater the volume of the solution. In obtaining comparable results in the adsorption of anions by barium sulphate we have introduced a correction necessary for the difference in volume. In Table III is a summary of the experimental results suitable for comparison:—

From the above results it will be seen that the actual adsorption by a mixture of barium sulphate and aluminium hydroxide is greater than the sum of the separate adsorptions in the following cases:—

$Cr_2O_7''$, $IO_3'$, $Fe(CN)_6'''$, $CNS'$ and $Cl'$

whilst it is less with $MnO_4'$, $BrO_3'$, $S_2O_3''$, $NO_2'$ and $Fe(CN)_6^{IV}$

It appears therefore that no definite conclusion with regard to the influence of one adsorbent on the adsorptive power of the other can be drawn from these experiments.

It will be interesting to observe that in many cases, the catalytic influence of a substance is greatly increased by the presence of another catalyst in small quantities. Thus the presence of small quantities of a ferrous salt largely increased the activity of cupric salts in accelerating the liberation of iodine by the inter-action of potassium iodide and potassium persulphate.

Small quantities of cupric salts also largely increase the activity of ferrous salts in the same reaction. Similarly the yield of ammonia in the Haber process is greatly increased by the presence of traces of tungsten. Many examples of promoter action are now known in the adsorption of gases by solid adsorbents. In the adsorption of anions by barium sulphate or aluminium hydroxide, no such marked promoter action is noticeable due to the presence of one adsorbent along with the other.

In the course of our experiments we noticed that along with anions the cations are also adsorbed and we obtained the following results on the adsorption of cations from $Na_3AsO_3$ and $K_2C_2O_4$ by barium sulphate.

| Electrolyte | Original concentration | Percentage of adsorption |
|---|---|---|
| $Na_3AsO_3$ | 0.08833 M | 3.7 |
| $K_2C_2O_4$ | 0.06894 M | 2.0 |

In this paper we have also determined the adsorption of cations by a mixture of barium sulphate and aluminium hydroxide and the following experimental results are obtained:—

| Electrolyte | Original concentration | Percentage of adsorption |
|---|---|---|
| KCl | 0.1029 M | nil |
| $K_2C_2O_4$ | 0.0068 M | 1.45 |
| $KBrO_3$ | 0.0742 M | 1.48 |

Our experiments on the precipitation of a mixture of barium sulphate and aluminium hydroxide in presence of KCl and $K_2C_2O_4$ show that the adsorption of $C_2O_4''$ ion is much greater than that of $Cl'$ ion, though according to our view of the Schulze-Hardy law[1] it should be otherwise. We have proved that along with the adsorption of $C_2O_4''$ ion by a mixture of barium sulphate and aluminium hydroxide, appreciable quantities of $K^{\cdot}$ ions are also adsorbed. The positively charged barium sulphate and aluminium hydroxide are capable of adsorbing $K^{\cdot}$ ions from $K_2C_2O_4$ and hence more of the oxalate ion would be necessary for the charge neutralisation and precipitation whilst in the case of KCl no $K^{\cdot}$ ion is adsorbed hence a small amount of $Cl'$ is sufficient for charge neutralisation. It is evident therefore that a colloid in the course of its precipitation can actually adsorb anion carrying the same charge as the colloid and this adsorption stabilises the colloid. Consequently if the amount of this adsorption is large deviations from Schulze Hardy law will take place.

We have drawn graphs of the amounts of adsorption against the concentration and the usual type of adsorption curves are obtained. By plotting the logarithms of the adsorption at different concentrations of the adsorbing ions against the logarithms of the concentration, straight-line curves are obtained.

[1] J. Phys. Chem., 28, 457 (1924).

## Summary

1. Experiments on the adsorption of anions by aluminium hydroxide and by a mixture of aluminium hydroxide and barium sulphate in the course of their formation have been carried on.

2. The experimental results show that in general the smaller the valency of an ion the greater is the adsorption.

3. In the adsorption of anions by barium sulphate or aluminium hydroxide no marked promoter action is noticeable due to the presence of one adsorbent along with the other.

4. Quantitative experiments show that $K^{\cdot}$ ion is also adsorbed by a mixture of barium sulphate and aluminium hydroxide from solutions of potassium oxalate and potassium bromate



*Chemical Laboratory,*
*Allahabad University,*
*Allahabad,*
*March 31, 1926.*

# THE WATER EQUILIBRIUM*

BY WILDER D. BANCROFT

Gelatine is peptized by potassium iodide solution much more readily than by a potassium chloride solution. It is a typical case of the Hofmeister series. The most obvious explanation is that the iodine ion is adsorbed much more strongly than the chlorine ion, and I have held to that as a working hypothesis for several years. The difficulty with it is that nobody has been able to show marked selective adsorption of iodine ion, as required by the hypothesis. Since potassium iodide is a more effective peptizing agent than potassium chloride both in slightly acid and in slightly alkaline solution, the explanation cannot be right, because there should then be a reversal of effect as one changes from positively charged to negatively charged gelatine or vice-versa.

We cannot be dealing with a solvent action of liquefied potassium iodide because the gelatine is peptized and not dissolved. It cannot be a peptization by liquefied potassium iodide because that would mean a selective adsorption of iodide, which we do not have. We have apparently excluded all direct action of potassium iodide on gelatine, in which case the only remaining possibility is an indirect action of potassium iodide on the gelatine. The potassium iodide may modify the water in such a way as to make the water more able to peptize gelatine at a given temperature. This hypothesis is the more plausible because the Hofmeister series crops up in one form or another in a large number of cases and the water seems to be the only thing in common. It cannot be a question of hydration alone, because the formation of hydrates of potassium iodide in solution would decrease the amount of free water and would therefore decrease and not increase the peptizing or liquefying action of the solution on gelatine.

Liquid water is usually considered to be an associated liquid in which we have equilibrium between hydrol ($H_2O$) and other forms, say dihydrol $(H_2O)_2$, trihydrol $(H_2O)_3$, and polyhydrols $(H_2O)_n$. For the present it is impossible to differentiate the hydrols to any great extent and I am therefore going to consider water temporarily as consisting of a mixture of a depolymerized form which I will call hydrol and a polymerized form which I will call polyhydrol. We know that the equilibrium between these two forms may be displaced by the addition of any other component. If the added component is more soluble in polyhydrol than in hydrol, the equilibrium will be displaced to the polyhydrol side. There have been quantitative studies of this sort of thing with $NO_2$ and $N_2O_4$ in different solvents[1] and Beckmann[2] has classified solvents according to their power of polymerizing organic acids.

It is evident that a polymerized form will not necessarily behave exactly like a depolymerized form and that therefore hydrol may have solvent or

---

* A paper presented at the Fourth Colloid Symposium in Cambridge, June 23.

[1] Cundall: J. Chem. Soc., 59, 1076 (1891); 67, 794 (1895).

[2] Z. physik. Chem., 6, 437 (1890).

peptizing powers which are not identical with those of polyhydrol. There is nothing new about this. H. E. Armstrong has blamed the physical chemists for decades because they treated water simply as water and not as a mixture of substances. Sutherland has calculated the amounts and the densities of two forms of liquid water under certain conditions. The orthodox explanation for the temperature of maximum density of water and the displacement of that temperature by the addition of salts is the occurrence of two forms of liquid water and the displacement of the equilibrium between them. In this very case we have a Hofmeister series for chloride, bromide, and iodide, though there seems to be some difficulty about sulphate. Bousfield[1] has laid great stress on the effects due to the depolymerization of water, and many other instances could be given.

All I am trying to do is to show, perhaps a little more specifically, the great importance of the water equilibrium for certain problems which are of great interest to the colloid chemist and to the physical chemist. In the particular case of gelatine our hypothesis means that one form of water does not peptize gelatine as readily as the other form, that potassium iodide displaces the water equilibrium so as to produce more of the form which peptizes gelatine readily, and that potassium chloride produces a lesser displacement of equilibrium in the same direction. There is nothing in the general hypothesis to show whether hydrol or polyhydrol peptizes gelatine more readily. Since potassium iodide lowers the temperature of the maximum density of water and since this lowering is believed to be due to increased formation of hydrol, we deduce that addition of potassium iodide causes increased formation of hydrol. If that is the case we ought to get an effect similar to that of potassium iodide by increasing the amount of hydrol in other ways, say by raising the temperature. As we all know, we can liquefy gelatine in hot water. This is of no real value as a proof because it is quite possible that we could have liquefied gelatine in hot water even if there had beeen no displacement of the water equilibrium. The fact that gelatine lowers the temperature of the maximum density[2] would be a proof that gelatine adsorbs hydrol if one could be sure that the effect was not due to salts in the gelatine.

It will be more interesting to consider a case in which the polymerized form of a liquid is the active substance. Pyroxylin is peptized by an ether-alcohol mixture and not by either pure liquid at room temperature. Ethyl alcohol causes pyroxylin to swell appreciably while ethyl ether does not. It has been shown by Lunge[3] and confirmed by Byron[4] in the Cornell laboratory that the ether apparently plays no direct part in the peptization of the pyroxylin. It must therefore activate the alcohol by increasing or decreasing the relative amount of depolymerized alcohol. If the depolymerized alcohol is the peptizing agent, it should be possible to peptize pyroxylin by alcohol alone at higher temperatures. If the polymerized alcohol is the peptizing agent, it

[1] Trans. Faraday Soc., **15**, 47 (1919).
[2] Jaffel: Trans. Faraday Soc., **19**, 97 (1923).
[3] Z. angew. Chem., **14**, 538 (1901).
[4] J. Phys. Chem., **30**, 1116 (1926).

should be possible to peptize pyroxylin by alcohol alone at lower temperatures. It has been shown by McBain[1] and confirmed by Byron that there is no appreciable peptization of pyroxylin by alcohol at 140°. It has been shown by Kugelmass[2] and by McBain, and confirmed by Byron, that pyroxylin is peptized by alcohol at very low temperatures. If the hypothesis is right, a colloidal solution prepared at low temperatures should become more viscous as the temperature rises because the relative amount of the peptizing agent decreases with rising temperature. It has been shown by McBain and confirmed by Byron that a colloidal solution of pyroxylin in alcohol, which is quite mobile at low temperatures, becomes a soft, flowing jelly at room temperatures. It has been shown by Byron that this soft, flowing mass becomes a stiff jelly when heated well above 100°, and that the tube can be turned upside down without the contents flowing out.

This is a striking illustration of the effect which may be produced by a polymerization of a liquid and it opens up a number of new problems, not the least interesting of which is to find out why ether increases the degree of polymerization of alcohol. For the present, however, I wish to call attention to certain problems which have troubled physical chemists for a generation. The first of these is the dilution law. I cannot guarantee an explanation of our difficulties; but I can suggest a new line of attack. The constancy of the dissociation constant depends of course on the constancy of the solvent because the dissociation constant is a function of the nature of the solvent. If the water equilibrium is displaced appreciably with increasing concentration of a salt, acid, or base, the dissociation constant will also vary. It is impossible to say that the dilution law will hold for strong electrolytes if we take this factor into account; but it is unjustifiable to say that it does not hold until we have taken this factor into account, and there is very little to be gained by devising empirical formulas which ignore this factor.

There is another case in which I can be more definite. The neutral salt effect has been a source of worry for many years and has given rise to innumerable papers. On adding sodium chloride to a hydrochloric acid solution we should expect a slight forcing back of the dissociation because we are adding a salt with a common ion. What we actually get is an increase in the rate of hydrolysis of the esters, in the rate of inversion of sugar, and in the apparent hydrogen ion concentration as determined potentiometrically. We have invented ingenious explanations for this neutral salt effect without troubling ourselves to make certain that any actual change of hydrogen ion concentration occurs. The first thing that strikes me is that our different methods of determining hydrogen concentration give us very different results. Akerlöf[3] found that four-normal sodium chloride increased the apparent hydrogen ion concentration of the hydrochloric acid by about five hundred percent and the rate of inversion of ethyl acetate by only about one hundred percent.

[1] McBain, Harvey and Smith: J. Phys. Chem., **30**, 312 (1926).
[2] Rec. Trav. chim., **41**, 751 (1922).
[3] Z. physik. Chem., **98**, 260 (1921).

Preliminary experiments in the Cornell laboratory show a different relation for the inversion of sugar. The freezing-point determinations give a third set of values and the conductivity measurements a fourth.

This makes it probable that there may be errors in some one—and perhaps in all—of our methods of determining hydrogen ion concentrations. Let us consider the potentiometric method first. If we have a cell $H_2 | c_1HCl | c_2HCl | H_2$ and we eliminate or correct for the potential difference between the two solutions, the electromotive force as calculated by the Nernst formula will be

$$E = \frac{RT}{nF}\left\{\log\frac{P}{p_1} - \log\frac{P}{p_2}\right\} = \frac{RT}{nF}\left\{\log\frac{P}{\alpha_1 c_1} - \log\frac{P}{\alpha_2 c_2}\right\}$$

where $\alpha_1$ and $\alpha_2$ are the percentage dissociations in the two solutions and consequently $\alpha_1 c_1$ and $\alpha_2 c_2$ are equal to (or proportional to) $p_1$ and $p_2$ respectively, the osmotic pressures of the hydrogen ions in the two solutions. If the second solution is so dilute that we may consider the dissociation as complete, and if the solution pressure term, log P, does not change with the concentration, the equation becomes

$$E = \frac{RT}{nF}\left\{\log\frac{P}{\alpha_1 c_1} - \log\frac{P}{c_2}\right\} = \frac{RT}{nF}\log\frac{c_2}{\alpha_1 c_1}$$

If we determine E, we can solve for $\alpha_1$ and that is the way in which we ordinarily determine hydrogen ion concentrations in principle, though we may actually measure the half-cell against a calomel electrode or against a standard hydrogen electrode, adding or subtracting a suitable constant in each case. If the solution pressure varies with the concentration, however, the equation becomes

$$E = \frac{RT}{nF}\left\{\log\frac{P_1}{\alpha_1 c_1} - \log\frac{P}{c_2}\right\}$$

and one cannot calculate the value of $\alpha_1$ because there are three (or two) unknown quantities in the equation.

I am not interested for the moment in the question whether the so-called solution pressure varies enough with the concentration to make all determinations of hydrogen ion concentrations of doubtful value. I am interested in the neutral salt effect because there it is not a question of quibbling over trifles. If we start with 0.1N HCl and add enough sodium chloride to make the apparent hydrogen ion concentration equivalent to 0.5 N HCl, which can be done without trouble, we cannot possibly be measuring changes in hydrogen ion concentration alone. No one would consider anything less than 60% dissociation for 0.1N HCl and most people would stand out for at least 85% dissociation. A 300% dissociation or higher is of course absurd and consequently we know that we are measuring something other than the change in hydrogen ion concentration. The other variable is, therefore, log P, the logarithm of the so-called solution pressure.

It may be well to substitute another phrase for the logarithm of the so-called solution pressure. In the case of a strictly reversible electrode we know that the potential difference is equal to the difference of the chemical potentials The chemical potential of the metal is of course a constant at constant temperature and pressure. We may, therefore, write, if we like

$$\pi = \frac{RT}{nF} \log A$$

The chemical potential of the ion for which the electrode is reversible is composed of two terms, one for the ion at unit concentration and one for the concentration. We may write

$$\pi_1 = \frac{RT}{nF} \log B + \frac{RT}{nF} \log p_1$$

The potential difference between the metal and the solution is

$$\pi - \pi_1 = \frac{RT}{nF} (\log A - \log B - \log p_1).$$

If we write $E'$ for $\pi - \pi_1$ and log P for log (A/B) we come right back to the Nernst equation

$$E' = \frac{RT}{nF} \log \frac{P}{p_1}$$

Since $\alpha_1 c_1$ is equal to (or proportional to) $p_1$, one can be substituted for the other.

We see, then, that a decrease in $E'$, the single-potential difference, may be due to an increase in the osmotic pressure (concentration) of the ion, to a decrease in the solution pressure P or to some combination of the two. Instead of a decrease in the solution pressure of hydrogen we may say that we have an increase in the chemical potential of hydrogen ion. The advantage of this is that it enables us to make plausible the relation between the potentiometric data and those on the color changes of the indicators. Few people would admit that the color change of an indicator depends on the solution pressure of hydrogen gas; but few would dare deny that it may depend on the chemical potential of hydrogen ion. There is all the difference in the world between tweedledum and tweedledee. With indicators showing large salt error, there is another factor which has not yet been determined.

In the case of the hydrolysis of the esters, the change in the solvent will produce an unpredictable change in the reaction velocity which need not stand in any necessary relation to the change in the apparent concentration of hydrogen ion.

The present line of thought causes me to criticize the distinctly formal treatment of equilibria by means of the activity concept.[1] "Although we have already seen that the molal free energy makes a very satisfactory quantitative measure of the escaping tendency, there are certain respects in which

[1] Lewis and Randall: "Thermodynamics," 190, 191, 254, 328 (1923).

this function is awkward. For instance, the molal free energy of a gas approaches an infinite negative value as the pressure approaches zero, and we shall see that this kind of inconvenience enters even more in the study of the partial molal free energy in solutions. For such reasons another scale of measurement of the escaping tendency is sometimes to be preferred, and we shall not hesitate to employ, side by side with the molal free energy, a second measure of the escaping tendency, which is called the *fugacity*.[1] . . .

"We may partially define the fugacity, $f$, in terms of the free energy, F, through the equation

$$F = RT \ln f + B,$$

where $B$ is defined no further than by the statement that it is a function of temperature only, or, in other words, that it is a constant at a single temperature."

"If we consider one constituent of a solution at two different concentrations, but at the same temperature, and if by some method we determine for this constituent $\Delta F = F - F'$ between these concentrations, then we have also determined the ratio of the fugacities. For, by Equation XVIII-7,

$$F - F' = RT \ln \frac{f}{f'}.$$

"Now we often have occasion to determine and to use such a ratio of fugacities when it is impossible or inexpedient to determine the numerical value of either fugacity; for example, we may be dealing with an almost involatile substance. It has therefore proved advantageous to consider, at a given temperature, the ratio between the fugacity $f$ of a substance in some given state and its fugacity $f^\circ$ in some state which, for temporary convenience, is chosen as a *standard state*. This relative fugacity[2] is called the activity and denoted by $a$. Thus in the standard state the activity is unity, $a^\circ = 1$, while in any other state it is given by the equations,

$$a = \frac{f}{f^\circ}; \quad F - F^\circ = RT \ln a$$

where at a given temperature, the molal free energy in any state is F, and in the standard state $F^\circ$."

"The mean activity of the ions, $a_\pm$, divided by the molality of the electrolyte, gives a quantity which has been called the thermodynamic degree of dissociation, since it may be used to replace the degree of dissociation as used

---

[1] Lewis: Proc. Am. Acad., **37**, 49 (1901); Z. physik. Chem., **38**, 205 (1901).

[2] Sometimes called also the relative activity; for Lewis first defined the absolute activity, as he defined the fugacity, by reference to the attenuated gaseous state, in which the activity was taken as equal to the concentration (Proc. Am. Acad., **43**, 259 (1907); Z. physik. Chem., **61**, 129 (1907)). More recently, however, it has become the general custom to use the term activity in the sense of relative activity, or relative fugacity, and it is in this sense that we shall use it henceforth.

in the older formulas. This quantity has also been called the activity coefficient,[1] and, in order to avoid any implication as to the molecular species which may be present, this is the term which we shall ordinarily employ henceforth.[2] It will be denoted by $\gamma$."

The question of activity is given in a condensed and perhaps more intelligible form by Dawson.[3] "Methods for the determination of the activities of the components of a solution—solute, solvent, molecules, and ions—have been worked out by G. N. Lewis and his collaborators. For a detailed account of these methods reference may be made to that extraordinarily interesting work by Lewis and Randall,[4] in which the authors describe and illustrate many novel applications of thermodynamics to chemical problems. The deviation of actual from ideal behaviour may be conveniently expressed by the activity coefficient ($a$ = ratio of activity to concentration), which may be defined as the factor by which the concentrations must be multiplied in order to make the expressions for mass action and free energy applicable to actual as distinguished from ideal solutes. Alternative and independent methods of evaluation are shown to afford consistent values for the activity coefficient."

In other words the activities are the values which one must substitute for the concentrations in order to make the formulas fit.[5] This means that we give up all attempts either to test or to improve our formulas. Lewis implies that his formulas are right because he has deduced them thermodynamically and that consequently he is justified in changing the facts to fit the formula.

The people interested in activities do not care whether the addition of a neutral salt does or does not change the actual hydrogen ion concentration of a solution or not. They are satisfied with their formulas and their formulas fit the facts when activities are substituted for concentrations, in other words when they make the facts fit the formulas. When the history of this period comes to be written, people will probably consider the activity craze as more foolish than the phlogiston theory.

If the addition of a second salt changes the water equilibrium, Debye's very ingenious theory of solubilities becomes a triumph of misapplied skill in calculation.

The general results of this paper are as follows:—

1. The displacement of the water equilibrium is apparently the important factor in the peptization of gelatine by potassium iodide solutions and in the effect of neutral salts on pH values.

---

[1] The term activity coefficient has been used in two senses, sometimes to mean the ion activity divided by the assumed ion molality, and sometimes to express the ion activity divided by the gross molality of the electrolyte. This latter usage, to which we shall find it desirable to adhere in thermodynamic work is more expressly designated by Bronsted (J. Am. Chem. Soc., **42**, 761 (1920)) as the *stoichiometrical* activity coefficient.

[2] For a weak binary electrolyte, when we do not choose to employ the convention that $a_+a_- = a_2$, we still write $\gamma = a_+/m$, but we cannot write $\gamma = a_2{}^{1/2}/m$.

[3] "Ann. Reports on the Progress of Chemistry," **21**, 24 (1924).

[4] "Thermodynamics and the Free Energy of Chemical Substances" (1923).

[5] Cf. Cartledge: "Inorganic Physical Chemistry," 296 (1924); Coates: "Ann. Reports on the Progress of Chemistry," **22**, 28 (1925).

2. The pH values, as at present determined, stand in no necessary relation to the actual concentrations of hydrogen as ion.

3. There is no satisfactory evidence as yet that the addition of sodium chloride to a dilute hydrochloric acid solution causes any increase in the actual hydrogen ion concentration.

4. It is possible that the displacement of the water equilibrium is of importance in causing the variations from the dilution law.

5. The agreement between the potentiometrically determined pH values and those determined by indicators is not an independent confirmation, because both depend on the chemical potential of hydrogen ion and not solely on the concentration of hydrogen ion.

6. Since the activities are, by definition, the values which must be substituted for the concentrations in order to make the formulas fit, it is impossible to test the accuracy of the formulas by means of the activity determinations.

*Cornell University,*
*May 24, 1916.*

# INFLUENCE ON THE SOLUBILITIES OF SALTS IN WATER BY THE ADDITION OF A NON-ELECTROLYTE TO THE SOLUTION

BY JOHN McAULAY

From the recent work of Prof. Debye and others on the interionic forces in solutions, it is but a small step to the influence on the solubility of salts by the addition of non-electrolytes to the solution. According to the Debye theory, the behaviour of salts in solution is largely determined by the electrical forces between the ions and also consequently by the dielectrical medium which separates them. The laws governing their behaviour are derived from classical thermodynamical considerations, together with Coulomb's Law for the electrical forces between the ions. On these foundations a theory has been built up, which has had considerable success in explaining very many phenomena covering a wide range of problems dealing with the behaviour of salts in solution. In this paper only the influence of non-electrolytes, in particular of acetone and alcohol on the solutions of various salts in water will be considered. Several previous attempts have been made to find a theory but no successful explanation seems to have been achieved.

When alcohol is added to the solution of a salt in water, the solubility of the salt generally decreases. This decrease, however is not exactly proportional to the quantity of alcohol added to the solution. It is quite natural to suppose that the chief factor in influencing the solubility will be that one which has the greatest influence on the electrical forces in the solution and especially on the work of solvation, with which we are mainly concerned here. Undoubtedly the greatest effect produced by the addition of alcohol in this respect, is the reduction in the value of the dielectric constant of the solvent medium between the ions and according to the "Interionic Attraction" theory the dielectric constant is an all-important factor for explaining the behaviour of electrolytes in solution.

If we consider a saturated solution of a salt in equilibrium with the solid phase, then the potential of one mol of the solid salt is equal to the potential of one mol of the salt in solution. Representing the potentials in the solid state and in the solution by $\Phi_s$ and $\Phi_l$ respectively and the activity or effective concentration by $\alpha$, then from ordinary thermodynamics $\Phi_s = \Phi_l$

where
$$\Phi = (\varphi + RT \ln \alpha)$$
being that part of the potential dependent on the pressure and temperature but independent of the concentration. Taking the general case of a salt of the type $K_mA_n$ dissociating into $m$ cations and $n$ anions, then

$$\Phi_s = (\varphi_A + \varphi_K)_s$$

and

$$\Phi_l = (\varphi_A + \varphi_K)l + RT \ln \alpha_A^n + RT \ln \alpha_K^m$$
$$= (\varphi_A + \varphi_K)l + (m + n)RT \ln \alpha_w$$

$\alpha_w$ being the activity of the salt in a water solution.

Hence
$$(\varphi_K + \varphi_A)_s - (\varphi_K + \varphi_A)_l = (m+n)RT \ln \alpha_w$$

For the left side of this equation we can put $-W_1$ as this is nothing more than the work required to remove one mol of the salt from the solution into the solid state. Again if we have the solid salt in equilibrium with its solution in a mixture of alcohol and water then

$$(\varphi_K+\varphi_A)_s-(\varphi_K+\varphi_A)_{al}=(m+n)RT \ln \alpha_{al}$$

the left side can again be replaced by $-W_2$ and we get

$$W_1=-(m+n)\ Rt \ln \alpha_w$$

$$W_2=-(m+n)\ RT \ln \alpha_{al}$$

Hence
$$\ln \alpha_w/\alpha_{al}=-\frac{(W_1-W_2)}{(m+n)\ RT}=-\frac{(W_1-W_2)}{(m+n)NkT}$$

where $k$ is the Boltzmann constant and N the Avogadro constant. With a ~~uni-univalent salt this becomes~~

$$\ln \alpha_w/\alpha_{al}=-\frac{(W_1-W_2)}{2NkT}$$

$(W_1-W_2)$ to a first approximation can be found from the difference of the work required to charge up the ions of one mol of the salt in water and in alcohol water solution at infinite dilutions. For this purpose the ions are considered as spheres of radius $a$ and sorrounded by a homogeneous medium of dielectric constant $D_o$ in the case of water and D in the case of alcohol water mixture as solvent. The work of charging an ion under such circumstances is $e^2/2Da$ and if it has a valency $z$ and the elementary charge is $\epsilon$, this becomes $\epsilon^2z^2/2Da$.

Hence
$$(W_1-W_2)=\frac{N\Sigma^i\epsilon^2z^2_i}{2a}(1/D_o-1/D)$$

and
$$\ln \alpha_w/\alpha_{al}=\frac{N\Sigma^i\epsilon^2z^2_i}{(m+n)\ 2NakT}(1/D-1/D_o).$$

or again in the case of a uni-univalent salt and using ordinary logarithms instead of the natural ones

$$\log \alpha_w/\alpha_{al}=\frac{\epsilon^2}{2\times 2.303.akT}(1/D-1/D_o).$$

In order to test the validity of this theory, several examples of salts in solutions of mixed solvents, where the solubilities of the salts and the dielectric constants of the solvents are known, were sought out from the literature on the subject. In this manner the only unknown quantity in the last equation is the value of the radius $a$. This however should, if the theory is true be of the correct order of magnitude, its actual value being of lesser importance, as it represents not the true radius of the ion but probably that of a hydrated one.

The values for the solubility of the alkali perchlorates in alcohol-water mixtures are especially suitable for the above purpose and the author is indebted to Prof. Treadwell for bringing to his notice the work of Flatt[1] from

[1] "Studie über Hydratation und Löslichkeit".

which the solubilities of these salts are taken. Flatt has measured the solubilities of $KClO_4$, $RbClO_4$ and $CsCl_4$ in 50% and 75% (vol) alcohol at 25°C and 40°C. In many of the calculations in this paper the activity has been used in place of the actual molar concentration. The activity may be called the fictive concentration and is the product of the molar concentration and another factor called the activity coefficient. Full details of the calculation of these activity coefficients can be found in the work of Hückel.[1]

The following values of $a \times 10^{-8}$ were obtained for the above-mentioned salts in alcohol water solutions at 25°C, the dielectric constants being interpolated from the values of Nernst.[2]

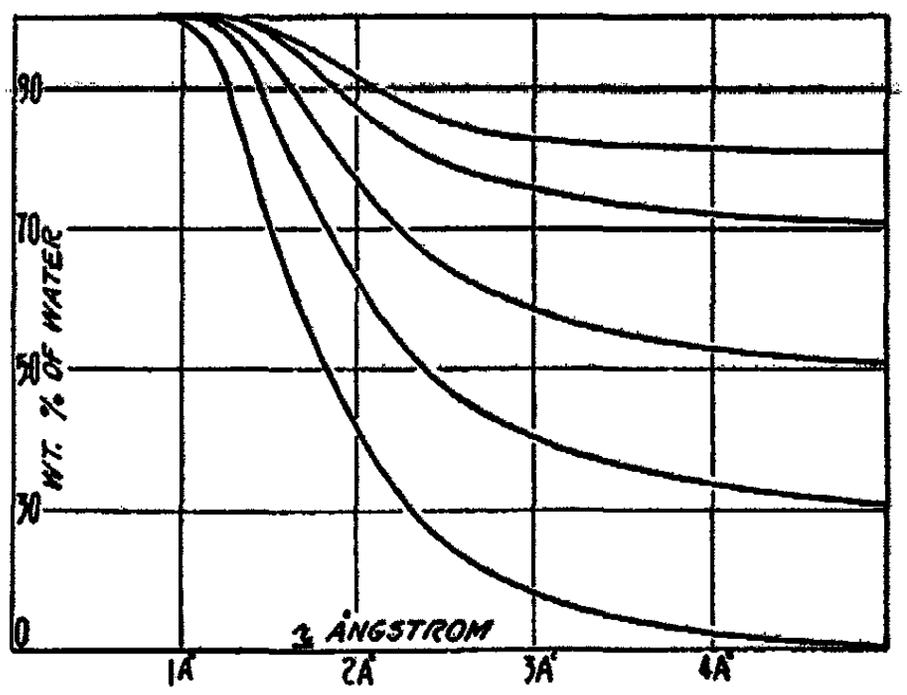



FIG. 1
Distribution of Alcohol-Water in the Vicinity of an Ion

Value of $a \times 10^{-8}$ at 25°C

| salt | $KClO_4$ | $RbClO_4$ | $CsClO_4$ |
|---|---|---|---|
| 0%—50% alcohol | 2.58 | 2.90 | 3.10 |
| 0%—75% " | 2.64 | 2.80 | 3.04 |
| 50%—75% " | 2.70 | 2.70 | 3.00 |

Value of $a \times 10^{-8}$ at 40°C.

| salt | $KClO_4$ | $RbClO_4$ | $CsClO_4$ |
|---|---|---|---|
| 0%—50% alcohol | 2.70 | 2.95 | 3.05 |
| 0%—75% " | 2.72 | 2.87 | 3.05 |
| 50%—75% " | 2.74 | 2.80 | 3.05 |

The solubilities of the above salts vary from about one hundredth of a mol, to one tenth of a mol pro litre, but even at such small concentrations the activity coefficient is about 0.5. In alcohol-water solutions however the actual variation for considerable range of salt concentrations is small. For instance, the following results obtained with $KClO_4$ at 25°C without using activity

[1] "Zur Theorie der Elektrolyte" (1924).
[2] Landolt-Börnstein: Tabellen, 5th Ed., Vol. 2, p. 1032.

coefficients and calculating only with the molar concentration $C$ instead of $\alpha$, show that in this case at least, the activity coefficients are unnecessary for our purpose

| % Alcohol | $a \times 10^{-3}$ |
|---|---|
| 0—50% | 2.95 |
| 0—75% | 2.85 |
| 50—75% | 2.75 |

This gives an average value of $2.85 \times 10^{-3}$ for $a$; using this value and knowing the solubility of $KClO_4$ in any mixture of alcohol and water from the solubility curve, it is possible to calculate the dielectric constant of the mixture for that temperature. Also where the variation of the dielectric constant of the solvent is known as a function of the concentration of the non-electrolyte, the solubility curves in that solvent can be calculated. The dielectric constants for 55% and 25% alcohol by weight were thus calculated and compared with values obtained by interpolation from the figures of Nernst for alcohol water mixtures at 20°C

| % Alcohol at 25°C | 55% | 25% |
|---|---|---|
| Calculated D. C. | 45.2 | 62.1 |
| Interpolated D. C. | 44.6 | 62.4 |

As the temperature coefficients of alcohol-water mixtures are not very accurately known and even different investigators give appreciably different values for the dielectric constants of the same liquids, these results are probably well within experimental error.

With the alkali perchlorates the concentrations are very small but it can be shown that the theory is by no means limited to these salts which are only soluble with difficulty. As a typical example of a comparatively easily soluble salt NaCl has been taken chiefly because the activity coefficients in this case can be calculated much more accurately from the somewhat complicated equations of Hückel in the work already referred to. This corrected formula is necessary, as the activity coefficient which has the value *one*, at very small concentrations gradually gets smaller with increasing concentration until a minimum is attained when it begins to increase and between four and five mols pro litre it again reaches the value *one* and with increasing concentration continues to increase rapidly. The activity coefficients so calculated for water solutions at such large concentrations, also, agree with those found by experiment, although the agreement may possibly not be so good with alcohol water as solvent.

The following results were obtained from the solubility figures for NaCl at 28°C in alcohol-water mixtures, by F. Fontein.[1]

| % Alcohol by weight | $a \times 10^{-3}$ |
|---|---|
| 0—20% | 1.57 |
| 0—30% | 1.60 |
| 0—50% | 1.53 |
| 0—80% | 1.37 |

[1] Z. physik. Chem., 73, 240 (1910).

From these values of $a$, assuming a mean of $1.52 \times 10^{-8}$, the solubility or rather the activity of NaCl in absolute alcohol at 28 C may be calculated assuming that the dielectric constant of alcohol at this temperature is 24.5. We find $\alpha = 0.00068$. L. de Bruyn gives the solubility of NaCl in alcohol as 0.09 gms. pro 100 gms solution at 17°C; if we take it as 0.1 at 28°C or as molar fraction 0.00079 and the activity as above, 0.00068, then we obtain the value $f = 0.86$ for the activity coefficient, a value which can be reasonably be expected.

For the type of uni-divalent salt $Ba(OH)_2$ is an eminently suitable example. In this case the equation becomes

$$\ln \alpha_w/\alpha_{al} = \frac{\epsilon^2}{2.303\ akT}(1/D - 1/D_o)$$

The solubilities of $Ba(OH)_2$ in acetone-water mixtures at 25°C are taken from the work of Herz and Knoch[1] and the dielectric constants of acetone-water mixtures from P. Drude[2]. The concentrations vary from 0.0004 to 0.02 mol pro litre and as the variations in the activity coefficients are rather large, the activities are used in place of the simple molar concentrations.

| % acetone by weight | $a \times 10^{-8}$ |
|---|---|
| 70%—60% | 1.56 |
| 70%—50% | 1.66 |
| 70%—40% | 1.63 |
| 60%—40% | 1.68 |
| 50%—40% | 1.55 |

Taylor[3] has measured the solubilities of $KClO_3$ in alcohol-water and in acetone-water mixtures at 30°C. These vary from 0.01 to 0.4 mol pro litre and as the activity coefficients in this case cannot be compared with experimental values, but have to be calculated from an approximate formula, which is only true at relatively small concentrations, it is to be expected that there will be considerable variation in the value of $a \times 10^{-8}$, for which the following were obtained.

| % non-electrolyte | alcohol | acetone |
|---|---|---|
| 90%—70% | 1.37 | 2.36 |
| 70%—50% | 1.92 | 2.67 |
| 50%—30% | 2.15 | 2.60 |
| 30%—20% | 1.59 | 2.45 |

The variation of $a$ in either alcohol-water or acetone-water is probably due to the method of calculating the activity coefficient but the large and persistent difference between the values for the two types of solvent presents a much more difficult problem. Prof. Debye has suggested a method which, though it has only been able to make a small correction in the radius, is nevertheless of great interest in giving a clear picture of the distribution of water and non-electrolyte in the immediate vicinity of an ion. A detailed account will be

[1] Z. anorg. Chem., 45, 268 (1905).
[2] Z. physik. Chem., 23, 288 (1897).
[3] J. Phys. Chem., 1, 720 (1897).

published shortly by Prof. Debye; but an outline of it may be given here, insofar as it applies to the problem on hand. In the work already referred to, Flatt is led by experimental facts to explain various phenomena by the supposition that the ions are hydrated in alcohol-water solutions. This is essentially the same conclusion to which one is led by the purely theoretical considerations of Prof. Debye.

Starting with the thermodynamical potential of an alcohol water mixture and the fact that the total number of molecules of water and of alcohol will not vary, although in the neighbourhood of an ion their distribution will be a function of the distance from the ion, the following equation has been derived giving the relation between the molar fraction $C_w$ of the water and the distance $r$.

$$\Omega_a \ln \frac{C_w}{\bar{C_w}} + \Omega_w \ln \frac{1-C_w}{1+C_w} = \frac{e^2}{8\pi r^4 RT\rho} F(D)$$

where $\bar{C_w}$ is the constant molar fraction at an infinite distance from the ion, $\Omega_a$, $\Omega_w$ are the molar volumes of alcohol and water respectively and $\rho$ the density of the alcohol water mixture, which will also vary with the distance $r$. If $D$ is a linear function of the weight concentration of water then F(D) has the value $1/D^2\,[(M_a D_w \Omega_a - M_w D_a \Omega_w) + (M_a\Omega_w - \Omega_a M_w)D]$

$D_w$, $D_a$, $M_w$, $M_a$ being the dielectric constants and the molecular weights of pure water and pure alcohol respectively. The curves showing the distribution of alcohol and water in the neighbourhood of an electric charge, for solutions of 90% to 20% by weight of alcohol are given here. It is seen that within a few Ångströms from the charge the concentration of water rises very rapidly even in the case of 90% alcohol and that near the surface of the ion only molecules of water are present. This is what one would naturally expect from the fact that the water molecules are much more easily polarised than those of alcohol. As a result of this the dielectric constant of the medium surrounding the ions is not the same as that of the rest of the solvent, but varies with the distance from the ion, the two becoming identical at large distances. By taking this into account, the size of the radius in the previous equations will be reduced. Whereas the work of charging the ion was formerly calculated as $e^2/2Da$, it will now be represented by $\int_{r=a}^{r=\infty} \frac{e^2 dr}{2Dr^2}$. The value of this integral can be obtained graphically as $C_w$ and hence D is known as a function of the distance $r$, from the distribution curves. This however is not the entire work of charging the ion, as there is a potential by no means negligible, due to the "piling up" of the water molecules. It is unnecessary here to give further details but this work may be calculated from the integral

$$W = kT \int_{r=a}^{r=\infty} 4\pi r^2 \left[\frac{C_a \ln c_a/\bar{c_a} + C_w \ln C_w/\bar{C_w}}{C_a\Omega_a + C_w\Omega_w}\right]$$

In this manner the total work required to charge up the ion is plotted against the distance $r$ and the difference in this work for different solvent media, with any value of $a$, can be found immediately from the graph. It can then be compared with that calculated from the solubilities and represented by $kT \ln \alpha_w/\alpha_{al}$, so that from the graph we can find that value of $a$ for which these two agree. The following were thus obtained for $a \times 10^{-8}$.

| % non-electrolyte | alcohol | acetone |
|---|---|---|
| 90%—70% | 1.18 | 2.16 |
| 70%—50% | 1.63 | 2.50 |
| 50%—30% | 1.85 | 2.50 |
| 30%—20% | 1.20 | 2.30 |

Comparing these figures with the previous ones, uncorrected for hydration, it is clear that the fundamental difference in the value of the radius for alcohol and acetone is not explained. In the above considerations however the molar concentrations have been used in place of the activities and this may probably account for the fact that the differences still exist. It is also possible however that the cause may lie in some other, so far neglected, properties in the acetone and alcohol molecules themselves.

## Summary

The calculations for the value of the average radius $a$ of the ions of a considerable variety of salts in mixtures of alcohol water and acetone water, show that it is possible by the means described in this paper.

1) To establish the relation between the solubility of a salt in a mixed solvent and the dielectric constant of the solvent.

2) Having the solubility curve given, to determine the dielectric constants of the mixtures.

3) Having the dielectric constants given, to determine the solubility curve at least to a fair degree of approximation.

Curves are also given showing the distribution of alcohol and water in the immediate vicinity of an ion.

*Physical Institute,*
*Polytechnikum,*
*Zurich.*
*March 1, 1926.*

# SOLUBILITY AND ELECTROLYTIC CONDUCTANCE OF MESITYLENE PHOSPHINOUS ACID

BY H. J. M. CREIGHTON

Mesitylene phosphinous acid, $(CH_3)_3C_6H_2 . P(OH)_2$, which was first prepared by Michaelis[1] by the action of water on mesitylene dichlorphosphine, which in turn was produced by the interaction of phosphorus trichloride and mesitylene in the presence of aluminium chloride, forms salts of the type, $[(CH_3)_3C_6H_2(PO_2H)]M'$, $[(CH_3)_3C_6H_2(PO_2H)]_2M''$, etc. Hence, it is a monobasic acid.

The mesitylene phosphinous acid[2] used in the following experiments had, after repeated recrystallization from hot water, a melting point of 147.35° (corr.).

The solubility of mesitylene phosphinous acid was determined as follows: A large excess of the finely powdered acid was placed in each of two bottles, which were three-quarters filled with "conductance water" and closed with tight-fitting glass stoppers. The bottles were then agitated in a large thermostat, the temperature of which was kept constant to within 0.05°. At the end of the period of agitation the bottles were removed from the shaking device and allowed to remain in the thermostat, until the finely divided acid had settled. The weight of acid contained in a known weight of saturated solution was determined by titration against a standardized solution of barium hydroxide. The values obtained for the solubility of mesitylene phosphinous acid at a number of temperatures are as follows:

| Temperature C°, | 1.0 | 25.0 | 35.0 | 45.0 | 65.0 | 85.0 |
|---|---|---|---|---|---|---|
| Grams acid per 100 grams soln., | 0.289 | 0.299 | 0.324 | 0.385 | 0.525 | 0.700 |

The conductance of aqueous solutions of mesitylene phosphinous acid and its sodium salt was measured at 25 ± 0.01°, by means of Kohlrausch's alternating current bridge method.

The sodium salt of the acid was prepared by exactly neutralizing the acid with a saturated solution of "carbonate free" sodium hydroxide. The conductance data obtained with solutions of the salt are given in Table I. The limiting value of the equivalent conductance ($\Lambda°$), given in the table, has been calculated by means of the equation[3]:

$$\Lambda_o = \frac{\sqrt[3]{V_2} \cdot \Lambda_2 - \sqrt[3]{V_1} \cdot \Lambda_1}{\sqrt[3]{V_2} - \sqrt[3]{V_1}}$$

[1] Michaelis: Ann., 294, 36 (1897).

[2] The writer is indebted to a former colleague, Dr. A. P. Tanberg, for this acid.

[3] Kohlrausch-Holborn: "Leitvermögen der Elektrolyte", 107 (1898).

TABLE I

Equivalent Conductance of the Sodium Salt of Mesitylene Phosphinous Acid, at 25°.

| V = | 100 | 200 | 400 | 500 | 800 | 1000 | ∝ |
|---|---|---|---|---|---|---|---|
| | *First Series* | | | | | | |
| $\Lambda$ = | 71.90 | 73.47 | 74.73 | 75.00 | 75.69 | 76.30 | |
| $\Lambda_o$ = | 79.48 | 79.55 | 78.74 | 79.58 | 80.15 | | 79.5 |
| | *Second Series* | | | | | | |
| $\Lambda$ = | 71.53 | 73.47 | 74.83 | 75.12 | 76.00 | 76.30 | |
| $\Lambda_o$ = | 80.89 | 80.08 | 78.90 | 81.05 | 76.12 | | 79.4 |

From the value of $\Lambda_o$ for the sodium salt of mesitylene phosphinous acid and that of the conductance (50.6) of the sodium ion, it follows that the conductance of the anion of the acid is 28.9, at 25°. On adding to this the value of the conductance (347) of the hydrogen ion at the same temperature, 376 is obtained for the limiting value of the conductance of mesitylene acid at 25°.

In Table II are given the data obtained for the equivalent conductance, the degree of dissociation and the mass-cation constant (K) of mesitylene phosphinous acid at different concentrations.

TABLE II

Conductance of Mesitylene Phosphinous Acid, at 25°

$\Lambda_o = 376$

| V | $\Lambda$ | $\alpha$ | $K \times 10^3$ |
|---|---|---|---|
| 88.27 | 233.2 | 0.620 | 11.46 |
| 176.54 | 270.6 | 0.720 | 10.49 |
| 353.08 | 296.4 | 0.788 | 8.29 |
| 706.2 | 312.1 | 0.830 | 5.74 |
| 1412.3 | 318.8 | 0.848 | 3.35 |
| 2824.6 | 320.1 | 0.851 | 1.72 |

It will be observed that the value of the mass-action constant of mesitylene phosphinous acid decreases steadily with the concentration of the acid. In this respect, the behavior of the acid is analogous to that of a number of the aromatic sulphinic acids[1].

[1] Cf. Asriel: Dissertation, Heidelberg (1900).

*Department of Chemistry,*
*Swarthmore College,*
*May 24, 1926.*

# THE SYSTEM: SODIUM SULPHATE, SULPHURIC ACID—ETHYL ALCOHOL

BY HORACE B. DUNNICLIFF, INDAR SAIN SIKKA ANDRATTAN CHAND HOON

Butler and Dunnicliff[1] showed that dry ethyl alcohol extracts two thirds of the sulphuric acid from pure dry sodium hydrogen sulphate and leaves behind a residue of the intermediate sulphate $3Na_2SO_4 . H_2SO_4$. The sulphuric acid dissolves in the alcohol and partial esterification takes place. The velocity of this esterification and the equilibrium in alcoholic sulphuric acids have been

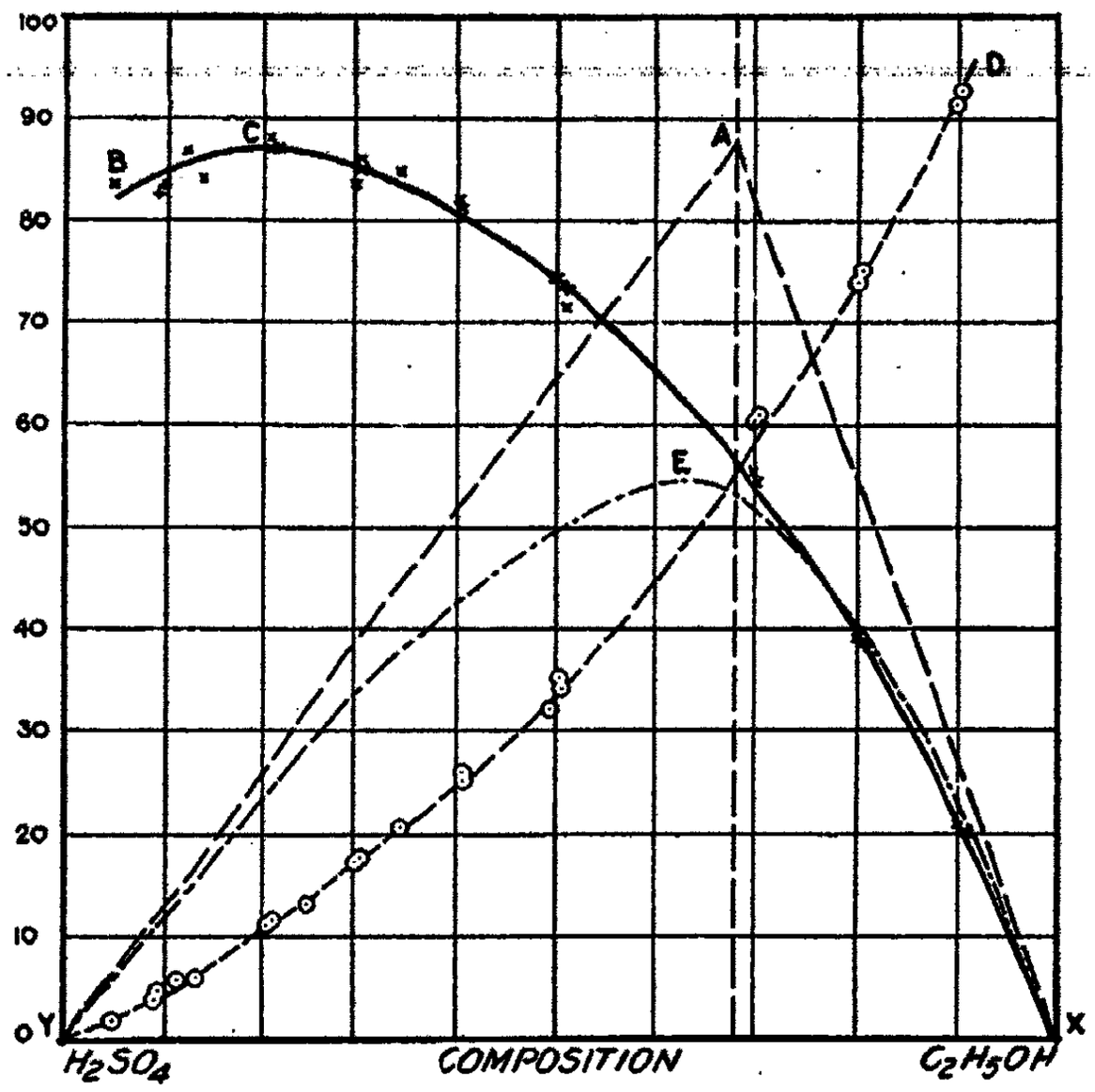



FIG. 1

Composition of Alcoholic Sulphuric Acid.
BCD Percentage esterification of Sulphuric Acid present.
YD Percentage of esterification of total Alcohol present.
YEX Percentage of Ethyl Hydrogen Sulphate present.
YAX Maximum possible percentage of Ethyl Hydrogen Sulphate present.

studied by the same authors[2]. At low concentrations of sulphuric acid, the rate of esterification is slow. The percentage conversion of both alcohol and sulphuric acid in alcoholic sulphuric acids has also been determined and the various equilibrium relationships are given in Fig. 1. This diagram is self-

[1] J. Chem. Soc., 117, 649 (1920).
[2] J. Chem. Soc., 119, 1386 (1921).

explanatory and was plotted from the experimental results on which the second paper referred to above was based.

The object of the work to be described was to investigate the equilibrium between sodium sulphate, sulphuric acid, and ethyl alcohol over a wide range of concentrations.

In the first series of experiments, dry sodium hydrogen sulphate was allowed to react with a known weight of dry ethyl alcohol in a thermostat maintained at 18.3 ± 0.5°C by electrical control. Pure sodium hydrogen sulphate, dry ethyl alcohol and alcoholic sulphuric acids were prepared by standard methods.

Weighed quantities of sodium hydrogen sulphate and alcohol were sealed off in glass bulbs of about 10 c.c. capacity and shaken for about 48 hours in the thermostat. The tube was then allowed to remain stationary in the bath until the solid phase had settled to the bottom. The liquid and the residue ("Rest") were separated and analysed as described below, the same method being used for each analysis.

Since the partial esterification of the sulphuric acid is a complicating factor in the problem, it is necessary to determine

(a) The acidity due to free sulphuric acid, together with that due to ethyl hydrogen sulphate. The latter was calculated as sulphuric acid and the acidity is called the "Direct Acidity".

(b) The amount of sulphuric acid converted into ethyl hydrogen sulphate.

(c) The sodium sulphate and

(d) the remainder of the constituents (by difference).

*Methods of Determination:—*

(a) A weighed amount of the substance was titrated against caustic soda using methyl orange as indicator and the acidity calculated as parts of sulphuric acid per 100 parts of the substance. This is the "Direct Acidity".

(b) The ester was determined[1] by method 3, and recorded in the Tables as "$H_2SO_4$ as ester", i.e. percentage of ester × 98/126.

(c) The sodium sulphate was determined by evaporating a weighed quantity of the substance to dryness in a platinum basin on a water bath. The residue was heated first in an air oven and finally by ignition over a blowpipe before and after treatment with a few drops of nitric acid.

Many estimations were made and a number of analysis are given in Table I. It was desired to find the best method of representing these results graphically and it was thought that, making certain limitations, this might be done by the usual method for a ternary system. Owing to the complication introduced by the esterification of the acid, it was necessary to consider which of three possible ways of condensing the system to one of three components would be best.

1. (a) sodium sulphate, (b) sulphuric acid assuming that no esterification had taken place, (c) alcohol.

[1] Butler and Dunnicliff: J. Chem. Soc., 119, 1385 (1921).

2. (a) sodium sulphate, (b) "direct acidity" (V.S.), (c) "Solvent" i.e., 100-(a+b).

3. (a) sodium sulphate, (b) sulphuric acid existing as such and omitting acidity due to the ethyl hydrogen sulphate. This is recorded in the tables as "Free $H_2SO_4$", (c) "Solvent" = alcohol + ethyl hydrogen sulphate + water.

The first method was shown to be inadmissible by plotting the results. It is not feasible to ignore esterification even though the values at low concentrations of sulphuric acid are small.

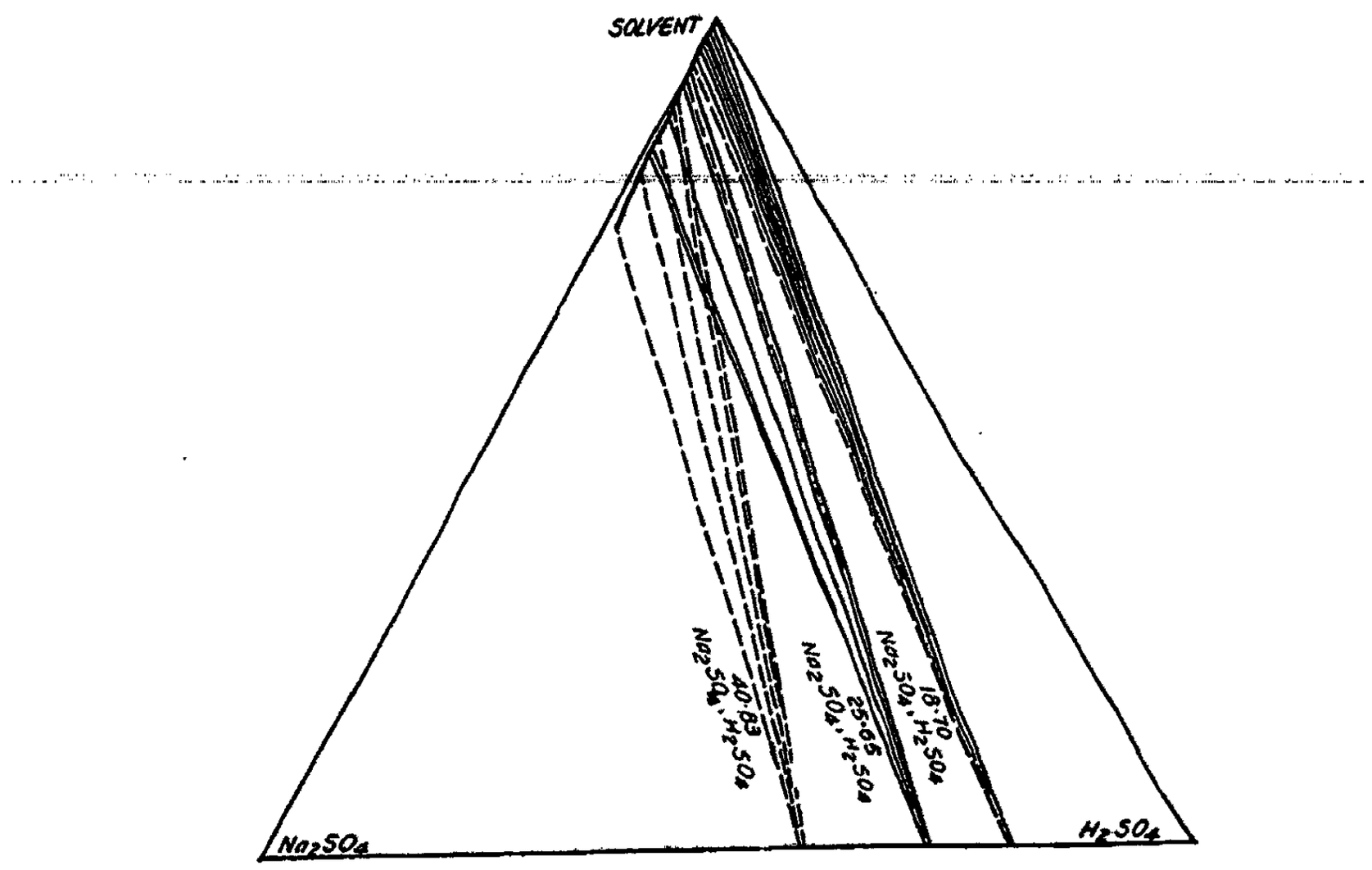



FIG. 2
The System Sodium Sulphate-Sulphuric Acid-Ethyl Alcohol

Method 2 gave a rough convergence of the conjugation lines but a much more satisfactory convergence of the lines to foci on the sodium sulphate—sulphuric acid line was given when the results were plotted according to method 3. These are shown in the continuous lines in Fig. 2 and indicate the existence of solid phases having the formulae $3Na_2SO_4$, $H_2SO_4$ and $2Na_2SO_4$, $H_2SO_4$.

It will be seen that the change in the solid phase occurs when the total sulphuric acid is between 5.5 and 6.8 per cent (Free $H_2SO_4$ = 4.5 − 5.7 per cent, ester 1.0 − 1.13 per cent) and the weight of alcohol used is about 4.5 times the weight of the sodium hydrogen sulphate. These results indicate that at low concentrations of ethyl hydrogen sulphate, the ester has only a small influence on the equilibrium. The effect of the ester on the equilibrium when it is present in large proportions is dealt with later.

TABLE I

Action of Ethyl Alcohol on Sodium Hydrogen Sulphate

| Parts of alcohol per unit of sodium hydrogen sulphate | $H_2SO_4$ as Ester % | Liquid Phase: Free $H_2SO_4$ % | Liquid Phase: $Na_2SO_4$ % | Liquid Phase: Solvent % | "Rest": $H_2SO_4$ as Ester % | "Rest": Free $Na_2SO_4$ % | "Rest": $Na_2SO_4$ % | "Rest": Solvent % | Calculated acidity of solid phase % | |
|---|---|---|---|---|---|---|---|---|---|---|
| 12.2 | 0.30 | 1.58 | 0.33 | 98.09 | 0.15 | 9.26 | 36.89 | 53.85 | 18.22 | |
| 9.9 | 0.34 | 2.20 | 0.42 | 97.38 | 0.20 | 7.68 | 27.36 | 64.96 | 18.65 | $3Na_2SO_4, H_2SO_4$ |
| 9.2 | 0.41 | 2.43 | 0.46 | 97.11 | 0.18 | 10.26 | 39.60 | 50.14 | 18.61 | requires |
| 8.2 | 0.41 | 2.90 | 0.46 | 96.64 | 0.20 | 10.17 | 37.43 | 52.40 | 18.75 | 18.70% $H_2SO_4$ |
| 6.1 | 0.80 | 3.55 | 0.47 | 95.98 | 0.40 | 12.04 | 44.21 | 43.75 | 19.17 | |
| 5.0 | 1.00 | 4.47 | 0.41 | 95.12 | 0.42 | 12.70 | 46.49 | 40.81 | 18.89 | |
| 4.0 | 1.13 | 5.70 | 0.40 | 93.90 | 0.77 | 10.94 | 19.80 | 69.26 | 26.30 | |
| 3.1 | 1.38 | 7.35 | 0.48 | 92.17 | 0.70 | 14.40 | 25.98 | 59.62 | 27.30 | $2Na_2SO_4, H_2SO_4$ |
| 2.1 | 1.42 | 9.20 | 0.49 | 90.31 | 0.51 | 16.26 | 31.84 | 51.90 | 26.40 | requires |
| 1.5 | 1.60 | 10.70 | 0.50 | 88.80 | 0.69 | 10.30 | 38.90 | 41.80 | 26.90 | 25.65% $H_2SO_4$ |
| 1.2 | 1.44 | 14.86 | 0.51 | 84.63 | 0.66 | 21.73 | 38.80 | 39.47 | 27.70 | |
| 0.8 | 3.24 | 14.51 | 0.52 | 84.97 | 1.04 | 22.24 | 42.40 | 35.36 | 27.70 | |

These results obtained graphically were checked by calculation. The "Rest" consists of true solid phase contaminated with true liquid phase, the composition of which has been determined. This contamination was allowed for by subtracting from the values found for free sulphuric acid and sodium sulphate in the "Rest", amounts calculated from the values in columns 4 and 5 respectively in the proportion of

$$\frac{\text{percentage of solvent in the solid phase}}{\text{percentage of solvent in the liquid phase.}}$$

From the net values so obtained for the sulphuric acid and the sodium sulphate in each case, the percentage acidity of each "True solid phase" was calculated and is shown in the 10th column in Table I. This would only be possible if the true solid phase contained no ester in combination. This was shown to be the case by drying a series of samples of "Rest" on porous tiles in desiccators. The maximum amount of ester obtained in the residue was 0.2% of ester and the composition of the "dried" residue corresponded with the values found by calculation and as indicated by the graphic method.

These results show that esterification was never complete (cf. Fig. 1). For this, not less than sixteen days would be necessary at the temperature of the experiment.

By the action of alcohol on sodium hydrogen sulphate, the maximum concentration of acid obtainable in the liquid phase is 17.75 per cent. If quantities of the salt sufficient to obtain higher concentrations are employed it is not possible to separate the liquid phase and the "Rest". Hence it is impossible to investigate this system further by this method.

The equilibrium may be studied at all concentrations of sulphuric acid in two other ways:—

(a) By the action of alcoholic sulphuric acids on sodium sulphate.

(b) By the action of alcoholic sulphuric acids on sodium hydrogen sulphate.

It has been shown (loc. cit.) that consistent or complete results are very difficult to obtain by method (a) probably owing to the protective action of the synthetic acid sulphates formed from and adhering to the surface of the particles of sodium sulphate. It was decided therefore to attack pure sodium hydrogen sulphate with alcoholic sulphuric acids prepared and estimated as described (loc. cit.). In order that equilibrium in the alcoholic sulphuric acids should be established, they were allowed to stand for a month before use. The liquid phase and "Rest" were analysed as described above and a number of results are shown in Table II. In these experiments many difficulties arose. In some cases the mixture set to a firm jelly, in others a hard crystalline deposit adhered to the sides of the tube; at the highest concentrations in many of the early experiments, the solid entirely disappeared. This may be due to the formation of a colloidal solution, a supersaturated solution or both. The difficulty due to gelatinisation was a maximum when the alcohol and sulphuric acid were mixed in the proportion of 30:70 to 65:35 by weight but gelatinisation was a more or less constant trouble and it was shown that

TABLE II

Action of Alcoholic Sulphuric Acids on Sodium Hydrogen Sulphate

| No. | $H_2SO_4$ as Ester. Before action % | After action % | Liquid Phase: Free $H_2SO_4$ % | $Na_2SO_4$ % | Solvent % | $H_2SO_4$ as Ester in "Rest" % | "Rest": Free $H_2SO_4$ % | $Na_2SO_4$ % | Solvent % | Calculated acidity of Solid Phase. % |
|---|---|---|---|---|---|---|---|---|---|---|
| 1. | 8.4 | 7.66 | 4.91 | 0.01 | 95.08 | 2.20 | 14.89 | 54.34 | 30.77 | 19.34 |
| 2. | 14.3 | 13.58 | 6.26 | 0.81 | 92.93 | 2.16 | 15.94 | 44.49 | 39.57 | 23.79 |
| 3. | 17.4 | 16.59 | 6.97 | 0.55 | 92.48 | 3.92 | 16.94 | 43.39 | 39.67 | 24.46 |
| 4. | 21.4 | 20.92 | 5.68 | 0.10 | 94.22 | 6.86 | 20.04 | 21.69 | 58.27 | 43.34 |
| 5. | 23.0 | 22.50 | 6.98 | 0.82 | 92.20 | 6.18 | 26.90 | 34.21 | 38.89 | 41.54 |
| 6. | 31.2 | 30.82 | 8.37 | 0.56 | 91.07 | 8.56 | 30.55 | 40.75 | 28.70 | 40.73 |
| 7. | 34.5 | 34.34 | 9.50 | 0.48 | 90.02 | 11.32 | 29.20 | 36.33 | 34.47 | 41.33 |
| 8. | 33.4 | 32.16 | 14.59 | 0.42 | 84.99 | 25.50 | 30.84 | 38.97 | 30.19 | 39.94 |
| 9. | 37.9 | 37.52 | 17.01 | 0.71 | 82.28 | 20.53 | 33.47 | 43.02 | 23.51 | 40.07 |
| 10. | 39.0 | 39.32 | 23.15 | 1.74 | 75.11 | 9.10 | 36.36 | 37.97 | 25.67 | 43.22 |
| 11. | 42.2 | 44.96 | 19.12 | 1.98 | 78.90 | 28.94 | 40.41 | 22.25 | 37.34 | 59.56 |
| 12. | 36.9 | 55.00 | 14.69 | 5.25 | 80.06 | 42.08 | 32.98 | 17.27 | 49.75 | 63.10 |
| 13. | 30.4 | 41.92 | 39.42 | 2.60 | 57.98 | 31.54 | 46.01 | 20.02 | 33.97 | 55.72 |
| 14. | 18.0 | 17.16 | 63.83 | 2.72 | 33.45 | 12.00 | 61.94 | 21.82 | 16.24 | 58.88 |

$3Na_2SO_4 . H_2SO_4$ requires 18.70% $H_2SO_4$; $2Na_2SO_4 . H_2SO_4$ requires 25.65% $H_2SO_4$; $Na_2SO_4 . H_2SO_4$ requires 40.83%; $H_2SO_4$ and $Na_2SO_4 . 2H_2SO_4$ requires 57.98% $H_2SO_4$.

the liquid phase contained the solid phase in colloidal solution. In order to ensure completion of the reaction the tubes were rotated in the thermostat for 14 days. In the case of the high concentrations (marked with an asterisk) it was not possible to keep the temperature at 18.3° owing to the beginning of the hot season having set in but the temperature in these instances did not exceed 20.4°C and the equilibrium is not very sensitive to a small range of temperature. The contents of many of the tubes became coloured, some pink, some red and, in two cases, brown.

An examination of the results in Table II shows that there are changes of solid phase at the concentration of the alcoholic sulphuric acid as follows:—

(1) The change of phase from $3Na_2SO_4$, $H_2SO_4$ to $2Na_2SO_4$, $H_2SO_4$ occurs when the concentrations are between the following limits:—

| | |
|---|---|
| Total acid | 12.56 to 19.84% |
| $H_2SO_4$ as ester | 7.65 to 13.58% |
| 'Free' $H_2SO_4$ | 4.91 to 6.26% |

Compare the range of concentration for the same change of phase in the first series.

| | |
|---|---|
| Total acid | 5.47 to 6.83% |
| $H_2SO_4$ as ester | 1.00 to 1.13% |
| Free $H_2SO_4$ | 4.47 to 5.70% |

(2) The change of phase from $2Na_2SO_4$, $H_2SO_4$ to $Na_2SO_4$, $H_2SO_4$ (= $NaHSO_4$) occurs when the concentrations are between the limits:

| | |
|---|---|
| Total acid | 23.56 to 26.60% |
| $H_2SO_4$ as ester | 16.59 to 20.92% |
| Free $H_2SO_4$ | 6.97 to 5.68% |

(3) The change of phase from $Na_2SO_4$, $H_2SO_4$ to $Na_2SO_4$, $2H_2SO_4$ occurs when the concentrations are between the limits:

| | |
|---|---|
| Total acid | 62.47 to 64.28 |
| $H_2SO_4$ as ester | 39.92 to 44.96 |
| Free $H_2SO_4$ | 23.15 to 19.12 |

(a) Results 1-10 are plotted in Fig. 2 and are indicated by broken lines. No. 11-14 are very irregular and are not shown in the diagram.

(b) Though in the first method of investigation the ethyl hydrogen sulphate appeared to be of minor importance, the results obtained by the second method indicate that this was on account of its low concentration. A study of the two tables will show that the higher the concentration of ester, the greater the concentration of free sulphuric acid with which a given solid phase can be in equilibrium. This influence is shown in Fig. 2 by the crossing of the two sets of lines.

(c) In some cases it will be observed that the percentage of ester in the liquid phase is less after the reaction than before the hydrogen sulphate was mixed with the alcoholic sulphuric acid. This is not due to the decomposition of the ester but to its diminution in percentage owing to the increase in the

amount of the free sulphuric acid present. This increase in the sulphuric acid is due to the extraction of sulphuric acid from the hydrogen sulphate by the alcoholic sulphuric acid. The free sulphuric acid is in excess of the amount possible in an equilibrium mixture of alcoholic sulphuric acids of those concentrations (Table II, Nos. 1-3, vide also Fig. 1) but the time taken by the experiment is insufficient to establish equilibrium in the liquid phase at the temperature of working.

(d) The analyses given in Table II, Nos. 4-10 show that the solid phase is practically unchanged. This is confirmed by the nearly equal values in columns 2 and 3 which give the percentage of combined acid in the alcoholic sulphuric acid before use and in the liquid phase respectively. The total acidity after the reaction is given by the sum of the figures in columns 3 and 4 and these totals are in ascending order of magnitude with the exception of Nos. 11 and 12, where the results are probably not so accurate as they are up to No. 10 inclusive. In Nos. 4-10 this total is found to be in close agreement with the strength of the alcoholic sulphuric acid before use (values not given in the table). It will also be observed that as the amount of esterification of the alcoholic sulphuric acid increases, it has a greater influence on the nature of the solid phase: compare Nos. 2 and 3, 2 and 4, 10 and 11, 12 and 14.

(e) Above 65% alcoholic sulphuric acid, the sodium hydrogen sulphate extracts acid from the liquid phase and forms a new solid phase. There is an indication of a compound $2H_2SO_4 . Na_2SO_4$ but the evidence is not conclusive in view of the complications which occur at high concentrations. When the percentage of sulphuric acid is 70 or over, the liquid phase becomes cloudy and a gelatinous substance is present. At concentrations of 80 per cent $H_2SO_4$ and over, the sodium hydrogen sulphate goes into solution. It was hoped that crystals of the true solid phase might be obtained by freezing and vigorous shaking but though the solution must have been highly supersaturated, all attempts were unsuccessful. In some tubes the solid phase adhered firmly to the walls of the tube as a hard crystalline mass and it is probable that the solid phases formed by the addition of alcoholic sulphuric acid of over 60% strength to sodium hydrogen sulphate were not uniform in composition. In one instance the centrifugalised liquid phase contained 11.5 per cent of sodium sulphate. This was present either as a colloidal sodium hydrogen sulphate probably having the composition $3H_2SO_4 . Na_2SO_4$ or as a supersaturated solution. Many repetitions failed to get absolutely uniform results and those quoted are typical of the values obtained.

*Punjab University,*
*Government College,*
*Lahore,*
*India.*

# A NOMOGRAM FOR THE VAN'T HOFF-ARRHENIUS TEMPERATURE EQUATION

BY OSCAR W. RICHARDS

The use that the biologists are making of the van't Hoff-Arrhenius temperature equation for the separation of various vital phenomena seems to warrant the construction of a nomogram or alignment chart with which one can readily discover the value of the thermal increment $\mu$. This equation is

$$K_2/K_1 = e^{\mu/2(1/T_1 - 1/T_2)} \qquad (1)$$

or

$$\mu = \frac{4.6(\log_{10}K_2 - \log_{10}K_1)T_1T_2}{T_2 - T_1} \qquad (2)$$

To use the accompanying nomogram a line is drawn connecting the two temperatures $T_1$ and $T_2$. Since in the construction, which will be explained later, the absolute temperature values are given in degrees centigrade it is unnecessary to use other than the centigrade values. A second line is drawn thru the two velocities $K_2$ and $K_2$ to the difference scale. Now, if a line is drawn from the point of intersection of the second line with the difference scale parallel to the first line to the $\mu$-scale it will indicate the numerical value of $\mu$. One must be careful to use the proper temperature and velocity scales.

As will be seen from Table I the value found of $\mu$ will be within 2-3% of the true value of $\mu$, or within, on the average about 300 units of the true value. An error of this magnitude is often of less importance as the characteristic values of $\mu$ are usually at least a thousand units apart when vital processes are measured. However, the chart is only intended to be a ready aid to the experimenter during the process of an investigation rather than for the calculation of critical values. The data of Table I with the exception of the last set are from actual experiments and the calculated value was made with the aid of a five or six place logarithmic table.

TABLE I

Values of $\mu$ from chart and from calculation

| $K_2$ | $K_1$ | $T_2$ | $T_1$ | $\mu$ Calc. | $\mu$ Chart. | Error | % Error |
|---|---|---|---|---|---|---|---|
| 10.0 | 3.2 | 30 | 22.5 | 27,175 | 27,600 | +425 | +1.6 |
| 139 | 9.67 | 45 | 25 | 25,230 | 25,300 | +70 | +0.3 |
| 15.7 | 1.55 | 49 | 38 | 22,526 | 23,500 | +947 | +4.4 |
| 4.55 | 1.7 | 38 | 32 | 31,120 | 31,000 | −120 | −0.4 |
| 26.0 | 16.1 | 30 | 22.5 | 11,431 | 11,200 | −231 | −2.0 |
| 33.8 | 26.5 | 30 | 22.5 | 5,806 | 6,000 | +194 | +3.3 |
| 31.6 | 28.2 | 30 | 22.5 | 3,374 | 3,250 | −124 | −3.7 |
| 10.0 | 5.7 | 30 | 20 | 9,970 | 10,000 | +30 | +0.3 |
| | | | | | Average | 271 | 2.06 |

Root-mean-square error 395.

The nomogram was constructed from the following equation which is derived from equation (1) which is

$$\log_{10}K_2-\log_{10}K_1=y=\frac{\mu}{4.6}\left(\frac{1}{T_1}-\frac{1}{T_2}\right). \qquad (3)$$

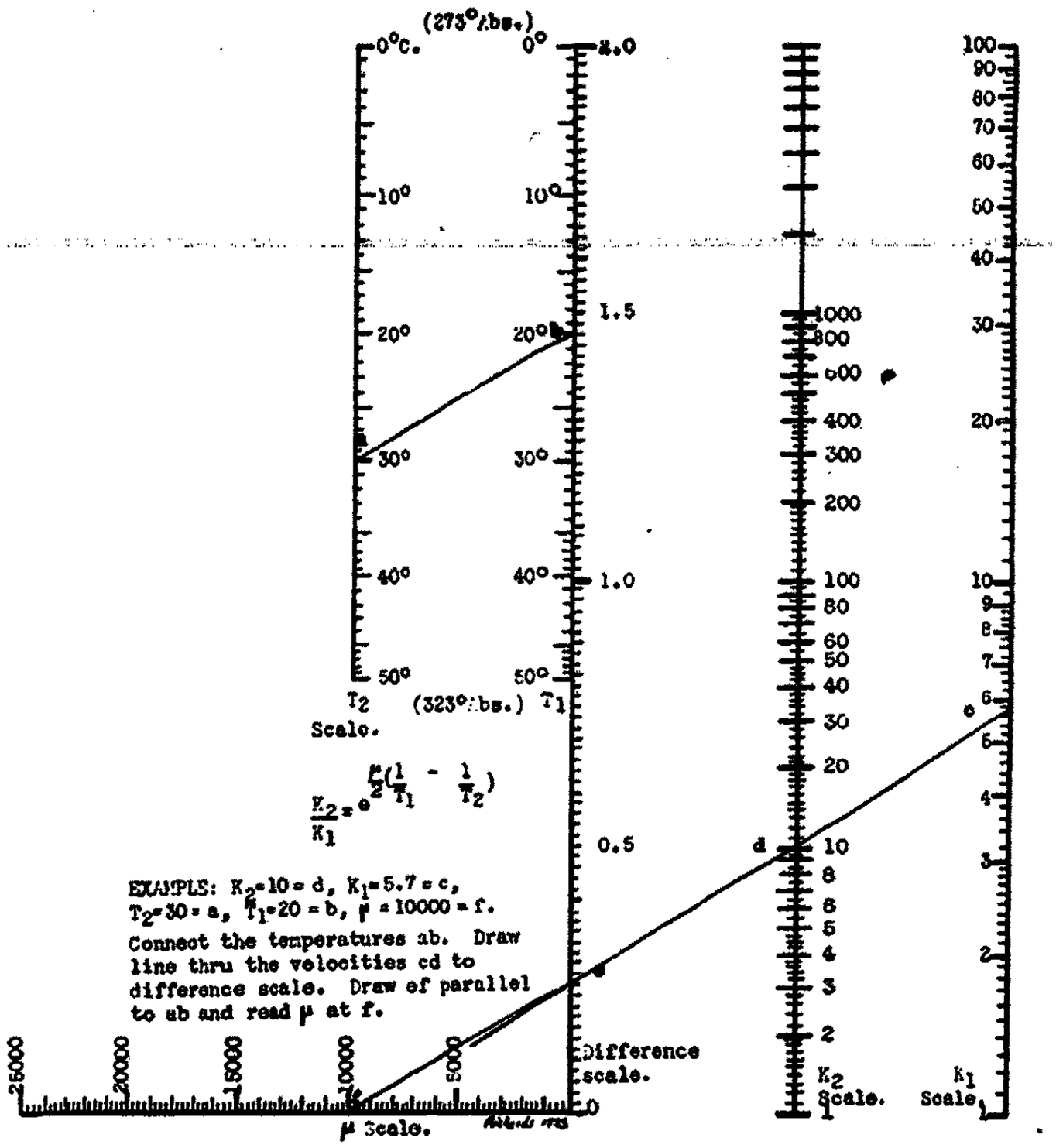



FIG. 1

The left hand member of (3) may be represented in the desired nomogram as a subtraction form, where the dividend scale $T_2$ has divisions one-half of the magnitude of those of the divisor scale $T_1$, and where both scales have logarithmic ruling. The difference scale is graduated equally to read in terms of the numerical differences of the logarithms. It may be conveniently graduated by noting that it will read 1 at the point of its intersection with a line connecting the values of $T_2=100$ and $T_1=10$.

To express the right hand member of (3) in the most compact form requires a nomogram of the subtraction Z-type.[1] The temperature scales are graduated in units of the reciprocals of the absolute temperatures on the parallel sides of the Z. For the convenience of the user the centigrade values were marked at the proper places. From trial the position of the bar of the Z was found to be almost parallel to the bases of the other scales. When the two nomograms are combined to give the graph of the complete equation it is convenient to place the difference scale and one limb of the Z on the same line. All of these scales may be extended by using the same scale factors and method of graduation as the particular scales now have and following the methods outlined in this description of the construction.

*Department of Zoology,*
*University of Oregon.*

[1] For the theory of these charts see J. B. Peddle: "The Construction of Graphical Charts." McGraw-Hill Co. 1910.

# THE ACTION OF METALS ON NITRIC ACID

BY E. J. JOSS

## Introduction

The results of this paper, which is one of a series from the Laboratory of Chemistry of Cornell University, contribute to the theory of the action of metals and various other reducing agents on nitric acid and its reduction products.

Previous papers[1] in this series have laid the foundation for this work. This paper comprises, in general, the rounding out of the theory and the proof of its veracity by application to the data of numerous investigators.

Too much credit cannot be given to the work of Freer and Higley, pioneers in this field, who would have completely solved the problem, had they not been too early to profit by the work of the investigators in the field of over-voltage.

## The Action of Metals on Nitric Acid

The interaction of metals and nitric acid is a problem that has caused chemists much difficulty for a great many years.[2] Much work has been done on this subject and many working hypotheses have been developed. The difficulty with these is that no one hypothesis will account for more than a few isolated facts.

In 1842 Millon[3] undertook to determine the temperature at which pure nitric acid, of varying concentrations, acts upon metals. He found that an acid having a specific gravity of 1.07 (12 %) does not attack copper at 20° C., but that, upon addition of a little potassium nitrite, action begins immediately, and from this he concluded that in the reduction copper nitrite is first formed, the latter being subsequently decomposed by the nitric acid. Millon's studies of the products of reduction were only qualitative. From these he concluded that the products obtained depended upon: 1. concentration of acid; 2. temperature; 3. the presence of nitrogen peroxide; and 4. solubility of the products.

Millon's work will be discussed later under the head of nitrous acid.

Gay-Lussac[4] added sulphuric acid (38 %) and nitric acid of specific gravity 1.07 (12 %), respectively, to copper in two test tubes, placing both in a freezing mixture, and thus found that there was no action in either case until nitrogen dioxide was added, whereupon both reacted with equal rapidity.

---

[1] Turrentine: Trans. Am. Electrochem. Soc., **10**, 49 (1906); Wilkinson: **13**, 309 (1908); Bancroft: J. Phys. Chem., **28**, 475, 973 (1924); Milligan: **29**, 554 (1924); Milligan and Gillette: **28**, 744 (1924); Nichols and Derbigny: **30**, 491 (1926).

[2] Bancroft: J. Phys. Chem., **28**, 475 (1924).

[3] Ann. Chim. Phys., (3) **6**, 95 (1842).

[4] Ann. Chim. Phys., (3), **7**, 385 (1843).

Gay-Lussac concluded that the experiment proved simply that "hyponitric acid" (nitrogen dioxide) is less stable than nitric acid. His work, like Millon's, was mainly qualitative.

In 1875 Acworth[1] made a series of quantitative experiments with the view of determining the proportions of nitric oxide, nitrous oxide, and nitrogen which are formed at different stages of the solution of copper in nitric acid; but no attempt was made to estimate the trioxide and dioxide of nitrogen produced, nor was any investigation undertaken of the effect of temperatures, above the ordinary. The conclusions of this investigator were:

1. Cold dilute nitric acid, acting on copper, gives almost pure nitric oxide, the gas evolved containing 90-95 % of that substance, but with increase of copper nitrate in the solution, the per cent of nitric oxide diminishes.

2. If the nitric acid is nearly saturated with cupric nitrate before the experiment, the action on copper yields as much as 85% of nitrous oxide with some nitric oxide and nitrogen.

3. Potassium nitrate in solution has little or no effect.

4. Ammonium nitrate added to the solution gives rise to the evolution, chiefly, of nitrogen and nitrous oxide.

3. Zinc, mercury, and iron, when treated with nitric acid and ammonium nitrate, evolve nitrogen chiefly.

Acworth recorded an experiment in which copper acting on a nitric acid solution almost saturated with copper nitrate gave a mixture of gases analyzing 85% of nitrous oxide, 4% nitric oxide, and 10% $N_2$.

In testing the action of copper on a solution of nitric acid almost saturated with cupric nitrate, Acworth and Armstrong[2] record an experiment in which 0.459 grams of copper are dissolved, and the analysis of the gases formed show 88% nitric oxide, 10% nitrous oxide, and 2% of nitrogen. This is only a slight decrease in nitric oxide yield (10%), as compared to an experiment in which only a small amount of cupric nitrate is added.

These two sets of data at first glance seem to be at variance with each other, but when the experimental conditions are investigated the differences become quite clear. Acworth used 15 grams of copper in his experiment, added successive portions of nitric acid, and allowed the reacting mixture to stand in contact with the reacting gases over night. Since the solutions in each case were almost saturated with cupric nitrate the only differences between the experiments are the quantities of reduction products in solution (only gaseous products were determined), and the time of contact of the resulting gaseous products with the solution covering the metallic reducing agent. It has been shown by Sabatier and Senderens[3] that moist metallic reducing agents will reduce nitric oxide to nitrous oxide. With the ordinary conception of the action of a moist solid and a gas, as consisting of an intermediate solution of the gas, it becomes quite clear why Acworth obtained such a large yield of nitrous oxide.

[1] J. Chem. Soc., 28, 828 (1875).
[2] J. Chem. Soc., 32, 67 (1877), Exp. XVII.
[3] Compt. rend., 114, 1476 (1892).

Further confirmation of the above view is found in the work of Russell and Lapraik[1] and of Cooke,[2] who find that nitric oxide will react slowly with water to give nitrogen, nitrous oxide, and nitrous acid. In the presence of a nitrous acid depolarizer (the metal), this reaction undoubtedly becomes a considerable factor.

The slightly decreased nitric oxide yield and increased nitrous oxide yield, with increase of cupric nitrate concentration, indicates that the solubility of nitric oxide, in a solution of nitric acid, increases with cupric nitrate concentration.

The result of Acworth,[3] confirmed by Acworth and Armstrong,[4] that the reaction on copper of a solution of nitric acid containing ammonium nitrate gives rise chiefly to nitrogen, may be explained as follows: It has been proved[5] that the first reduction product of nitric acid is nitrous acid. The action of copper on a solution of nitric acid containing ammonium nitrate thus results first in the formation of some ammonium nitrite. Ammonium nitrite solutions decompose[6] under ordinary conditions, giving nitrogen and water. If this reaction goes on rapidly enough to use up the ammonium nitrite before it is reduced further, the gaseous product will be chiefly nitrogen. These are the results recorded.

Acworth and Armstrong[7] made the first real step forward in the study of the action of metals on nitric acid. They advanced the following theory: "We regard the action of the metal as consisting simply in the displacement of the hydrogen of the acid and the formation of the corresponding nitrate in the manner expressed by the following equation, in which R denotes the amount of any metal which is equivalent in combining or displacing power to two atoms of hydrogen:

$$R + 2\,HNO_3 = R(NO_3)_2 + 2\,H$$

"Under no circumstances however, is the hydrogen thus displaced evolved as such, it at once acts on the free acid present . . ., reducing it more or less completely to nitrous acid, nitrosidic (hyponitrous) acid, hydroxylamine, or ammonia, as shown by the following equations:

$$HNO_3 + 2\,H = HNO_2 + H_2O$$
$$HNO_3 + 4\,H = HNO + H_2O$$
$$HNO_3 + 6\,H = NH_2OH$$
$$HNO_3 + 8\,H = NH_3 + H_2O$$

---

[1] J. Chem. Soc., **32**, 35 (1877).
[2] Chem. News, **58**, 155 (1888).
[3] J. Chem. Soc., **28**, 837-839 (1875).
[4] J. Chem. Soc., **32**, 67 (1877).
[5] Gladstone and Tribe: J. Chem. Soc., **33**, 139 (1878); Müller and Weber: Z. Elektrochem., **9**, 955 (1903).
[6] Arndt: Z. physik., Chem., **39**, 64 (1901).
[7] J. Chem. Soc., **32**, 58 (1877).

"The gases which are evolved on dissolving metals in nitric acid result, we believe, from the decomposition of these reduction products and from their action upon each other.

"The nitric oxide is chiefly, if not entirely, formed by the decomposition of nitrous acid, in accordance with the equation

$$3\ HNO_2 = 2\ NO + HNO_3 + H_2O$$

"The nitrous oxide is in all probability chiefly the product of two distinct changes, viz., . . .

$$2\ HNO = N_2O + H_2O$$
$$NH_2OH + HNO_2 = N_2O + 2\ H_2O$$

"Finally we regard the nitrogen as chiefly the product of the action of nitrous acid on ammonia:

$$NH_3 + HNO_2 = N_2 + H_2O,$$

but it is perhaps in some cases in part, and in others entirely, the product of the action of nitric action on nitrosidic acid."

Bancroft[1] pointed out that the part of the theory of Acworth and Armstrong that deals with the solution of the metal, is nothing more than a special case of the electrolytic theory of corrosion, as developed by Whitney[2] in 1903.

Thorpe[3] found that the copper-zinc couple will reduce nitrates to ammonia. This result was confirmed by Gladstone and Tribe,[4] who proved the action to be electrolytic in nature, the reduction taking place at the cathode metal, that is, the copper.

In 1883 Divers[5] showed that metals which are acted on by nitric acid may be divided into two classes. The metals of the first class (copper, silver, bismuth, and mercury), when treated with nitric acid, form neither ammonia or hydroxylamine, while those of the second class (including tin, magnesium, zinc, cadmium, aluminum, and iron) produce ammonia or hydroxylamine, or both.

Divers advances a theory for the action of the two classes of metals: "there seems to be but one way of interpreting the action of the silver class of metals upon nitric acid, and that is to recognize that these metals combine with the nitrogen of the acid, and do not decompose its hydroxyl. . . . The metals of the tin-zinc class, characterized by forming ammonia with nitric acid, have certainly the power to displace hydrogen of the hydroxyl of such acids as sulphuric acid, and thus may directly form nitrate by displacing the hydrogen of nitric acid."

The conclusions Divers draws do not seem to follow as a logical consequence of his results. He gives no reason why a given metal should fall in one class rather than the other.

---

[1] J. Phys. Chem., 28, 478 (1924).
[2] J. Am. Chem. Soc., 25, 394 (1903).
[3] J. Chem. Soc., 26, 541 (1873).
[4] J. Chem. Soc., 33, 139 (1878).
[5] J. Chem. Soc., 43, 455 (1883).

Up to this time no investigators with the exception of Acworth and Armstrong had attempted to account for all the metal dissolved. Their analyses were only of gaseous products, and consequently there are discrepancies in their results of 20% or more between the equivalents of products obtained and the weight of metal employed.

Freer and Higley,[1] Higley,[2] and Higley and Davis[3] made a rather exhaustive study of the action of metals on nitric acid. The work of these investigators is very interesting, because they are the first to attack the action of a metal on nitric acid with the view that it differs only from the electrolytic reduction of the acid with the metal as cathode, in that in the reduction by electrolysis the metallic ions are not present. This, it will be shown, is by no means the whole story, but it is distinctly a valuable step in the right direction. In their work a hint of consideration is given also for the specific effect (catalytic effect plus overvoltage) of the metal itself. "If hydrogen, occluded and energized by the undissolved metal, is the reducing agent with dilute acid, then an electrolysis of the same acid in cells provided with anodes of platinum and cathodes of silver, copper, and lead, respectively, should at the latter poles yield products differing qualitatively and quantitatively somewhat as do those obtained by the solution of the same metals without the electric current, the acid being of the same specific gravity."

This, of course, was long before the days of overvoltage, so Higley cannot be blamed for not having solved the problem completely when it was so close in his grasp.

Bancroft,[4] in his presidential address before the American Electrochemical Society, gave the first clear, concise statement of this method of attack: "the most striking characteristic of an electrolytic action is that it occurs in two places—at the anode and at the cathode. This peculiarity can be made less marked by bringing the electrodes nearer and nearer together. When the distance between them vanishes, we have a chemical reaction in the ordinary sense of the word and not an electrochemical reaction. Any chemical reaction, therefore, which can be made to take place electrolytically, must consist of an anode and a cathode process.[5] Considering the matter in this light, we see that there is a possibility of the anode and cathode processes interfering and of one perhaps masking the other.

"In some cases it is easy enough to tell what the anode and the cathode processes are. If we dissolve zinc in sulphuric acid, the formation of zinc sulphate is the anode process and the evolution of hydrogen is the cathode process. Now we know that pure zinc does not dissolve readily in sulphuric acid. Consequently we should expect to find a difficulty of some sort if we electrolyze sulphuric acid between the electrodes. We find this in the form

[1] Am. Chem. J., 15, 71, 378 (1883); 21, 377 (1899).
[2] Am. Chem. J., 17, 18, (1895).
[3] Am. Chem. J., 18, 587 (1896).
[4] Trans. Am. Electrochem. Soc., 9, 13 (1906).
[5] Cf. Traube: Ber., 26, 1473 (1893); Haber: Z. physik. Chem., 34, 514 (1900).

of the so-called 'excess voltage' at the cathode; and in the electrolytic process we can obtain a more or less quantitative measurement of the phenomenon thought we are still far from knowing the cause of it.

"A less simple case is that of copper in dilute nitric acid. Copper reacts chemically with dilute nitric acid, setting free nitric oxide. The formation of copper nitrate must be the anode process and the reduction of the nitric acid the cathode process. . . .

"These experiments were performed to prove that the difference between the electrochemical and the chemical corrosion of copper by nitric acid was an apparent one only and due to an unsuspected difference in the conditions. In addition they illustrate the superior flexibility of the electrochemical method over the chemical method. In the electrochemical method there is no difficulty in varying the concentration of the copper salt at the cathode between any desired limits, while this is very difficult to do in the case of the chemical method. This is in addition to the advantage, which the electrochemical method always has, of permitting a wide variation in the rate of reaction for constant temperature and constant concentration. If we are ever to have a thorough knowledge of the chemical reactions between nitric acid and the metals we must study the problem electrochemically."

Later Bancroft[1] gave the scheme of attack which has been followed in this problem:

"On the assumption that all corrosion is electrolytic in nature, it is evident that at least three independent factors must be taken into account in the reduction of nitric acid by a metal: the specific reducing power of the metal which may be measured by the hydrogen over-voltage in a corresponding sulphuric acid solution; the catalytic action of the metal on the various reduction products; and the catalytic action of the metallic nitrate on the various reduction products. This analysis of the problem is of no value unless we can devise methods of distinguishing the effects due to these three causes. Fortunately that is a very simple matter. We can determine the reduction products on adding different, dissolved, reducing agents having no catalytic action, which will give us the reduction products due to different electromotive forces. Of course it is possible that any given reducing agent may exert a catalytic action itself or through one of its oxidation products. The catalytic action can be recognized and eliminated by using other reducing agents of about the same reducing power or by adding the same reducing agent to solutions of the different reduction products of nitric acid. This last method will be effective only in case the catalytic action is on one of the first reduction products of nitric acid, such as nitrous acid. There is no reason at present to suppose that there will be any special difficulty in distinguishing between reducing action and catalytic action.

"Electrolysis of a nitric acid solution with the metal under consideration as cathode will give the combined effect of the specific reducing action of the cathode plus the possible catalytic action of the cathode metal. If the elec-

[1] J. Phys. Chem., 28, 479 (1924).

trolytic reduction agrees with those obtained by the corresponding chemical reduction,[1] the cathode metal has no catalytic action. If there is a difference between the sets of results, the difference gives us valuable information in regard to the catalytic action of the cathode metal. It will probably not be difficult then to formulate the catalytic action of the metal clearly and definitely.

"The catalytic action of the metallic nitrate can be detected by adding the salt to nitric acid and then repeating the experiments with the dissolved reducing agents. These results will be supplemented by repeating the electrolytic reductions in presence of the metallic nitrate, after which there should be no difficulty in accounting for all the products obtained when the metal reacts direct with the nitric acid under the conditions of ordinary corrosion."

Bancroft accepts Armstrong's views on the gaseous reduction products of nitric acid and adds to them several of his own.

"It is evident from what has already been done that Armstrong was right in saying that the direct reduction products are $HNO_2$, $H_2N_2O_2$, $NH_2OH$, and $NH_3$, while $NO_2$, NO, $N_2O$ and $N_2$ are formed by secondary reactions, very probably as follows:—

$$HNO_3 + HNO_2 = 2\ NO_2 + H_2O$$
$$3\ HNO_2 = 2\ NO + HNO_3 + H_2O$$
$$H_2N_2O_3 = 2\ NO + H_2O$$
$$H_2N_2O_2 = N_2O + H_2O$$
$$HNO_2 + NH_2OH = N_2O + 2\ H_2O$$
$$2\ HNO_3 + 2\ NH_2OH = 2\ HNO_2 + N_2O + 3\ H_2O$$
$$H_2N_2O_2 + 2\ NH_2OH = 2\ N_2 + 4\ H_2O$$
$$HNO_2 + NH_3 = N_2 + 2\ H_2O$$

"The reaction between nitric and nitrous acids to form nitrogen peroxide will increase relatively with increasing concentration of nitric acid. It is simply the reverse of one of the reactions in the synthesis of nitric acid by the arc process. It is sometimes stated that the formation of nitrogen peroxide is due to the oxidation of nitric oxide by concentrated nitric acid; but this is clearly a mistaken way of looking at things. There is no reason to postulate an intermediate formation of nitric oxide.

"We get nitric oxide by the decomposition of nitrous acid and this reaction will predominate as the concentration of nitric acid decreases and that of nitrous acid increases. This equilibrium was studied carefully by Noyes and Edgar[2] over a dozen years ago.

"We get nitrous oxide either through the dehydration of hyponitrous acid or through the interaction of nitrous acid and hydroxylamine.[3] If this second reaction passes through the hyponitrous acid stage as seems probable, those are merely different ways of saying the same thing.

[1] The author here refers to the chemical reduction with an agent having the same reduction potential as the metal would have if it were reacting. This agent must of course have no catalytic effect of its own. This undoubtedly is a rather large order.

[2] J. Am. Chem. Soc., 33, 292 (1911).

[3] V. Meyer: Ann., 175, 141 (1875).

"It is usually assumed that nitrogen comes from the interaction of nitrous acid and ammonia, apparently because ammonium nitrite will decompose into nitrogen and water under certain conditions. This seems to me inadequate because we get nitrogen evolved in cases where there is no reason to suppose that ammonia is formed at all. We must therefore postulate a reaction between hyponitrous acid and hydroxylamine.

$$H_2N_2O_2 + 2\,NH_2OH = 2\,N_2 + 4\,H_2O$$

Oesterheld[1] was forced to the same conclusion when he found that the electrolytic oxidation of an alkaline hydroxylamine solution at a platinum anode gave a mixture of gases approximating 51% $N_2$ and 49% $N_2O$. 'The formation of nitrous oxide is undoubtedly due to the oxidation of hydroxylamine to hyponitrous acid which then breaks down into nitrous oxide and water:

$$NH_2OH + O = NOH + H_2O$$
$$2\,NOH \longrightarrow H_2N_2O_2 \longrightarrow N_2O + H_2O$$

"It is impossible, however, that the nitrogen formed from the hydroxylamine can be a decomposition product of ammonium nitrite as was assumed to be the case when studying the oxidation of ammonia. In the first place there is no ammonia present and, in the second place, there can be no oxidation of hydroxylamine to nitrous acid at the low anode potential which was maintained. The simplest explanation is that the nitrogen is due to the reaction between hydroxylamine and nitroxyl which is the first oxidation product,

$$O{:}NH + NH_2OH = N_2 + 2\,H_2O$$

A. Angeli has observed the same reaction when nitroxyl splits off from benzene sulphohydroxamic acid in presence of hydroxylamine. While two molecules of nitroxyl may combine to form hyponitrous acid or nitrous oxide and water, yet there is a quantitative evolution of nitrogen so long as there is a sufficient excess of hydroxylamine.

"It is also possible that nitrogen may be formed simultaneously with nitrous oxide by a different decomposition of hyponitrous acid,[2] perhaps

$$5\,H_2N_2O_2 = 4\,H_2O + HNO_3 + 4\,N_2$$

"While it is perfectly certain that nitrogen peroxide, nitric oxide, nitrous oxide, and nitrogen are due to secondary reactions and are not direct reduction products of nitric acid, this does not mean that hydroxylamine and ammonia may not be formed by reduction of the oxides of nitrogen. In fact, we know that under certain conditions this may happen. The simplest supposition to make would be that the stages were $NO_2 \longrightarrow NO \longrightarrow N_2O\ (\longrightarrow N_2) \longrightarrow NH_2OH \longrightarrow NH_3$; but there seems to be good reason to believe that matters are not so simple as this. It seems probable that hydroxylamine is not always a preliminary stage to the formation of ammonia, that nitrous oxide is not always a preliminary stage in the formation of hydroxylamine or ammonia

[1] Z. anorg. Chem., **86**, 129 (1914).

[2] Berthelot and Ogier: Compt. rend., **96**, 30, 84 (1883); Hantzsch and Kaufmann: Ann., **232**, 317 (1896); Ray and Ganguli: J. Chem. Soc., **91**, 1866 (1907).

from nitrogen peroxide or nitric oxide, and that the reduction of nitrogen peroxide does not necessarily give rise to nitric oxide as an intermediate stege."

With this line of attack in mind, we can now avail ourselves not only of the data on the chemical action of metals on nitric acid, but also of those on the electrochemical reduction, keeping always in mind the chemistry of our problem, that is, the interaction of the various constituents present in a given mixture.

Points of extreme importance in this consideration are: The reduction scheme of nitric acid consists of direct reduction reactions and of secondary reactions. The quantity of the various products we shall obtain in a given case depends, therefore, wholly on the various reaction velocities. If the secondary reaction has a high velocity while the direct reaction has a low one, the products of the secondary reaction will predominate. If the reverse is true the products of the direct reaction will predominate. There can be all intermediate gradations of these two cases.

The velocity of the direct reactions may be controlled in the electrochemical process by controlling the current density, while, as pointed out be Bancroft[1] the chemical process is not so flexible. This may be effected to some degree however by controlling the concentration of reducing agent.

The velocities of the secondary reactions may depend on a multitude of factors; catalytic effect of the reducing agent, of the products of its oxidation, of the reduction products of the acid itself (no cases of this have been found), temperature, solvent, etc.

Practically all the reactions in the reduction scheme of nitric acid are reversible, hence the time factor must be considered in ways other[2] than as a component of reaction velocity. Especially is this true in the case of gaseous products.

The study of the electrolysis of solutions of nitric acid has received much attention for many years. Faraday[3] has shown that when strong nitric acid is electrolyzed, no hydrogen appears at the cathode, but a yellow or reddish color, thought to be due to nitrous acid, is seen. A different result was, however, obtained on mixing the acid with an equal or greater volume of water, for then hydrogen was produced, the amount of the gas depending both upon the concentration of the acid and upon the current employed. To use Faraday's own words, "that acid from which no gas separated at the cathode with a weak voltaic battery, did evolve gas there with a stronger; and that battery which evolved no gas there with a strong acid, did cause evolution with an acid more dilute."

A little later Schönbein[4] made a series of determinations of the electrolytic reduction of nitric acid at a platinum cathode, with acids ranging from 1.49 to 1.70 in specific gravity, his object being to determine the conditions under which all the hydrogen is depolarized.

[1] Trans. Am. Electrochem. Soc., 9, 15 (1906).

[2] See pages 1223 for an example.

[3] Phil. Trans., 124, 96 (1834).

[4] Pogg. Ann., 47, 563 (1839).

In 1871 Bourgoin[1] found that electrolysis of a very dilute nitric acid solution causes no reduction of the acid, hydrogen being evolved at the cathode. He found that with an acid $HNO_3 + 6.25$ aq., hydrogen was first evolved, this was followed by nitrogen, while finally, ammonia is produced, and with $HNO_3 + 19$ aq., hydrogen and subsequently nitrogen are obtained; the latter gradually increasing in quantity, reaching a maximum and, in the end, disappearing. No nitrous acid could be detected. When, in subsequent experiments, a more concentrated solution was employed, no hydrogen was evolved at first, however, a blue coloration, "probably due to nitrous acid," was observed around the cathode; finally, the electrolysis of $HNO_3 + 1\frac{1}{2}$ aq. produced pure nitric oxide for a time and, afterwards, a mixture of nitric oxide hydrogen.

Gladstone and Tribe[2] electrolyzed acid of specific gravities 1.40, 1.20, and 1.13, respectively, in a *Hofmann* apparatus with presumably platinum electrodes, employing various current densities. They found that from the first concentration, neither ammonia nor hydrogen was obtained with any current employed; with the second neither of the above compounds was evolved. When the current from a single Grove cell was employed, but with increased current density hydrogen was obtained.

The results of Gladstone and Tribe are not surprising when the work of Ihle[3] is considered. This author showed that for a given concentration of acid a definite current density was required to effect reduction to ammonia, and that this value increased with increasing concentration of acid.

Gladstone and Tribe, in their work, also confirmed the report of Bourgoin and of Schönbein regarding the ceasing of the mysterious initial evolution of hydrogen. "In the first, second, third, and fourth experiments with the 1:1 acid, the evolution of hydrogen gas at the cathode ceased almost entirely and quite suddenly in three minutes, and with the first experiment with the 1:2 acid in 40 minutes."

This result was accounted for as follows: "We . . . have traced it to the presence of nitrous acid, which we find almost entirely prevents the escape of hydrogen."

Their conclusions are quite correct but no satisfactory explanation of the effect of nitrous acid is given. This will be discussed later under nitrous acid.

Freer and Higley had made by far the most exhaustive study to that time. Their results, as well as all those of other workers in the field, could not be explained on the basis of the theories advanced, simply because they assumed the action of metals on nitric acid depended on too few factors, or upon factors that had only an apparent effect.

A summary of their work is given in their final article.[4]

---

[1] J. Pharm., (4), **13**, 266-270 (1871).
[2] J. Chem. Soc., **35**, 172 (1879).
[3] Z. physik. Chem., **19**, 572 (1896).
[4] Am. Chem. J., **21**, 389 (1899).

"Silver, copper, iron, and electrolytic hydrogen have nearly the same effect on concentrated nitric acid, nearly pure nitrogen dioxide being evolved."

"In respect to their action on dilute nitric acid, the order of the metals silver, copper, lead and iron is that of the potential series.

"The activity of electrolytic hydrogen depends, in a marked degree, upon the character of the electrode upon whose surface it is liberated.

"Electrolytic hydrogen, in contact with cathodes of copper and of silver, effect reduction of nitric acid in proportion to the current density.

"When nitric acid having a specific gravity of 1.05 is subjected to electrolysis in cells having cathodes of silver and lead, respectively, on the surface of whose cathodes there is equal current density, the reduction products are the same, i. e., nitrogen and ammonia, in approximately the same proportions.

"Silver and lead when dissolved in acid of specific gravity 1.05, yield reduction products which are widely different, both qualitatively and quantitatively, since from the silver there is obtained only nitric oxide and nitrogen dioxide equivalent respectively to 95% and 5% of the metal dissolved, while with lead the products are nitric oxide, nitrogen dioxide, and nitrous oxide, equivalent in the order named, to 2.5, 7.5, and 90% of metal dissolved.

"Lead reduces nitric acid of specific gravity 1.05 much more completely than copper, yielding about five times more nitrous oxide than the latter. On the other hand, copper, when made the cathode of an electrolytic cell containing the same strength of acid, has a much greater energizing effect upon the hydrogen deposited upon its surface than is shown by lead under the same circumstances, and produces about three times as much ammonia as the latter. This conclusion is much more emphatically impressed on us by the comparison of the results with lead and silver.

"Since in the electrolysis of nitric acid with a constant current, the action of the metallic ions is excluded, and the reduction must be effected by the hydrogen ions[1] in contact with the surface of the different metals, and since, therefore, the hydrogen ion, in contact with the respective metals, is the sole reducing agent [illegible]lows that the widely different products obtained when lead and si[illegible]solve in nitric acid cannot be attributed to the action of the hydrogen at[illegible]s alone, but must also involve the direct deoxidizing effect of the metals themselves. Undoubtedly with the concentrated, and hence not ionized, acid, the metals alone cause the change, but with greater dilution both metals and hydrogen unite in causing reduction. The theory of nascent hydrogen cannot therefore be held in regard to the stronger acids, in which only nitrogen dioxide and nitric oxide are given off, but, subject to the modifications given above, is undoubtedly valid in relation to dilute acid."

Let us first consider the case of lead, silver and copper. The products of reduction are the same when the reduction is electrochemical, hence there is no catalytic effect of the metal itself, but the quantity of ammonia produced at the lead cathode is higher. This at once tells us that the specific reducing power of copper and of silver is the same, while that of lead is greater. This

[1] Here the author obviously means what we now know as monatomic hydrogen.

is confirmed by measurements of their hydrogen overvoltages[1] under comparable conditions. Lead was found to be highest, while silver and copper have approximately the same value.

The difference between the electrochemical process and the chemical process can be due only to the metal ions in solution. When lead reacts with nitric acid, under the conditions stated, the chief product is nitrous oxide, hence the nitrous oxide is the product of a secondary reaction, and this reaction is catalyzed by the lead ions present at the place of reaction. Another way of saying the same thing is: the velocity of the secondary reaction is so great as compared to that of the direct reaction, that the intermediate products yield nitrous oxide almost entirely.

This point is confirmed by the work of Alexeeff[2] who found that ammonium sulphate upon oxidation at a lead peroxide anode gives chiefly nitrous oxide and nitrogen.

The nitrogen is undoubtedly the product of the interaction of hydroxylamine and hyponitrous acid.

He also notes that in an excess of ammonia, the oxidation goes entirely to nitrogen while with an excess of sulphuric acid yields only nitrous oxide. This parallels the observed effect of acid on reducing agents, that is their reducing power decreases, hence the oxidation can be carried farther in their presence.

When silver and copper, respectively, react with nitric acid, under the stated conditions, the chief product in each case is nitric oxide. With the same reasoning as above, we can say that the secondary reaction yielding nitric oxide is catalyzed by silver and copper ions respectively.

The case of copper was treated very thoroughly by Turrentine,[3] who proved the catalytic effect of the copper ions on the reaction by carrying out the chemical reaction under such conditions that no appreciable concentration of copper ions was present. Under these conditions ammonia was formed acidity

In the analytical methods for the reduction products of nitric veloped by Milligan,[4] nitric oxide is determined by absorption in phuric of two per cent nitric acid in concentrated sulphuric acid, the ric d by being determined by estimation of the nitrosylsulphuric with ganana titration.

This method of procedure at once causes one to wonder what would happen to the nitric acid if such a solution were to act on copper. The nitric oxide would not be evolved because by definition it is absorbed, and hence, we have a product in solution (a more correct term would be, in combination), capable of further reduction, in contact with copper, a metal with a reducing potential high enough to cause ammonia formation. The answer is obvious. Ammonia should be formed.

---

[1] Foerster: "Elektrochemie wässeriger Lösungen," 310 (1922).

[2] J. Russ. Chem. Soc., 41, 1155 (1909); abstracted J. Chem. Soc. 98 II, 98 (1910).

[3] Trans. Am. Electrochem. Soc., 10, 49, (1906). See also Bancroft: 9, 13 (1903), J. Phys. Chem., 12, 118 (1908); 28, 479, 798 (1924).

[4] J. Phys. Chem., 28, 544 (1924).

This experiment was tried, but the mixture of Milligan would not attack copper appreciably. The sulphuric acid was then diluted by addition of more concentrated nitric acid until the copper was attacked somewhat. The final mixture used was thirty cubic centimeters of concentrated nitric acid in one hundred cubic centimeters of concentrated sulphuric acid. At lower concentrations gases were evolved. The action was extremely slow since the copper salt formed was almost insoluble in the mixture. The mixture was placed, with a large quantity of bright copper foil, in a glass stoppered Erlenmeyer flask, and tightly sealed. This was allowed to stand for a month, with daily shaking to dislodge the layer of copper salt formed on the foil. At the end of this time much copper had been dissolved, and there was no pressure in the flask on opening. A portion of this solution was made alkaline with sodium hydroxide and tested for ammonia. There was sufficient per cent to give a decided test with litmus.

Thus it has been shown that under conditions such that gases cannot be evolved, the product of the action of copper on nitric acid is ammonia, *even in the presence of copper ions.*

Luckow,[1] Vortmann,[2] Ulsch[3] and, Easton[4] all developed methods for the estimation of nitrates by electrolytic reduction. A feature of all of these methods is the presence of copper sulphate and sulphuric acid in their solutions. This is obviously the condition under which we would expect to get nitric oxide, yet the methods give quantitative yields of ammonia.

The reason why nitric oxide was not evolved must be merely a question of reaction velocity, that is, the velocity of the direct reduction (dependent only on the current density) must be so great as compared to the velocity of decomposition of the intermediate product, giving nitric oxide, that this latter of ntion is unappreciable.

hydrog was tested by repeating Easton's experiments using a current density therefor mately one hundredth of the lowest value he recommends. Under reducin nditions no ammonia was formed, even after two weeks of continuous lead folysis.

To prove that nitric oxide will be formed by electrolysis of nitric acid in the presence of copper ions, a solution similar to that used by Easton was prepared, using instead of potassium nitrate, concentrated nitric acid in such quantity as to make its concentration ten per cent. This solution was electrolyzed in a cell similar to the one used by Patten,[5] except that no anode eudiometer was used. The cathode was a very large sheet of platinum foil. When electrolysis was started only traces of gases were evolved at the cathode, but when the copper ions had almost all migrated into the cathode chamber

[1] Z. anal. Chem., 19, 11 (1880).
[2] Ber., 23, 2798 (1890).
[3] Z. Elektrochem., 3, 546 (1897).
[4] J. Am. Chem. Soc., 25, 1042 (1903).
[5] Trans. Am. Electrochem. Soc., 12, 333 (1908), Figure 4.

(shown by a deep color with an almost colorless solution outside) gases were evolved rapidly. A sample of the gases evolved analyzed ninety one per cent nitric oxide.

The concentration of copper ions necessary for the production of nitric oxide is fairly sharp. This is probably one of the reasons why the analytical methods were at all useful.

A further point to be settled is why sulphuric acid is desirable in these methods. It has been shown that sulphuric acid increases the solubility of nitric oxide in nitric acid. Thus any sulphuric acid in the mixture decreases the tendency for nitric oxide to be evolved.

In connection with the above effect of the sulphuric acid, a study was made of the evolution of nitric oxide from solutions of nitric and sulphuric acids, of varying concentrations of the latter acid, when acted on by copper. The addition of sulphuric acid should cause a slight retardation of the time necessary for the first bubbles to appear.

A solution of oxide-free nitric acid (17%) that would cause the evolution of nitric oxide in ten minutes, when acted on by copper was chosen. Solutions of this concentration of nitric acid with varying concentrations of sulphuric acid were allowed to attack copper and the time noted when bubbles first began to form.

As was expected a retardation did take place, a solution containing one per cent sulphuric acid required twenty-one minutes while three per cent sulphuric acid required forty-six minutes. However, higher concentrations than this decreased the time necessary, until at eleven per cent sulphuric acid the copper was attacked faster than with nitric acid alone. This is explained on the basis of increased acidity causing increased corrosion. The reason we get a maximum in the first part of the curve is due to the factor of increased solubility first being the determining factor, while later the increased acidity becomes the determining factor.

The curve would approach infinity at very high concentrations of sulphuric acid, as has been shown by the experiment in which ammonia was formed by the action of copper on a mixture of nitric and sulphuric acids.

The accelerating effect of sulphuric acid is apparent in the action of ferrous sulphate on oxide-free nitric acid. Here the retardation cannot be noted for ferrous sulphate will not attack pure nitric acid in a reasonable length of time.[1] This will be discussed later under nitrous acid.

This leaves the problem of which ion of copper, the cuprous or cupric, is the catalyst. At first thought one would think that at no time was there an appreciable amount of cuprous ion in the solution to cause a catalytic effect. This is quite true, but the concentration we must consider is the concentration at the point of reduction. This of course is at the metal surface where the solution of the copper is taking place in two stages, first the oxidation of metal to cuprous ion, and secondly the oxidation of cuprous to cupric ion.

[1] This is confirmed by Mellor: "Modern Inorganic Chemistry," 519 (1912).

This problem was solved by Milligan and Gillette[1]. These investigators found that nitric acid reacts with stannous chloride to give almost entirely nitrous oxide. When copper sulphate was added to the nitric acid and the stannous chloride then added, there was no change in the products formed, hence cupric ion has no directive influence. The ion that catalyzes the secondary reaction with the production of nitric oxide, when copper acts on nitric acid, is then the cuprous ion. In these experiments the nitric acid was in excess, so the stannous chloride would not have an opportunity to reduce the less thoroughly oxidizing agent.

The views of Higley[2] on the action of metals in concentrated nitric acid is a possibility, which under all ordinary conditions need not be considered. We will attempt to show that the electrolytic corrosion theory will suffice in all cases.

TABLE I

Action of Metals on Nitric Acid (Divers)

| Metal and Second Acid | $NH_2OH$ | $NH_3$ | Remarks |
|---|---|---|---|
| Sn | little | much | |
| Sn + HCl | much | some | Ammonia yield increases and hydroxylamine decreases on standing with excess metal |
| Sn + $H_2SO_4$ | much | some | |
| Zn | little | much | |
| Zn + HCl | some | much | Same as tin |
| Zn + $H_2SO_4$ | some | much | |
| Mg | no | much | |
| Mg + HCl | trace | much | |
| Mg + $H_2SO_4$ | no | much | |
| Cd | no | some | |
| Cd + HCl | little | some | |
| Cd + $H_2SO_4$ | little | some | |
| Pb | no | some | |
| Pb + HCl | no | some | |
| Pb + $H_2SO_4$ | no | some | |
| Al + HCl | trace | some | Acids quite dilute |
| Fe | no | much | |
| Fe + HCl | no | much | |
| Fe + $H_2SO_4$ | no | much | |
| Na amalgam | no | much | Excess acid |
| Cu | no | no | |
| Hg | no | no | |
| Ag | no | no | |
| Bi | no | no | |

[1] J. Phys. Chem., 28, 750 (1924).

[2] Am. Chem J., 19, 18 (1895). See also Bancroft: J. Phys. Chem., 28, 492 (1924).

The investigations of Divers[1] are of much interest. He was interested only in the production of hydroxylamine, so gaseous products were not analyzed and in many cases not even mentioned. It is difficult to tell from his paper what quantities of the recorded products were actually formed. The summary of his results is given in Table I.

Divers found that high temperature is detrimental to the stability of hydroxylamine.

These data do not agree in all details with those of Higley.[2] This last investigator reports no ammonia in the reaction of lead on nitric acid. The amount found by Divers, however, was quite small.

This point was tested, that is, whether the specific reducing power of lead is sufficient, under ordinary conditions, to yield ammonia. An electrolytic couple was arranged in the following manner: A stick of especially pure lead (Kahlbaum) was connected to a smooth platinum electrode. A diaphragm cell, consisting of a porous cup filled with nitric acid standing in a beaker of hydrochloric acid of the same strength, was prepared, and the couple was immersed in it in such a way that the platinum electrode was in contact with the nitric acid and the lead electrode dipping into the hydrochloric acid.

In a cell of this type the lead goes into solution, and the hydrogen is depolarized at the platinum. It is easy to see that the reducing potential (specific reducing power) at this platinum electrode, is that of the lead going into solution in the nitric acid, less the hydrogen voltage at smooth platinum, measured under these conditions. This is nothing more than the principle of the Gladstone and Tribe[3] couple whose action was explained in 1878, except that the anode and cathode reactions are separated when the couple is arranged in this manner.

After standing for several days the cathode solution (nitric acid) was analyzed and an appreciable quantity of ammonia and no hydroxylamine was found.

A second experiment was run, in which everything was exactly the same with this exception, a small quantity of lead nitrate was added to the cathode solution. Ammonia was obtained, but after a few hours tiny bubbles of a gas, presumably nitrous oxide, were noticed on the cathode.

From these experiments, those of Freer and Higley, and those of Divers, we can draw the conclusion that the reducing potential of lead in nitric acid solution is sufficient for the production of ammonia, and that the reason ammonia is not always obtained, is because the secondary reactions by which an intermediate product decomposes to give nitrous oxide, is catalyzed by lead ions, until it predominates over the direct reduction.

This method of attack is an exceedingly valuable one, since by means of this cell we can pick apart, and analyze, each of the three factors affecting the reduction.

---

[1] J. Chem. Soc., 43, 455 (1883).

[2] Am. Chem. J., 17, 18 (1895).

[3] J. Chem. Soc., 33, 139 (1878).

Before discussing further the work of Divers we will turn to the work of Tafel.[1] He disputed flatly the identity of chemical and electrochemical reaction, and substantiated his belief by what seemed to be conclusive evidence. The experiments were all made with solutions containing both nitric and sulphuric acids.

His results may be stated as follows: When nitric acid is electrolyzed, it suffers reduction, and in order to diminish the action of nitric acid as an electrolyte a relatively large amount of sulphuric or hydrochloric acid was added to the solution. The product of the reduction is largely dependent on the nature of the metal used as electrode. With platinum, no ammonia or hydroxylamine was formed, and with palladium the reduction is extremely slow. The chief products of the reduction are hydroxylamine and ammonia. The largest proportion of the hydroxylamine is formed when mercury is used as cathode, and the conversion of the nitric acid into this can be carried out almost quantitatively. With lead electrodes, about forty per cent of the nitric acid is converted into hydroxylamine, and with copper electrodes only about fifteen per cent; if the copper be in the form of a spongy mass, only about one per cent of the acid is transformed into hydroxylamine, the remainder being reduced to ammonia. When an amalgamated (lead, tin or copper) cathode is used, the reduction takes place in the same way as when a mercury cathode is employed.

TABLE II

Electrolytic Reduction of Nitric Acid (Tafel)

| Cathode Material | Surface | Time in Hours | Hydroxyl-amine | Ammonia | Nitrous Acid | Gas | Sum |
|---|---|---|---|---|---|---|---|
| Lead | prepared | 2.5 | 26.8 | 57.6 | 1.5 | 7.0 | 91.4 |
| " | " | 2.5 | 25.2 | 57.6 | 0.6 | 8.4 | 91.2 |
| " | " | 2.5 | 22.2 | 64.6 | 0.3 | 6.5 | 93.3 |
| " | amalgamated | 2.5 | 69.7 | 16.9 | 0.1 | 9.2 | 95.8 |
| Tin | polished | 3.0 | 45.8 | 38.3 | 0.8 | 7.7 | 91.8 |
| " | " | 3.0 | 40.8 | 42.5 | 0.6 | 6.9 | 90.2 |
| Copper | " | 2.5 | 11.5 | 76.8 | Trace | 7.1 | 95.4 |
| " | spongy | 2.5 | 1.5 | 93.8 | 0.1 | — | —— |
| " | " | 2.5 | 1.0 | 92.3 | Trace | 3.4 | 96.7 |
| Silver | polished | 3.0 | 18.4 | 47.2 | 1.5 | 21.0 | 86.6 |
| " | " | 3.0 | 25.3 | —— | —— | 18.5 | —— |

Hydroxylamine, it is said, is not reduced when subjected to electrolysis between copper electrodes. It is then proved that the reduction of nitric acid does not, at least between copper electrodes, always go through the hydroxylamine stage.

[1] Z. anorg. Chem., **31**, 289 (1902). See also for translation of parts, Bancroft: J. Phys. Chem., **12**, 110 (1908).

Tafel is interested primarily in the yield of hydroxylamine. In a few of his experiments he reports also ammonia yield and quantities of the nitrogenous gases evolved. The gases were not analyzed however. The amounts were always small.

Table II shows the general order of his results. One must not be misled by the apparent excellence of his analytical results. The data are not reproducible within ten per cent.

In the experiments shown the conditions were: "0.4 grams nitric acid, 20 ccm. 50% sulphuric acid, 10 sq. cm.,[1] cathode surface, 2.4 amp., cooled with ice."

The amount of hydroxylamine produced is greater as the solution of nitric acid is more dilute; in order to obtain the largest proportion, a very dilute solution of nitric acid should be used, and more added as the reduction proceeds. When the amount of sulphuric acid present falls below forty per cent, the quantity of hydroxylamine formed decreases appreciably, but otherwise the concentration of the sulphuric acid exerts no influence on the reaction.

Tafel performed a few experiments on the action of various metals on a mixture of sulphuric and nitric acids. He finds that with mercury or copper neither hydroxylamine nor ammonia is produced, and with lead, reduction to nitrous acid takes place.

In the production of hydroxylamine, the current yield is greatest for lead, slightly less for amalgamated lead, and decidedly less for copper. The presence of nitrous acid is said to exert no appreciable influence on the reduction of nitric acid at cathodes of these metals.

Incidentally he finds that hydroxylamine sulphate is very stable in the presence of sulphuric acid, and the solution may be warmed to about 40° without any decomposition taking place.

Tafel believed the electrolytic reduction of nitric acid would prove the best method for the production of hydroxylamine. This method is being used for its commercial production at present.[2]

He confirms the work of Divers,[3] on the effect of sulphuric and hydrochloric acid concentration on hydroxylamine yield. They both find that with increasing sulphuric acid or hydrochloric acid concentration the hydroxylamine yield increases, although Divers finds that in the case of hydrochloric acid the yield passes through a maximum. A point of much interest in connection with the effect of sulphuric acid is noted in a paper by Patten[4] "Thus, the conclusion of Tafel is confirmed, that the ammonia yield increases with increased concentration of sulphuric acid at a copper cathode, and that the hydroxylamine, on the other hand, forms in greatest quantity in dilute sulphuric acid."

---

[1] The author gives this as "qdm." which is doubtless a misprint.
[2] Schoch and Pritchett: J. Am. Chem. Soc., 38, 2042 (1916).
[3] J. Chem. Soc., 43, 455 (1883.
[4] Trans. Am. Electrochem. Soc. 12, 325 (1907).

What Tafel[1] actually said is as follows: "In the percentage conversion of nitric acid into hydroxylamine . . ., with a copper cathode, the best case gave fifteen per cent, the latter result I obtained by careful work with polished copper electrodes, in the presence of fifty per cent sulphuric acid. On the other hand using a copper electrode, which had been covered with a layer of spongy copper, only very slight quantities of hydroxylamine, about one per cent, were obtained, whereas almost all the nitric acid was reduced to ammonia." At this point a note appears referring to the work of Ulsch[2] who reduced nitric acid quantitatively to ammonia at a copper cathode in very dilute sulphuric acid.

The statement of Patten is incorrect, and I am inclined to the view that his experimental results are in the same category. His data conflict with those of Tafel and of Divers, and with my own. On attempting to repeat his work, satisfactory results could not be obtained. His method of analysis, in my mind, is to be condemned, for checks could not be obtained within twenty per cent. If his method for hydroxylamine yield is followed, the endpoint of the permanganate titration varies with temperature, rate of stirring, and rate of addition of the standard permanganate. The results of Tafel were found to be reproducible qualitatively only.

An explanation of the effect of sulphuric and hydrochloric acid on the yield of hydroxylamine was offered by Divers.[3] "There is no reason to believe that the action of the hydrochloric or sulphuric acid upon the metal is instrumental in forming hydroxylamine. The second acid serves to decompose the metal nitrate as fast as it is produced. In this way; (1) it holds the hydroxylamine in a state more stable than the nitrate; (2) it preserves the hydroxylamine from the destructive action of the nitrous acid, by preventing the formation of this substance which would otherwise result from the reaction between the metal yielding hydroxylamine and its own nitrate, and (3) it determines the reduction of all the nitric acid to hydroxylamine by supplying the hydrogen for reproducing it, and so keeping it free to the last."

Divers' second postulate was shown to be wrong by Tafel[4] who showed that nitrous acid had little effect on the reduction under these conditions. His third postulate becomes very doubtful in very concentrated solutions since there the hydrogen ion is likely quite low. The reason for this last statement is that when a number of cells of the type of Tafel's containing various concentrations of sulphuric acid, are electrolyzed in series, the cells containing the highest per cent of sulphuric acid have a much greater heating loss (higher resistance) than the cells containing the more dilute acid. This indicates a low concentration of ions.

The first postulate seems quite reasonable in the light of the data of Flaschner.[5] This investigator in a large part repeated the work of Tafel obtaining

[1] Z. anorg. Chem., 31, 290-291 (1902).
[2] Z. Elektrochem., 3, 546 (1897).
[3] J. Chem. Soc., 43, 465 (1883).
[4] Z. anorg. Chem., 31, 289 (1902).
[5] Monatshefte, 28, 216 (1907).

decomposition curves and time current curves at constant cathode potential, to follow the reduction, instead of analyzing for the products formed. He finds that hydroxylamine lowers the decomposition voltage of twice normal sulphuric acid at a mercury cathode only slightly, while twice normal nitric acid lowers it almost 0.4 volt. This indicates that nitric acid is a better oxidizing agent than hydroxylamine under these conditions, hence, when undergoing reduction, will be used up instead of the hydroxylamine.

This of course leaves a loophole, for we have said nothing about the oxidizing power of nitrous acid. Later in this paper it will be shown that nitrous acid is a slightly less powerful agent than is nitric acid, which clears up this point.

There is much of Flaschner's work that does not agree with Tafel's. We could not expect a very close agreement however, for Tafel used principally fifty per cent sulphuric acid solutions while Flaschner's highest concentration of sulphuric acid was about ten per cent.

Flaschner finds that hydroxylamine and nitric acid also, have approximately the same effect on the decomposition voltage of a twice normal sulphuric solution at a copper cathode, as was found with mercury, except that the hydroxylamine was a better depolarizer at the copper cathode. This does not at all agree with the fact that Tafel could get no reduction of hydroxylamine at a copper cathode, while it was reduced at an amalgamated cathode. Flaschner was able to reduce hydroxylamine to ammonia at a copper cathode. Tafel and Bahl[1] pointed out that Flaschner did not reduce hydroxylamine under the conditions stated by Tafel, in the experiment in which hydroxylamine was not reduced by electrolysis at a copper cathode. They say that addition of water causes hydrolysis of the hydroxylamine salt and it is probably this hydrolyzed part that undergoes reduction.

If Tafel's results are right, and quite likely they are, it means that in fifty per cent sulphuric acid, hydroxylamine does not depolarize the decomposition of sulphuric acid at a copper cathode. That the depolarizing power of hydroxylamine does bear a queer relationship to the acid concentration, is borne out by the report of Müller[2] who finds that the oxidizing power of hydroxylamine is greater than either nitrate or nitrite in alkaline solution. Müller observes that this is paralleled by the fact that he has never been able to obtain any appreciable yield of hydroxylamine in the electrolysis of neutral solutions.

The reason why Tafel was able to get reduction of hydroxylamine to ammonia at an amalgamated cathode while he was unable to do so at the copper cathode is without doubt due to the high hydrogen overvoltage of the former.

Frankly, we do not thoroughly understand the relation of sulphuric acid to hydroxylamine yield.

The reduction of hydroxylamine to ammonia at a copper cathode, under Tafel's conditions, should be tried, and if no ammonia is obtained the de-

[1] Z. anorg. Chem. **56**, 375 (1908).
[2] Z. anorg. Chem., **26**, 1 (1900).

composition voltage curves of Flaschner should be redetermined, using the solutions of Tafel. These two must show the same results. These experiments were not carried out, due to lack of time. This will be the next step in the study of nitric acid carried out in this laboratory.

Flaschner showed that the decomposition voltages of concentrated nitric acid solutions were very low. This offers an explanation of why Bourgoin[1] was unable to reduce concentrated nitric acid to ammonia, since the lower reduction products would not be reduced until the nitric acid was practically used up

Divers[2] found that tin reacts with a mixture of sulphuric acid to give a mixture of hydroxylamine and ammonia. Tafel finds the same results on electrolysis, but infers that there is some chemical reaction of the acid with his cathode, hence this cannot be taken as reliable electrochemical data. It seems conceivable that if ammonia was produced at all by this reaction, it might be the major reaction if the disturbing factors were removed. This was tested by means of the diaphragm cell used in the case of lead. The couple of smooth platinum and tin was immersed, the tin in contact with the hydrochloric acid, and the smooth platinum in the nitric acid. The tin was dissolved rapidly and ammonia was formed in the cathode chamber. There was no hydroxylamine formed. The experiment was repeated with conditions the same except that a small quantity of stannic chloride was added to the nitric acid. The products under these conditions were ammonia and hydroxylamine, thus proving definitely that the stannic ion catalyzed the decomposition of an intermediate product with the formation of hydroxylamine. The reducing power of tin in a solution of nitric acid is then more than enough to reduce nitric acid to ammonia.

The most striking generality in the work of Tafel is the very high yield of hydroxylamine he obtains in all experiments in which mercury was present at the cathode. With all his amalgamated electrodes the results are the same which proves that it is a specific property of the mercury, since no mercury ions are present.

With mercury, a metal with an extremely high overvoltage,[3] we should expect the reduction to go to ammonia, providing no disturbing factors enter.

To find out just how good a reducing agent mercury is, the diaphragm cell used above was resorted to. The anode in this experiment was a pool of mercury in a tiny dish. This was connected by means of a platinum wire to the platinum cathode. The rest of the experiment was exactly as described before, and ammonia was formed.

Thus it is proved that the reducing potential of mercury is more than enough to form ammonia. The only difference between these experiments and those of Tafel's, in which hydroxylamine was formed at a mercury cathode in dilute nitric acid, is that no mercury is present at the point of reduction. The metallic mercury therefore catalyzes the decomposition of an intermediate product with the formation of hydroxylamine.

[1] J. Pharm. (4) 13, 266-270 (1871).

[2] J. Chem. Soc., 43, 443 (1883).

[3] Föerster: "Elektrochemie wässeriger Lösungen," 310 (1922).

Tafel showed that mercury acted on nitric acid to give nitric oxide. "It has long been known that in the presence of very concentrated sulphuric acid mercury reduces nitric acid readily to nitric oxide, and mercury is used in Lunge's nitrometer for the quantitative determination of nitric acid. That a more dilute acid acts in the same way and that not a trace of hydroxylamine is formed by the action of mercury on nitric acid, has been proved by me in special experiments so contrived as to duplicate the conditions of electrolysis as closely as possible."

The results of his electrolysis experiments have been given before. These experiments, together with those on copper form the basis for his entire objection to the theory of the identity of chemical and electrochemical reactions.

Wilkinson,[1] working in this laboratory, straightened out this point in an admirable fashion, using the same method as Turrentine[2] used in the case of copper.

He repeated that experiment of Tafel, in which a solution of nitric acid and sulphuric acid was electrolysed in a diaphragm call, with a mercury cathode. The only difference between the experiments of the two investigators was that Wilkinson covered his cathode with a layer of mercurous sulphate. Under those conditions he obtained sixty per cent of nitric oxide. The electrolysis had taken place in the presence of mercury ions which catalyzed the decomposition of an intermediate product yielding nitric oxide.

To further prove his point he let mercury act on nitric acid in such a way that no high concentration of mercury ions could build up. Under these conditions hydroxylamine was obtained.

The above experiments furnish the proof that when mercury acts on nitric acid in the absence of mercury as ion, the product is hydroxylamine, whether done electrolytically or chemically.

Divers[3] proved that iron acts upon a mixture of nitric and sulphuric acids to give ammonia. He was not interested in gaseous products, so these were not analyzed. Freer and Higley[4] found that iron acts on nitric acid to give nitric oxide, nitrogen peroxide, and ammonia, the nitrogen peroxide yield increasing and the ammonia yield decreasing with an increase in acid concentration. The nitric oxide yield increases slightly with increasing concentration of acid.

When electrolyzed[5] at an iron cathode, nitric acid gives the same products as when acted upon by iron, but the low concentrations give little or no nitric oxide. This indicates that the decomposition yielding nitric oxide is catalyzed to a slight extent by the presence of metallic ions.

---

[1] Trans. Am. Electrochem. Soc., 13, 309 (1908).
[2] Trans. Am. Electrochem. Soc., 10, 49 (1906).
[3] J. Chem. Soc., 43, 453 (1888).
[4] Am. Chem. J., 21, 377 (1899).
[5] Freer and Higley: Am. Chem. J., 21, 377 (1899).

Scheurer-Kestner[1] says that dilute nitric acid acts on iron to give only ferrous ions, and this is confirmed by Ordway.[2] The catalyst therefore is ferrous ion.

Acworth and Armstrong[3] studied the reaction of zinc on nitric acid and found the gaseous products to be nitric oxide, nitrous oxide, and nitrogen. This was confirmed by Deville.[4] According to Divers[5] a trace of hydroxylamine and much ammonia is formed with nitric acid alone, if the acid is allowed to act only slightly and is then poured off. Divers and Shimidzu[6] found that much hydroxylamine was formed if mixed sulphuric and nitric acid were acted on by zinc. Montemartini[7] contradicts Divers saying that no hydroxylamine is formed with nitric acid alone. He also finds nitrite and hyponitrite in small amounts, and reports nitrogen peroxide, nitric oxide, nitrous oxide, and nitrogen as gaseous products, the peroxide being formed only in concentrated acid. With the dilute acids much ammonia is formed.

Kinnear[8] was able to get rapid quantitative reduction of nitric acid to ammonia in very dilute solution (one part nitric nitrogen to five thousand parts water), by sulphuric acid and zinc.

From the above it is easily seen that the reducing potential of the zinc is sufficient to carry nitric acid to ammonia. The products obtained are qualitatively the same[9] as those obtained by electrolyzing at a platinum cathode, an electrode we know has no catalytic action, hence neither the zinc metal, nor the zinc ions have any catalytic action.

Kippenberger[10] finds that magnesium, manganese, and aluminum readily reduce dilute solutions of nitrates to nitrite, then hydroxylamine, and finally ammonia. Since these are the products obtained by electrolysis at an inert cathode neither the metallic ions nor the metals themselves have any catalytic effect.

Personne[11] and Maumené[12] found that phosphorus arsenic, and antimony, when treated with nitric acid yield ammonia.

Montemartini let antimony, molybdenum, and bismuth act on nitric acid and obtained only nitrous acid, nitric oxide, nitrogen trioxide, and nitrogen peroxide. With cadmium, nickel, and cobalt he obtained the above and also hyponitrous acid, nitrous oxide, nitrogen and ammonia. His acids were mostly quite concentrated and much in excess of that required for solution of the metal.

---

[1] Compt. rend., 47, 927 (1858).
[2] Am. J. Sci., 190, 316 (1865).
[3] J. Chem. Soc. 36, 54 (1877).
[4] Compt. rend., 70, 22, 550 (1870).
[5] J. Chem. Soc., 43, 447 (1883).
[6] J. Chem. Soc., 47, 597 (1885).
[7] Gazz., 22 II, 250, 277, 384, 426 (1892).
[8] Chem. News, 46, 33 (1882).
[9] See products obtained at cathode with Grove-Bunsen cell, Allmand and Ellingham: "Applied Electrochemistry," 209 (1924).
[10] Chem. Ztg., 19, 1269 (1895); abstracted J. Chem. Soc., 70 II, 522 (1896).
[11] Bull., (2), 1, 163 (1864).
[12] Ann. Chim. Phys., (4) 3, 344 (1864).

Assuming that Personne and Maumené are right regarding the ammonia from the action of nitric acid on antimony, it becomes apparent that the specific reducing powers of antimony, arsenic, cadmium, nickel, and cobalt are sufficient to reduce nitric acid to ammonia. With molybdenum and bismuth we have not sufficient data to say with certainty, but from their position in the electrochemical series (both above silver), in seems quite likely that they too have specific reducing power enough to form ammonia from nitric acid.

### Catalytic Action of Nitrous Acid[1]

In 1842 Millon[2] showed that copper reacts with twenty per cent nitric acid at 20° only when nitrous acid is present in the solution. When no reaction occurs, bubbling nitric oxide through the solution immediately starts the action.[3] The reaction is negligible if some substance such as urea, which uses up the nitrous acid as fast as it is formed, is present in the solution.

Millon considers that nitrites are the first products formed, and that these are decomposed by nitric acid yielding the metallic nitrate and regenerating the nitrous acid. He worked with copper, mercury and silver.

Russell[4] confirmed Millon's results, and found also that bubbling a stream of an inert gas through a solution of nitric acid, in contact with a metal, hindered the action of the nitric acid by removing the nitric oxide, and thus keeping the acid free from nitrous acid. He also postulated the intermediate formation of nitrates.

Veley's[5] results confirm the results of previous investigators. He interprets his results on the assumption that nitrous acid is reduced to nitric oxide.

"The experiments detailed above for the metals, copper, mercury, and bismuth, to which, according to Russell's experiments, silver must also be added have established the following facts:—(1) the primary change is that between the metals and nitrous acid; (2) no gas is evolved at first from the surface of the metal; (3) the amount of nitrous acid increases up to a constant and maximum proportion; and (4) those conditions which increase the amount of metal dissolved per unit time, are equally those conditions which increase this constant proportion of nitrous acid. If then a trace of nitrous acid becomes once formed, and if, also, the quantity of nitric acid is present in very considerable excess, it would appear that these results may be explained as follows:—(1) the metal dissolves in nitrous acid to form the metallic nitrite and nitric oxide; (2) the nitrite formed is decomposed by the excess of nitric acid to reproduce the nitrous acid; and (3) the nitric oxide formed in (1) is not

---

[1] For more detailed account of early work and his formulation of the problem, see Bancroft: J. Phys. Chem. 28, 973 (1924).

[2] Compt. rend., 14, 904 (1842).

[3] This was noted also in the case of iron by Young and Hogg: J. Phys. Chem. 19, 647 (1915).

[4] J. Chem. Soc., 24, 8 (1874).

[5] Phil. Trans. 182 A, 279 (1891). See also Bancroft: J. Phys. Chem., 28, 973 (1924).

evolved as such, but reduces the nitric acid or the nitrate to produce a further quantity of nitrous acid. These changes may be presented thus, taking copper for example:

$$(1)\ Cu + 4\ HNO_2 = Cu(NO_2)_2 + 2\ H_2O + 2\ NO$$
$$(2)\ Cu\ (NO_2)_2 + 2\ HNO_3 = Cu\ (NO_3)_2 + 2\ HNO_2$$
$$(3)\ 2\ NO + HNO_3 + H_2O = 3\ HNO_2$$

"The same equations apply to the other metals, mutatis mutandis. The condition of the increase in amount of the nitrous acid is satisfied, for at the start four molecular proportions take part, while five are ultimately produced; the non-evolution of nitric oxide in the earlier stage of the change is also accounted for. But when the amount of nitrous acid has reached a certain point, the reverse of equation (3) takes place, and the nitric oxide is evolved from the liquid.

$$(4)\ 3\ HNO_2 = HNO_3 + 2\ NO + H_2O.$$

"At this point the nitrous acid is decomposed as fast as it is formed, the amounts of the reactions (3) and (4) per unit time being doubtless dependent as in other similar cases, upon the relative masses of the nitrous and nitric acids, upon the temperature and other conditions of the experiment.

This explanation is, however, only valid provided that the mass of nitric acid be in very large excess over that of the nitrous acid, for it is evident from the experiments described above, that, if there is no very great difference between the masses of the two acids, the nitric acid serves to impede rather than to promote the chemical change, a result which is probably due to the greater stability of nitrous acid in the presence of a small quantity of nitric acid.

"There yet remains one further point; if these metals by themselves do not dissolve in dilute nitric acid by itself, by what manner of means is the necessary nitrous acid formed initially? It is, of course, possible that the metal will enter into chemical change with an amount of nitrous acid less than that detected by the meta-phenylene diamine; it is also possible that some metallic impurity forms with the metal a couple which electrolyzes the nitric acid, thereby producing nitrous acid. As regards this latter point, it is worthy of remark that, of the metals experimented with, mercury was less susceptible of chemical change than copper, and copper in its turn than bismuth. This order is equal to that of their probable degree of purity.

"A few experiments were accordingly made to determine the amount of a foreign metal which could be added to pure mercury without promoting its reaction with nitric acid. These showed that one part in a thousand of pure copper and one part in eight hundred of pure silver added to mercury did not render the latter susceptible of chemical change, even with nitric acid of 30.5 per cent concentration, and heated to 28.5°, provided that both metal and acid were stirred continually. If both were at rest, then as in the previous experiments, the change commenced immediately."

Veley has given no proof for his explanation. His assumption regarding the action on copper is superfluous for what he really assumes is that nitrous acid is the depolarizer. This involves the reduction of the depolarizer to nitric oxide. Armstrong[1] showed that nitric oxide is not a direct reduction product of nitrous acid, so his views seem quite improbable.

If Veley's three equations are grouped the result is

$$Cu + 3\,HNO_3 = Cu(NO_3)_2 + HNO_2 + H_2O$$

This does not preclude the possibility of nitrous acid forming an intermediate product in the course of its catalytic action, and quite probably it does in some cases as will be shown below; but we shall prove that nitrous acid is not the depolarizer.

Burch and Veley[2] attempted to prove that nitrous acid is a stronger oxidizing agent than nitric acid, and would therefore be reduced first, though this was not compatible with the marked building up of nitrous acid concentration.

Their general conclusions are as follows:—

"1. The experiments detailed above show that when the metals, copper, silver, bismuth, and mercury are introduced into purified nitric acid of varying degrees of concentration, and a couple made with platinum, the electromotive force of such a cell increases considerably until it reaches a constant and (in most cases) a maximum value. This rise of electromotive force is attributed to the production of nitrous acid by the decomposition of the nitric acid, and the final value is considered to be due to the former acid only, while the initial value is due for the most part to the latter acid, though it is affected to a remarkable degree by the amount of impurity of nitrous acid either initially present or produced by minute and unavoidable uncleanliness of the metallic strips and the containing vessel.

"2. If nitrous acid has been previously added to the nitric acid, then the maximum electromotive force is reached at once.

"3. If the conditions, namely, increase of temperature, of impurity, and of concentration of acid, are such as could favour a more rapid production of nitrous acid, then the rise of electromotive force is concomitantly more rapid.

"4. Conversely, if the conditions are unfavourable to the production of nitrous acid, the rise of electromotive force is less rapid.

"5. If any substance, such as urea, be added, which would tend to destroy the nitrous acid as fast as it may be formed, then the rise of electromotive force is extremely slow, being dependent upon the number of molecular impacts of nitrous acid upon the surface of the metal. Thus the results obtained by the electrometer and of the chemical balance are in every way confirmatory, the one of the other. These results open out the further question as to whether the electromotive force of batteries, in which concentrated nitric acid forms an ingredient, is dependent not upon the nitric acid per se, as hitherto supposed

[1] J. Chem. Soc., 32, 57 (1877).
[2] Phil. Trans., 132 A, 319 (1891).

but upon the nitrous acid present in the fuming nitric acid, and formed also by the reduction of the acid by the hydrogen, which would otherwise be given off from the zinc and sulphuric acid."

Ihle[1] found Burch and Veley to be incorrect. "The two English investigators always observed a rise of the electromotive force to a constant (maximum) value and also found that the time of this increase depended exclusively on the presence or absence of nitrous acid, addition of this acid causing a very considerable shortening of the time necessary to reach the maximum value. Conditions such as higher temperature, increased concentration of the nitric acid, etc., which favor the formation of nitrous acid, accelerate the increase of the electromotive force, while substances, such as urea, which decompose the existing or nascent nitrous acid, retard the increase of the electromotive force. They account for these phenomena by the assumption that the lower initial value of the electromotive force is a measure of the potential of the nitric acid, while the higher final value measures the potential of the nitrous acid. The rate of increase of the electromotive force depeds solely on the number of nitrous acid molecules which are formed from the nitric acid. According to this point of view, the finally reached maximum of the electromotive force should be higher, the more nitrous acid there is in the nitric acid. Exactly, the opposite is true, as was observed by Burch and Veley; and I have myself confirmed this result. In order to clear up this contradiction Burch and Veley[2] assumed that nitrous acid ready formed is not so active a material as nitrous acid in the alternative process of formation and decomposition. The inadequacy of this hypothesis here is evident."

Ihle found that "nitrous acid lowers the potential of nitric acid, the lowering being greater the more nitrous acid is added. On the other hand the addition of nitrous acid increases the rate of oxidation of the nitric acid and therefore decreases very markedly the time necessary for a dilute nitric acid solution to give the maximum value. If one adds nitrous acid to a very dilute nitric acid before this solution gives its maximum value, the addition apparently causes a rise of potential. The resulting value is lower, however, than that which would have been reached in time by the nitric acid solution alone.

"The addition of urea causes the destruction of nitrous acid and raises the potential of the nitric acid. Addition of urea to solutions containing less than 35-40% nitric acid causes an apparent lowering of the potential, because at these concentrations the rate of change of the nitric acid decreases very much, the Grove cell changing to the Smee cell at about this concentration. Since the measurement of electromotive force involves some flow of current, because the capacity of the capillary electrometer is fairly large, every observation is accompanied by some transfer of electricity, even though a very

[1] Z. physik. Chem., **19**, 577 (1896).

[2] Phil. Trans., **182 A**, 330 (1891).

small one, and consequently by some chemical change. If the chemical changes take place very slowly, the measurements of electromotive force may be affected seriously thereby."

Bancroft[1] pointed out further evidence that contradicts Veley. "We can see in another way that there is nothing to Veley's assumption that the metal dissolves to nitrite. If we add nitrous acid to the Grove cell or to the Smee cell, we increase the depolarizing action of the nitric acid; but no metal dissolves in the nitric acid solution and consequently there is no formation of nitrite. The behavior of these two cells was discussed by Ihle[2] in an earlier paper. "If one dilutes the concentrated nitric acid in the Grove cell gradually and measures the electromotive force (of the cell at the same time, one finds that the electromotive force) remains nearly constant until the concentration of the nitric acid drops to about 38%. At slightly lower concentrations the cell shows, though at first only for a very short time, a changed and much smaller electromotive force than the 1.8 volt characteristic of the Grove cell; it corresponds rather to the 0.7 volt of the Smee cell. If one dilutes the nitric acid more and more, the time during which the cell stays at the lower potential increases until at a nitric acid content of 27-28% the element keeps the low elecromotive force of the Smee cell permanently.

"To carry out this experiment, one pours dilute nitric acid into an ordinary battery jar and puts into this two small, porous cups. In one of the cells is placed an amalgamate zinc rod and a zinc sulphate solution while a platinum electrode and the nitric acid to be tested are placed in the other porous cup. The two poles of the cell are connected through a galvanometer. Since the resistance remains the same in all the experiments, changes in the electromotive force of the cell will show as changes in the deflection of the galvanometer.

"It seemed probable that the peculiar relation between the concentration of the nitric acid and the electromotive force of the cell was due to nitrous acid present in the nitric acid solution or formed in it while the circuit is closed. This guess has been confirmed. If one adds a small amount of potassium nitrite to a cell containing less than 28% nitric acid and therefore giving permanently the potential of the Smee cell, the galvanometer needle swings at once to the deflection corresponding to the electromotive force of the Grove cell. If one removes the nitrous acid again by adding potassium permanganate,[3] hydrogen peroxide, or urea, the galvanometer needle goes back at once to the original value which corresponded to the Smee cell.

"Just as one can make dilute nitric acid active as a depolarizer by means of nitrous acid, so one can also remove the depolarizing power of concentrated nitric acid containing more than 38% $HNO_3$, by removing continuously the

[1] J. Phys. Chem., 28, 978 (1924).

[2] Z. Elektrochem., 1, 174 (1895).

[3] On adding potassium permanganate there is at first an increase in electromotive force corresponding to the high potential of permanganic acid; but the galvanometer needle goes back to the value corresponding to the electromotive force of the Smee cell as soon as the permanganic acid in immediate contact with the platinum electrode is used up.

small amounts of nitrous acid which are always present in so strong nitric acid by means of urea or potassium permanganate and can thereby convert a Grove cell into a Smee cell. With very concentrated acid containing 50-60% $HNO_3$, the conversion is only temporary because more nitrous acid forms soon. From this it follows that nitrous acid is the real depolarizer in the Grove cell and not nitric acid as is usually assumed, or at any rate, that it is only in presence of nitrous acid that the oxygen of the nitric acid reacts with hydrogen set free electrolytically at the platinum.

"The question arises as to how this action takes place and it seems probable that we are dealing with a case of catalysis. Nitrous acid plays the part of a catalyzer here just as it does in other cases, such as the action of nitric acid on metals studied by V. H. Veley."

Ihle's measurements were made with a galvanometer, which we now know is a decidedly unsatisfactory method for measuring the electromotive force of cells that undergo polarization. The galvanometer undergoes deflection by virtue of the current which passes through it, and a flow of current requires that a small quantity of the depolarizer be used up. If nitric acid is a stronger oxidizing agent than nitrous acid, as Ihle says it is, it will undergo reduction with the formation of more nitrous acid, which, being a catalyst for the depolarization of the nitric acid, will cause the nitric acid to build up rapidly to its maximum value, that is, would accelerate the decomposition of the depolarizer until only the ohmic resistance of the circuit opposes the flow of current. However, if the nitric acid is so dilute that its concentration also becomes a determining factor in the reaction, the nitrous acid formed may diffuse away before sufficient has accumulated to allow the voltage to rise to its full value; that is, to allow the reaction to proceed fast enough to prevent polarization. This is the reason why Ihle was able to obtain a maximum of only 0.7 volts from the Smee cell.

Now if the electromotive force of the Smee cell, prepared from oxide-free nitric acid, were measured with a device which draws absolutely no current, it should give the maximum attainable voltage of the Grove cell, since the ratio of concentration of depolarizer to concentration of the product of depolarization is at a maximum.

Vieweg[1] repeated the work of Ihle using a Leeds and Northrup Student Potentiometer. This instrument furnishes a method for measuring electromotive forces, using practically no current when the instrument is nearly balanced. With this device he was able to obtain an electromotive force of 1.92 with cells of nitric acid concentration as low as fifty grams per liter. This is, of course, analogous to the 1.8 volts obtained by Ihle for the Grove cell, the 0.12 volts difference being the current-resistance product for the circuit as measured by Ihle. The maximum value was not reached, however, for about two hours, with the cell of lowest nitric acid concentration.

The criticism might be offered that electromotive force is a measure of the tendency to react, and not of the reaction itself. This is quite true, but the

[1] Unpublished data from this laboratory.

reaction must occur to at least a slight extent before a potential is built up on the electrode. There will always be a reaction, and in this instance a polarization, as a product of the depolarization makes its appearance in the slow building up of the electromotive force.

Vieweg carried out experiments in which the platinum electrode was rotated. This should cause a decrease in the concentration of the nitrous acid at the electrode and, consequently (since the condition of zero flow of current is not experimentally realizable with the apparatus used), a fall in the electromotive force obtained. This is found to be the result with the dilute, but not with the concentrated acids. The reason no decrease is obtained with the latter is the fact that the concentrated acids reach their maximum electromotive force practically instantaneously.

These experiments are confirmed by the work of Brown[1] upon passivity of iron. The electromotive force of a cell, consisting of a platinum and an iron electrode dipping into a solution of nitric acid, was measured with a galvanometer condenser device whereby very little current was used. The electromotive force of the cell could be followed rapidly. Nitric acid of various strengths were used, and no precautions were taken to have it free from oxides. The measurements were made with the iron electrode in motion, and then suddenly brought to rest, the electromotive force being followed throughout the experiment. The values obtained were fairly constant throughout the time of rotation, but upon being brought to rest the electromotive force rose immediately to a higher value where it once more became constant. This is exactly the result Vieweg found with a rotating platinum electrode. The rotation prevented a building up of the concentration of nitrous acid at the electrode, and hence polarization prevented the cell from giving its maximum value.

The explanation given by Brown is as follows: "That this rise is due to ferrous nitrate is shown by the fact that when a quantity of this salt is added to the dilute acid[2] the cell has an electromotive force of 1.5 volts from the start, whether the electrode is in motion or at rest."

It certainly does not seem probable that the rise obtained by Vieweg upon bringing his platinum electrode to rest, or upon addition of nitrite, was due to ferrous ions.

The ferrous nitrate added by Brown, being a weak reducing agent, caused the formation of nitrous acid. The rotation of the electrode could not sufficiently dissipate the nitrous acid concentration to allow polarization, when only a small current was drawn, hence the cell gave the maximum value.

The measurement of cells of this type and microscopic examination of the iron electrode, comprise the entire experimental work reported by Brown, and upon these determinations he bases his theory of the passivity of iron. He draws conclusions that active iron (the metal) is ferrous, while passive iron is ferric. This is the theory of Smits.[3]

[1] J. Phys. Chem., **25**, 434 (1921).

[2] The most dilute acid used was approximately eleven per cent nitric acid. E. J. J.

[3] "The Theory of Allotropy," 342-377 (1922).

The results of Brown may be explained on the oxide film theory of passivity.[1] Everyone will admit that an electrode with a film of an oxide on it will have different properties from an uncoated electrode. The electromotive force of such an electrode is shown by the passive iron portion of Brown's curves,[2] if correction is made for the potential of the platinum against the solution. If the film were not continuous or too thin to give its full effect,[3] a value intermediate between that of active and passive iron would be noted. If a concentration of nitric acid were used that would partially prevent the formation of such a film, or partially dissolve it if already formed, we should expect to get a different equilibrium value than that which we would get with an acid that would completely dissolve the film. This is shown by the various maximum values attained with varying strengths of nitric acid. The case in which the acid dissolves the film already formed is shown by the acid whose density was 1.01. When an electrode, that has been rendered passive by dipping into a strong nitric acid solution, is dipped into acid of 1.01 density, it becomes active and reaches the maximum value very quickly.

Urea is an agent which has a specific reaction with nitrous acid (diazo reaction), thereby destroying it. This, if added to the nitric acid of a Smee cell should have an effect paralleling that of the rotation of the platinum electrode. This Vieweg found not to be true. When urea was added to the nitric acid, after the cell had reached its maximum value, the electromotive force was not altered. If this result is right, it means that the urea does not react so completely with the nitrous acid that it is all removed. This postulate receives support from the experiments of Ihle in which he was unable to get any lowering of the electromotive force of cells containing nitric acid of greater concentration than 35-40 %. However, this result will have to be checked.

Vieweg showed that addition of nitrite to the nitric acid of a Smee cell, after the maximum value had been reached, had no effect whatever. This contradicts Ihle's statement on this point. On repeating the experiment measuring the electromotive force of a cell, in the manner of Ihle, Vieweg confirmed his own result. The "Galvanometer" used by Vieweg was a high resistance voltmeter which gave him a value of 0.78 volts as compared to the 0.7 volts obtained by Ihle, so it is very probable that the resistance of this instrument is higher than Ihle's.

It is a known fact that the nitrous acid concentration does not build up when a solution of nitric acid undergoes electrolysis, even in the cases where there is no evolution of gases. This does not seem correct if nitric acid were the depolarizer, for it should be almost entirely removed before the nitrous is attacked. This points at once to the necessity of postulating some method of removal of the nitrous acid. Bancroft[4] pointed out that a case of a dynamic

[1] Faraday: Phil. Mag., (3) 9, 57 (1836).
[2] J. Phys. Chem., 25, 438 (1921).
[3] A similar case is treated by Shepherd: J. Phys. Chem., 7, 15 (1903).
[4] J. Phys. Chem., 28, 980 (1924).

equilibrium was especially desirable in cases of this type. "I think that this critical study of the literature shows that nitrous acid is not the actual depolarizer but that it acts as a catalytic agent making the nitric acid active. The next question is as to the way in which nitrous acid acts and I think that the answer to this question is suggested by the previously quoted statement by Burch and Veley[1] that 'nitrous acid ready-formed is not so active a material as nitrous acid in the alternative process of formation and decomposition.' If one substitutes nitric acid for nitrous acid in this statement, we have made a real step forward. I have pointed out in another paper[2] that any reaction between so-called saturated compounds involves either a preliminary dissociation which means the breaking of a regular bond, or a preliminary association which means the opening of a contravalence or residual valence. In the case of a solid catalytic agent the thing of real importance is not the formation of a definite intermediate compound or the formation of an adsorption complex but is the formation of the free radical, taking the term in its broadest sense—which is the real reacting substance. In so far as we can duplicate photochemically the action of a contact catalyst this must be so, because light can activate a substance only by opening a normal valence or a contravalence. We can word this in a different way, if it will make it clearer to anybody, by saying with Daly[3] that activation means opening up fields of force, because 'it is a necessary deduction that the condensing together of the lines of force must result in a decrease of chemical activity, and, indeed, it would seem to follow that the true chemical affinity of any molecule cannot be exhibited until the condensed systems of force lines within each molecule have been unlocked or opened by some means.'

"If we apply this point of view to the case that interests us at the moment, we see that a dynamic equilibrium must represent a more active state then a static one. In the case of the reversible reaction

$$HNO_3 + HNO_2 \rightleftarrows 2\ NO_2\ (\text{or}\ N_2O_4) + H_2O,$$

the nitric acid is continually going over to nitrogen peroxide and being formed from the latter. During the moments of change and nitric acid, the nitrogen atom, or some radical containing nitrogen and oxygen must be in a different state from what it would be if no nitrous acid were present and if this reaction were not taking place. If the particular intermediate stage involved in this reaction is one which permits more rapid reaction with nascent hydrogen, our problem is solved. Actually, we have merely formulated our problem in a new way."

Bancroft's summarized statement is:—

"It seems probable that the activation of nitric acid depends on the dynamic equilibrium represented by the equation

$$HNO_3 + HNO_2 \rightleftarrows 2\ NO_2 + H_2O."$$

[1] Phil. Trans., **182** A, 330 (1891).
[2] Bancroft: Ind. Eng. Chem., **16**, 270 (1924).
[3] J. Chem. Soc., **101**, 1469, 1475 (1912).

This view may seem a little more definite if we say it in this manner. The activation of nitric acid depends upon the formation of an intermediate product in the dynamic equilibrium as given above, and this product is the real depolarizer in the reduction of nitric acid. This may be represented as follows:

$$HNO_3 + HNO_3 \rightleftarrows (H_2N_2O_5) \rightleftarrows 2\ NO_2 + H_2O$$

This intermediate product, nitrosic acid as we will call it after Oddo, gives upon reduction another product which may decompose partly into nitrous acid and be reduced partly.

This view finds support in the work of various investigators. Armstrong, in a note appended to a paper by Divers[1], discussed the possibility of such an intermediate product. Veley's[2] own work gives perhaps the most conclusive evidence: "Lead is attacked to a less degree by nitric or nitrous acid, taken separately, but to a greater degree by mixtures of the two acids, the reaction between the metal and acid mixture being the most intense the more nearly equal in the proportion between nitric and nitrous acids."

Luther and Schilow[3] in studying induced, or coupled, reactions have considered the case of nitric acid. "If we study the first of the above mentioned reactions ($HNO_3$ is Actor, Zn or Cd is Inductor, and HI is Acceptor) it is probable that the total reaction can be divided into the two following equations:

$$HNO_3 + Zn = ZnO + HNO_2,$$
$$2\ HNO_2 + 2\ HI = I_2 + 2\ NO + H_2O.$$

"In this case the primary reactions are linked together by an *intermediate stage of the Actor*, which becomes existent in the oxidation-reduction reaction (Actor + Acceptor), and so far as it itself is concerned, reacts in a similar manner with the acceptor.

"In the following example the current acts as inductor. If one reduces an acidified nitrate solution containing iodide ions by means of an unattackable electrode, then the iodide ion is oxidized to iodine. The procedure may be shown by the following equations:

$$HNO_3 - F = HNO_2,$$
$$HNO_2 + HI = \tfrac{1}{2}\ I_2 + NO + H_2O$$

"Such cases may be termed electrolytic induction.[4]"

It is apparent that this second case of Luther and Schilow is the same as the first.

Oddo[5] found evidence for the existance of $H_2N_2O_5$, formed by the interaction of water and nitrogen peroxide, in freezing-point determinations in nitrobenzene. He gave it the name of nitrosic acid.

---

[1] J. Chem. Soc. **43**, 456 (1883).
[2] J. Soc. Chem. Ind. **10**, 210 (1891).
[3] Z. physik. Chem., **46**, 797, 801 (1903).
[4] This case is mentioned by Turrentine: Trans. Am. Electrochem. Soc., **13**, 291 (1908).
[5] Gazz., **45** I, 413 (1915).

The presence of nitrosic acid in solutions of nitric acid may be explained on the basis of the work of Reynolds and Taylor,[1] who found that light decomposes nitric acid vapor according to the equation:

$$2\,HNO_3 = 2\,NO_2 + H_2O + O$$

The formation of nitrosic acid is nothing more than the intermediate step in one of the reactions for the preparation of nitric acid,[2] by fixation of atmospheric nitrogen in the arc process.

Most reducing agents will not react appreciably with nitric acid in the absence of nitrosic acid. Ferrous sulphate, sodium sulphite, stannous chloride, and titanous chloride react with pure nitric acid only after long standing, but upon addition of a small amount of a nitrite the reaction occurs with great rapidity.

Bourgoin, Schönbein, and Gladstone and Tribe[3] noticed, that upon electrolysis, solutions of nitric acid first gave an evolution of hydrogen, which ceased abruptly in from three to forty minutes. Gladstone and Tribe traced the sudden stoppage of the evolution to the presence of nitrous acid in the solution. Thus it is seen, as was shown by Luther and Schilow[4] that the presence of nitrosic acid is essential for the reduction of nitric acid, whether it be by chemical or electrochemical means.

Quite likely the reason Veley and others felt it incumbent upon them to show the formation of a metallic nitrite, is because in some cases it is possible to separate the nitrite from solution. In the case of silver the nitrite is only slightly soluble while the nitrate is very soluble, hence silver nitrite may be crystallized from the reaction mixture.

Mercury offers the same problem. This was encountered by Rây.[5] "Mercurous nitrite is the sole product[6] other than water, of the immediate action of mercury on dilute nitric acid containing any nitrous acid. In the absence of the latter acid, the former is quite inactive. The formation of the salt may be expressed by the equation

$$2\,Hg + NO_2H + HO.NO_2 = Hg_2(NO_2)_2 + H_2O,$$

but it is in part converted by nitric acid into nitrate and nitrous acid. At suitable temperatures and in the presence of the right proportions of water and nitric acid, a stage is soon reached in which the quantity of nitrite produced by nitrous acid is just balanced by that decomposed by nitric acid. There then ensues for some time a steady accumulation of mercurous nitrite, during which the production of permanent nitrite is due wholly to nitric acid, as expressed by the equation:

$$4\,Hg + 4\,HNO_3 = Hg_2(NO_2)_2 + Hg_2(NO_3)_2 + 2\,Hg_2O$$

---

[1] J. Chem. Soc., **101**,

[2] Foerster and Koch: Z. angew. Chem., **21**, 2161, 2209 (1908).

[3] See page 1231.

[4] Z. physik. Chem., **46**, 797, 801 (1903).

[5] Proc. Chem. Soc., **20**, 217 (1904).

[6] Without doubt the author means in solution.

So long as this equation is valid, there is present in the solution an unvarying quantity of nitrous acid, acting as it were, catalytically. Analyses of portions of the solution drawn off close to the surface of the mercury give support to the foregoing theoretical considerations. When working at 35°, the mercurous nitrite and mercurous nitrate are present in molecular proportion."

It will be noted in the above that Rây did not assume that the nitrous acid alone is the depolarizer.

It is of much interest to note that one of the more recent writers has also made the mistake of assuming that the nitrous acid is the depolarizer. Bagster[1] offers the following theory for the action of copper on nitric acid. "The following explanation of the process, in terms of well known electrochemical theory is suggested: (1) Oxidation of the hydrogen film on the copper by the nitrous acid, which itself is reduced to hyponitrous acid, the copper passing into solution to replace the hydrogen removed; (2) oxidation of the hyponitrous acid to nitrous acid by nitric acid, which itself is reduced to nitrous acid."

Bagster offers no proof of the reaction between nitric acid and hyponitrous acid.

Klemenc[2] offers an explanation of the action of nitric acid on metals that is very hypothetical in its nature. Everything is based upon the assumption of an intermediate compound between nitric and nitrous acids. This compound is designated as "E acid" and is given the formula $H_2N_3O_8$. The various reactions of this acid with the metals, and with its reduction products, are given, and the usual products accounted for in this manner. There is no proof given for these hypotheses.

## Action of Reducing Agents in Solution

The first systematic work on oxidation and reduction potentials was done by Bancroft,[3] who pointed out that these potentials were a measure of the oxidizing or reducing power of a reagent. The formulation of the theory of electrode potentials is due primarily to Nernst.[4] The formulation, as we ordinarily use it, is a modification of the van't Hoff reaction isotherm due to Haber.[5] However, this was merely following the lead of Peters[6] who developed a similar formulation a few years earlier. The formulation as it is used today is:

$$E = (RT/nF) \ln K - (RT/nF) \ln C_1/C_2,$$

where E is the reduction potential, K is the equilibrium constant for the reaction, and $C_1$ and $C_2$ refer to the actual concentrations of the reducing agent and products of reduction. This relationship holds rigidly only in cases of strictly reversible reactions.

The higher the value of E, the more powerful is the reducing agent we are dealing with, and the further we would expect it to reduce nitric acid, other factors remaining constant.

---

[1] J. Chem. Soc., **119**, 82 (1921).
[2] Z. Elektrochem, **32**, 150 (1926).
[3] Z. physik. Chem. **10**, 387 (1892); See also Neumann: **14**, 228 (1894).
[4] Z. physik. Chem., **4**, 129 (1889).
[5] Z. Elektrochem., **7**, 1045 (1901). See also Bancroft: Trans. Am. Electrochem. Soc., **28**, 362 (1915).
[6] Z. physik. Chem., **26**, 193 (1893).

For purposes of comparison the value of E is measured with normal concentrations. Tables of oxidation-reduction potentials are given by Bancroft[1], Neumann[2] and various other investigators.[3] These data are none too plentiful, and none too accurate.

In Bancroft's original paper the effect of hydrogen ion concentration on oxidation-reduction potentials is considered. "A free acid is a stronger oxidizing agent than the corresponding salt, but the reverse is true with a reducing agent."

This is a factor that must be considered throughout the treatment of reducing agents. A factor of even greater importance is the interaction of nitric acid and its various reduction products, and their action among themselves.[4] A third very important factor is, that exactly as in the case of the action of metals on nitric acid, we are dealing with the same reduction scheme, consisting of direct reductions and secondary reactions. The products obtained in any instance are a result of the various reaction velocities. The factor of diffusion does not enter here so much as in the case of the action of metals.

When the reducing agent is added to the nitric acid we would expect an entirely different result than if the order of addition were reversed, if the reaction is rapid.

In the first case there is never an appreciable concentration of the reducing agent, hence its potential is low, and the reduction will not go so far. There is also plenty of opportunity for the excess nitric acid to react with some of the intermediate products.

In the second case there is always an excess of reducing agent and the reduction should go to a lower stage than in the first case. There is also little chance for the nitric acid to react with the intermediate products.

However, when the reaction is slow, the order of addition is a factor of little importance, but the presence of an excess of one or the other reagent has a marked influence. An excess of reducing agent will cause more complete reduction to a lower stage. An excess of nitric acid will cause loss of the products due to interactions with the excess nitric acid.

A very complete study of the action of reducing salts upon nitric acid was made by Milligan and Gillette.[5]

"When small amounts of nitric acid are added to an excess of ferrous chloride solution containing free hydrochloric acid, and the mixture is boiled in the absence of air, the nitric acid is quantitatively reduced to nitric oxide which is expelled from the boiling solution; and this procedure has been made the basis of a method for the quantitative determination of nitrates.[6]

---

[1] Z. physik. Chem.; 10, 387 (1892).

[2] Z. physik. Chem., 14, 228 (1894).

[3] See references in Creighton and Fink: "Electrochemistry," 228-229 (1924).

[4] See page 1228.

[5] J. Phys. Chem., 28, 744 (1924).

[6] Method of Schloesing and Grandeau: Ann. Chim. Phys., (3) 40 (1850); Fresenius: Z. anal. Chem., 1, 38 (1862); modified by Tiemann and Schulze: Z. anal. Chem., 9, 401 (1870); Ber., 6, 1041 (1873).

"With low concentrations of ferrous ion and nitric acid at room temperature, the reaction takes place with extreme slowness, but there does not appear to be a limiting concentration below which some reaction will not occur. Strong ferrous sulphate solutions containing a few drops of nitric acid will remain a light green color for a long time, but eventually (months) will turn red-brown, indicating the formation of nitric oxide which combines with the ferrous sulphate to give the same more or less unstable complex compound[1] which results when nitric oxide is passed into cold ferrous sulphate solution.

"Boiling the ferrous sulphate-nitric acid solution accelerates the reaction and renders the complex compound unstable, at once expelling nitric oxide.

"Experiments were made to determine the reactions taking place when ferrous sulphate solutions were treated with an excess of free nitric acid. When 35% nitric acid is added in large excess to a strong solution of ferrous sulphate at room temperature, so that the final mixture contains about 20 gms. of nitric acid per 100 cc of solution, no evidences of reaction appear for a while. Then, suddenly, the dark red-brown color indicative of the ferrous sulphate-nitric oxide complex appears at one spot and spreads rapidly throughout the whole solution. This condition persists only for a few minutes, however, and then the color bleaches rapidly to a light yellow-green with an attendant formation of small bubbles of gass. These phenomena are interpreted to represent: first an induction period; second the formation of nitrous acid and nitric oxide according to the reactions,

$$2\,FeSO_4 + HNO_3 + H_2SO_4 = Fe_2(SO_4)_3 + HNO_2 + H_2O$$

$$3\,HNO_2 = HNO_3 + 2NO + H_2O$$

and combination of the nitric oxide with the ferrous sulphate to give the red-brown color; and third the decomposition of this complex compound with evolution of the nitric oxide, due to the fact that diminishing ferrous sulphate concentration and rising temperature (from the heat of reaction) have rendered it unstable.

"It is not improbable that the reaction goes through other unstable intermediate stages. The hypothetical compound $H_2N_2O_5$, of which $N_2O_4$ is the anhydride, is quite likely to be the first reduction product, and Angeli's nitrohydroxylamic acid ($H_2N_2O_3$) probably stands between nitrous acid and nitric oxide.

"When a considerable amount of sulphuric acid has been added to the reaction mixture the period of induction is especially notable, and in this event the addition of a small quantity of nitrous acid seemed to act as a positive catalyzer."

"When an excess of nitric acid of 15-20% strength is reduced at 20° C by ferrous salt solutions, first the reaction passes through an induction period and then the solution becomes dark red-brown indicative of the formation of the $Fe^{++}.NO$ complex which is rapidly decomposed, nitric oxide being the

[1] See, for instance, Schlesinger and Salathe: J. Am. Chem. Soc., 45, 1871 (1923).

principal product but considerable nitrogen peroxide being formed also. When small amounts of nitric acid are added to an excess of boiling ferrous salt solution, nitric oxide only is produced."

The reason for the "extreme slowness" of the reaction between the dilute nitric acid and ferrous ion has been given in the treatment of nitrous acid.[1]

Boiling of the reaction mixture speeds up the reaction for two reasons, (1) the increase in reaction velocity due to rise of temperature, and (2) the decrease in the solubility of the nitric oxide in the reaction mixture removes a product of the reaction.

In the treatment of iron[2] it was indicated that the ferrous ion had a slight directive influence upon the formation of nitric oxide, but since there is not a trace of a lower reduction product it may be said that the reducing potential of ferrous sulphate is sufficient only for reduction to nitric oxide. Since acidified ferrous sulphate is a weak reducing agent, this is almost what one would expect.

Maumené[3] treated nitrates with stannous chloride in acid solutions, and obtained crystalline hydroxylamine hydrochloride from the solution.

Dumreicher[4] has shown that stannous chloride in acid solution reduces nitric acid to hydroxylamine and this again to ammonia.

Milligan and Gillette studied this case. "In order to get an idea of the general behavior of stannous chloride solutions when treated with an excess of nitric acid, experiments were made by mixing these reagents either with or without the addition of sulphuric acid, and the mixtures were warmed up in a water bath until decomposition took place. This began spontaneously at a fairly definite temperature, as shown by violent bubbling, the development of a yellow color in the solution starting at the top and working downward, and the evolution of light brownish-colored fumes. This temperature was noted as being a measure of the stability of the solution or an inverse measure of the rate of reaction. On this basis it was found, as would be expected from the mass law, that increasing the concentration of the nitric acid or stannous chloride lowered the decomposition temperature. Increasing the concentration of sulphuric acid in a solution in which the concentration of nitric acid and stannous chloride were kept constant, also lowered the decomposition temperature, serving to increase the effective concentration of the solution. Thus a solution containing 15 gm $SnCl_2$, 6 gm HCl, 25 gm $HNO_3$ and 22.7 gm $H_2SO_4$ per 100 cc, decomposed at 64°C under a definite set of conditions, but when the $H_2SO_4$ content of this same solution was raised to 60.5 gm the decomposition temperature was lowered to 32°.

"The preceding experiments indicate that when stannous chloride solutions are treated with an excess of nitric acid, hydroxylamine salts are the first end-reduction product produced in the solution; but that the hydroxy-

[1] See page 1255.
[2] See page 1244.
[3] Compt. rend., 70, 147 (1870).
[4] Monatshefte, 1, 724 (1880).

lamine salts are often oxidized to gaseous products if the concentration of nitric acid is sufficiently great. When stannous chloride is in excess, at least a part of the hydroxylamine is reduced to ammonium salts.

"If this is the true mechanism of the reaction, and the presence of the tin ions have no specific catalytic effect, then the gaseous products given off when nitric acid is added in excess to stannous chloride solutions should be the same as those produced when excess nitric acid is added to solutions of hydroxylamine salts. Experiments were made to test this point, and these confirm the mechanism postulated for the reaction. The fact that small amounts of $NO_2$, NO, and $N_2$ accompany the production of $N_2O$ as the main product when hydroxylamine salts are oxidized with nitric acid seems to the writers to indicate that the reaction goes through unstable intermediate stages. On this basis the fact that hydroxylamine alone seems to be the primary end-reduction product between stannous chloride solutions and an excess of nitric acid, would be interpreted to mean that the concentration of the intermediate stages under these conditions never reaches the point where decomposition to gaseous products takes place.

"When an excess of nitric acid of 10-50% strength is treated in the cold with stannous salt solutions, hydroxylamine salts are the primary end-product of the reaction, but when the conditions of temperature and concentration are such that the nitric acid and the hydroxylamine salts react, then nitrous oxide is the chief product together with small amounts of nitric oxide, nitrogen and traces of nitrogen peroxide. No ammonium salts are formed. When stannous salts are used in excess over the nitric acid, the reaction takes place with hydroxylamine and ammonium salts as the products either in hot or cold solutions, but the reaction is very slow in the latter case."

It has been proved[1] that stannic ion has a specific catalytic action resulting in the formation of hydroxylamine. In the cases where excess stannous chloride was used ammonia was formed. Dumreicher[2] has shown that hydroxylamine may be reduced to ammonia by means of acidified stannous chloride. Acidified stannous chloride then has a reducing potential sufficient for the production of ammonia, but since the stannic ion catalyzes the formation of hydroxylamine, this latter product is ordinarily obtained.

One peculiarity of stannous chloride as a reducing agent is its extraordinary change of reducing power with change in acidity. With most reducing agents the reducing potential decreases with an increase in acidity, but with stannous chloride the reverse is true. An explanation for this was offered by Goldschmidt and Ingelbrechtsen.[3]

The reduction of nitric acid by titanous salts was also studied by Milligan and Gillette. "Titanous salts are stronger reducing agents in acid solutions

[1] See page 1242.

[2] Monatshefte, 1, 724 (1880).

[3] Z. physik. Chem., 48, 435 (1904); see also Nichols and Derbigny: J. Phys. Chem., 30, 902 (1926).

than are corresponding stannous salts, as shown both by electromotive force measurements[1] and by reduction experiments.[2]

"It has just been shown that stannous salts reduce nitric acid to hydroxylamine and eventually to ammonium salts, and therefore it would be expected, reasoning purely from the apparent reducing strength of the solutions, that ammonium salts would be the chief reduction product with titanous salts and nitric acid; but, on the contrary, nitric oxide is mainly formed. When, for instance, a few drops of titanous chloride solution are added to 20% nitric acid, an instantaneous evolution of gas occurs and analysis shows it to be more than 50% nitric oxide. If stannous chloride were used under these same conditions there would be no obvious reaction, but hydroxylamine salts would be slowly formed in the solution. In terms of the reaction mechanism previously postulated, this is interpreted to mean that titanous salts exert a specific catalytic effect on the decomposition of nitrohydroxylamic acid, producing nitric oxide in quantity before much of the nitrohydroxylamic acid has a chance to be further reduced.

"No complete experiments were made in which dilute nitric acid was added to an excess of titanous chloride solution, but experiments in connection with the development of the titanous salt method for the determination of hydroxylamine[3] showed that ammonium salts are not a product under these conditions. This, and other phenomena noticed in those experiments, indicates that the reaction proceeds to practically the same products with titanous salt and nitric acid no matter which constituent is in excess. Support is thereby supplied to the view that the 'ous' salt of titanium is the catalytic agent causing the decomposition of nitrohydroxylamic acid and splitting off of nitric oxide. Further confirmation was obtained by adding titanic salt to a solution containing nitric acid and stannous chloride, in which case the reaction did not appear to be affected, and nitric oxide did not split off preferentially as should have been the case if the 'ic' salt of titanium were the catalyzer.

"When an excess of nitric acid is treated with titanous salt solutions, the reaction takes place very rapidly with the formation of nitric oxide as the chief product together with a considerable amount of nitrous oxide, a smaller amount of nitrogen, and traces of nitrogen peroxide and also of hydroxylamine salts. No ammonium salts are formed. The reaction appears to progress in practically the same way no matter whether the nitric acid or the titanous salt is in excess, neither hydroxylamine nor ammonium salts being formed in the latter case.

"Titanous salts are stronger reducing agents than corresponding stannous salts and yet the chief product produced by the former acting on an excess nitric acid is nitric oxide; whereas the chief product from the latter is hydroxylamine, which is a 'more reduced' compound but is produced by the weaker

[1] Foerster: "Elektrochemie wässeriger Lösungen," 217 (1922).

[2] Knecht and Hibbert: Ber., 36, 166, 1549 (1903); 38, 3318 (1905); Stähler: 42, 2695 (1909); Bray, Simpson and MacKenzie: J. Am. Chem. Soc., 41, 1363 (1919).

[3] See previous paper on analytical methods. Milligan: J. Phys. Chem. 28, 544 (1924).

reagent. This shows that catalytic effects play an important part, and evidence indicates that the 'ous' salt of titanium is the catalyzer for the decomposition of nitrohydroxylamic acid and production of nitric oxide."

The reduction of nitric acid by sulphur dioxide and hydrogen sulphide is treated by Spiegel,[1] "sulphurous acid reduces nitric acid very slowly unless sulphuric acid is present. If one boils one volume of nitric acid (sp. gr. 1.4) with five volumes of aqueous sulphurous acid, nitric and nitrous oxides are formed; in presence of less water there is a sudden, violent evolution of nitric oxide before boiling begins. A mixture of nitric and sulphuric acids reacts with sulphurous acid in different ways, depending on the concentration. If sulphur dioxide is passed into a mixture of oil of vitriol with ten per cent of strong nitric acid, lead chamber crystals are formed if the saturated mixture is left to itself for twenty-four hours. If these are redissolved and more sulphur dioxide is passed in, the liquid becomes dark violet if left standing in a tightly closed bottle, and contains a mixture of sulphurous acid, which passes off in the air or in a vacuum, and nitrous acid.[2] A mixture of nitric acid and dilute sulphuric acid (at least sp. g. 1.34) is readily reduced by sulphurous acid to nitric oxide. If one drops liquid sulphurous acid into pure nitric acid monohydrate, there are formed red fumes and lead chamber crystals, which disappear again when an excess of the reducing agent is added, so that finally there is only a slightly colored sulphuric acid. On heating a mixture of the two acids, Fremy observed a formation of nitrous oxide.

"Hydrogen sulphide is not attacked at ordinary temperature by nitric acid containing no oxides of nitrogen, and there is no reaction when hydrogen sulphide is passed into a pure acid of 1.18 sp. g. If the nitric acid contains only so much of the oxides of nitrogen as forms on standing exposed to air at 25°, the whole of the acid will be decomposed with formation of sulphur, sulphuric acid, ammonia, nitric oxide, and nitrogen.

"Nitrous acid in a good deal of water loses two thirds of its oxygen in presence of sulphurous acid and is reduced to nitrous oxide. When less water is present or when sulphur dioxide is passed into a solution of nitric acid in sulphuric acid of 1.4 sp. g., nitric oxide is formed. Nitrous acid dissolved in oil of vitriol does not react at all with sulphurous acid."

The products obtained from the action of various oxidizing and reducing agents on nitric acid and its derivatives are shown by Milligan and Gillette.[3]

These authors also discuss the effect of sulphuric acid. "In special solvents, new stability relations may be set up. Thus nitrosylsulphuric acid formed from nitrous acid (or nitrogen trioxide) and a large excess of concentrated sulphuric acid, according to the reaction

$$HNO_2 + H_2SO_4 \longrightarrow NOHSO_4 + H_2O,$$

may be considered to be simply nitrous acid stabilized by solution in concentrated sulphuric acid. When solid nitrosylsulphuric acid crystallizes from the

[1] "Der Stickstoff," 571 (1903).

[2] Girard and Palst: Bull., (2) 30, 531 (1878).

[3] J. Phys. Chem., 28, 755 (1924).

solution, it is simply that the system has become supersaturated with respect to this particular compound, under the conditions of the experiment. Dilution of the sulphuric acid with water decreases the stability of the nitrosyl-sulphuric acid; nitrous acid is re-formed, and is decomposed at least partially into nitric oxide and nitric acid."

The above shows that the reduction potential of sulphurous acid is sufficient for the production of nitrous oxide, while the potential of hydrogen sulphide is sufficient for the formation of ammonia.

### The Reduction of Nitrogenous Gases

Very probably the first work done on the reduction of nitrogen was by Davy[1] in 1807. "To make the experiment in as refined a form as possible, I procured two hollow cones of pure gold containing about 25 grains of water each, they were filled with distilled water, connected together by a moistened piece of amianthus which had been used in the former experiments, and exposed to the action of a voltaic battery of 100 pairs. . . . In 10 minutes the water in the negative tube had gained the power of giving a slight blue tint to litmus paper and the water in the positive tube rendered it red. The process was continued for 14 hours; the acid increased in quantity during the whole time, and the water became at last very sour to the taste.

"It was natural to account for both these appearances, from the combination of nascent oxygene and hydrogene respectively; with the nitrogene of the common air dissolved in water."

Lord Rayleigh[2] contradicted Davy's statements. "I endeavored to repeat Davy's experiment nearly in its original form. The water was contained in two cavities bored in a block of paraffin, and connected by a wick of asbestos which had been previously ignited. By means of platinum terminals connected with a secondary battery, a potential difference of 100 volts was maintained between the cups. The whole was covered by a glass shade, to exclude any saline matter that might be introduced from the atmosphere. But, under these conditions, no difference in the behavior of litmus when moistened with water from the two cups could be detected, even after 14 days' exposure to the 100 volts. When, however, the cover was removed, the litmus responded markedly after a day or two."

Rayleigh's work suffers the criticism that he did not repeat the experiment of Davy in all its details. His electrodes were platinum while Davy's were made of gold. The current density undoubtedly was not the same.

Following Rayleigh's work a patent[3] was granted in Germany for the electrolytic production of ammonia and ammonium nitrate from atmospheric nitrogen. The method of Davy modified by working under high pressure, was to be used.

Tiede and Schlede[4] were unable to get reduction of elementary nitrogen even under one hundred and fifty atmospheres pressure.

---

[1] Phil. Trans., 97, 1 (1807).
[2] J. Chem. Soc., 71, 181 (1897).
[3] D. R. P. 95532 (1897).
[4] Z. Elektrochem., 27, 112 (1921).

Fichter and Suter,[1] however, were able to get reduction of nitrogen under a pressure of two hundred atmospheres. Large heavily platinized platinum electrodes were used, the electrolyte being one per cent sulphuric acid. An average yield of 0.3 milligrams of ammonia per 160 ampere minutes was obtained.

Of course this experiment does not tell whether or not Davy's results are correct, but it does tell us that elementary nitrogen may undergo electrolytic reduction. Neogi and Adhikary[2] attempted to reduce elementary nitrogen by passing it, together with an excess of hydrogen, over heated iron and heated nickel. Negative results were obtained.

The Haber process for synthetic ammonia is an example of a success along the lines of the above experiment.

A quantitative method for the reduction of nitrous oxide was developed by Winkler[3] in which the gas was subjected to slow combustion with hydrogen at a red-hot platinum surface; nitrogen and water being obtained. Kemp[4] using this method found that ammonia also was formed. Lunge[5] modified the method, using a lower temperature and obtained only nitrogen and water. Milligan[6] obtained satisfactory results by using an excess of hydrogen, a platinum spiral heated to redness, and passing the gas slowly over the spiral.

Sabatier and Senderens[7] reduced nitrous oxide with metals at high temperatures. Nitrogen is the product formed. Iron causes reduction at 170° while copper requires a temperature of 250°.

Pascal[8] states that sulphur dioxide reduces nitrous oxide to nitrogen if the concentration of sulphur dioxide and the temperature are kept high. Coblens and Bernstein[9] obtained complete reduction of nitrous oxide to ammonia by shaking the gas with a solution of titanous chloride.

A very complete study of the action of various reducing agents in solution upon nitrous oxide was made by Nichols and Derbigny[10] in this laboratory. The results of these investigations are as follows:

"Nitrous oxide is reduced by aqueous solutions of titanous chloride, stannous chloride and sodium sulphite, with the formation of ammonia, hydroxylamine, and nitrogen respectively.

"From the preceding experimental work it has been shown that, with all of the reducing agents used, the percentage reduction for a definite time of contact, (1) increases with an increase in concentration of the reducing agent, (2) decreases with a rise in temperature and, (3) in the case of titanous chloride and of stannous chloride, decreases with increased acid concentration. The

[1] Helv. Chim. Acta, 5, 246 (1922).
[2] Z. anorg. Chem., 69, 209 (1910).
[3] "Lehrbuch tech. Gasanalyse," 3rd Ed. 190 (1901).
[4] Chem. News, 71, 108 (1895).
[5] Ber., 14, 2190 (1881).
[6] J. Phys. Chem., 28, 544 (1924).
[7] Compt. rend., 120, 618 (1895).
[8] "Synthesis and Industrial Catalysis," 348 (1925).
[9] J. Phys. Chem., 29, 750 (1925).
[10] J. Phys. Chem., 30, 491 (1926).

experimental work also shows that the only effect of these variables is to change the percentage reduction and never the nature of the final reduction product with a given reducing agent.

"It would be natural to expect in the reduction of a gas by liquid reagents that no reduction would take place, except with gas which dissolves in the liquid. In the reduction with stannous chloride the only product obtained is hydroxylamine, which can only be explained on the assumption that hydration of nitrous oxide occurs, which we believe takes place with the formation of hyponitrous acid.

$$N_2O + H_2O = (NOH)_2$$

On this basis it is possible to explain all the results obtained. A direct reduction of nitrous oxide without the addition of water would give an unsymmetrical product and only a fifty per cent yield of hydroxylamine.

"Since in every case with a given reducing agent the final product is always the same, the reducing power of the agent employed must govern the nature of the product and the quantity of the product obtained must depend upon the velocity at which the total process of reduction occurs. The total process of reduction takes place in two steps: (1) the dissolving of the $N_2O$ with the formation of $(NOH)_2$ and (2) the reduction of the $(NOH)_2$ formed, by the different reducing agents. It is highly improbable that these two reactions will take place at the same rate under varying conditions and the velocity of the total reaction will be dependent upon the rate at which the slower reaction occurs.

"In all of the experiments where the concentration of the reducing agent was varied, the acid concentration was very low or zero and the temperature was kept at 20° C. Unless then, the concentration of the reducing agent itself has some effect, the first reaction in the process should take place at constant speed, and the total velocity of the reaction will depend upon the speed of the second reaction. Since the speed of a reaction is proportional to the active mass of the reactants, it would be expected that an increase in the concentration of the reducing agent would increase the velocity of the reaction. Also, an increase in the time of contact should increase the total amount of reduction which occurs. The curves (Fig. 2) shows that this is true.

"It has already been stated[1] that the decrease in the reduction of NO with $SnCl_2$ at high temperatures is probably due to the decreased solubility. Since nitrous oxide is only sparingly soluble at high temperatures, any increase in the temperature will decrease the amount of $N_2O$ that would be dissolved when equilibrium is reached in the first reaction. This would decrease the concentration of $(NOH)_2$ and result in a decreased percentage of reduction for a given time of contact. Increased time of contact would give increased reduction. The curves (Fig. 3) show that results of this nature were found.

"The decreased reduction with increased acidity might be due to any of the following causes: (1) A decrease in the velocity of the reduction of $(NOH)_2$ because of (a) a decrease in the concentration of the $Ti^{\cdots}$ of $Sn^{\cdot\cdot}$

[1] Bancroft: J. Phys. Chem., **28**, 488 (1924).

ions due to the repression of the ionization by HCl or (b) a decrease in the reducing power of the $TiCl_3$ and $SnCl_2$ with increased acidity. (2) The acidity of the solution decreasing either the rate of attainment of equilibrium in the formation of $(NOH)_2$, or the equilibrium concentration of $(NOH)_2$.

"Experiments No. 9, Table III and No. 7 Table VI show that it cannot be due to decreased ionic concentration. In these experiments, hydrochloric acid was added and then neutralized with sodium hydroxide. The amount of reduction in these cases was much greater than when the equivalent amount of the HCl was present, although the concentration of the $Cl'$ ion was approximately the same in both cases.

"The e. m. f. measurements of the reducing power of titanous chloride decrease with increased quantities of HCl, whereas those for stannous chloride increase under the same conditions (Table IX, and Fig. 5), The case of titanous chloride is that we would expect, while that of stannous chloride at first seems anomalous. Goldschmidt and Ingebrechtsen[1] have shown that the increased reducing power of stannous chloride on nitro bodies with increased acidity is due to the formation of $HSnCl_3$. Since, however, the rate of reduction of $N_2O$ by either $TiCl_3$ or $SnCl_2$ decreases with increased acidity the change in the reducing power of the solution is not the essential factor.

"The controlling factor must be that the increased acidity decreases the rate at which equilibrium is attained in the formation of $(NOH)_2$. If this is the case, then, an equivalent amount of some other acid would have the same effect. This was proved by the use of an equivalent amount of sulphuric acid in experiment No. 8, Table VI and experiment No. 8, Table III. The slightly increased reduction can be accounted for by the difference in the ionization of the acids. Also the presence of some catalyst like platinized platinum shoul increase the amount of reduction by increasing the rate at which equilibrium in the first reaction is attained. This was found to be the case as shown by experiment No. 10, Table III, and shows that it is the rate of formation of $(NOH)_2$ which is affected by the acid, and not the equilibrium concentration of $(NOH)_2$.

"Since the reducing power of titanous chloride decreases and that of stannous chloride increases with increased acidity it would seem probable that the same reduction product should not always be obtained under all of the conditions under which the experiments were performed. However, as the voltage measurements show, the oxidizing power of the nitrous oxide increases with increased acidity. The total effect of the reaction must be represented by the algebraic sum of these two measurements which is shown by the curves (Fig. 5). It is seen that the total reducing power in the case of titanous chloride and nitrous oxide decreases rapidly at the start and then remains practically constant. In the case of stannous chloride the total reducing power increases rapidly at the start but later the rate of increase decreases. This is probably due to the formation of large amounts of $HSnCl_3$ with increased concentration of HCl.

---

[1] Goldschmidt and Ingebrechtsen: Z. physik. Chem., 48, 435 (1904).

$$\frac{(HSnCl_3)}{(SnCl_2) \times (HCl)} = K$$

The rate of change of reducing power of stannous chloride solutions will naturally decrease as the concentration of HCl increases.

"Since the above mentioned curves do not intersect at any point in the region of the values used in these experiments and since the reducing power of sodium sulphite is less than that of either stannous chloride or titanous chloride, the fact that only one primary reduction product is obtained with each reducing agent is readily explained.

"With higher concentrations of hydroxylamine in the presence of an excess of stannous chloride, other experimenters have found[1] that ammonium salts may result. Stannous chloride is therefore capable of reducing hydroxylamine to ammonia, but the low concentrations of hydroxylamine developed in the solutions of this work probably account for the fact that no ammonia was found.

"From the fact that the reduction of nitrous oxide to ammonia, hydroxylamine, or nitrogen is dependent upon the reducing power of the salt used, the following is suggested as the mechanism of the reactions.

$$N_2O + H_2O = H_2N_2O_2$$
$$H_2N_2O_2 + 2H = 2\ H_2O + N_2$$
$$H_2N_2O_2 + 4H = 2\ NH_2OH$$
$$H_2N_2O_2 + 8H = 2\ NH_3 + 2\ H_2O$$

This view was also advocated by Milligan and Gillette."

It has been pointed out[2] that the reducing potential of stannous chloride in high concentration is sufficient to reduce nitric acid to ammonia. It is apparent, therefore, that stannous chloride should reduce nitrous oxide to ammonia, if there are no disturbing influences. It has been shown that the decomposition of an intermediate product due to the catalysis by the stannic ion, is responsible for the hydroxylamine obtained in the case of nitric acid. Hydroxylamine is obtained in this case also.

The reduction of nitric oxide has been studied by numerous investigators. Ludwig and Heim[3] passed nitric oxide through a hot concentrated solution of acidified stannous chloride and obtained hydroxylamine. Cold dilute hydrochloric acid and tin give the better yield. Ammonia was produced when zinc was used.

Maumené[4] reports that nitric oxide is reduced chiefly to hydroxylamine by stannous chloride and hydrochloric acid.

Divers and Haga[5] also studied the action of stannous chloride on nitric oxide. "The reaction between acid stannous chloride and nitric oxide is not

[1] Milligan and Gillette: J. Phys. Chem., 28, 744 (1924).
[2] See page 1260.
[3] Ber., 2, 671 (1869).
[4] Compt. rend., 70, 147 (1870).
[5] J. Chem. Soc., 47, 623 (1885).

quite simple, however. The greater part of the nitric oxide becomes hydroxyammonium chloride, but a part of it is always converted into nitrogen. No nitrous oxide is formed. Since much of the nitric oxide passes unabsorbed, we could not well take the proportions of it to the hydroxyamine formed at the same time. But we many times collected it in quantity, the nitric oxide we were using being tested and found pure, as from its source it was sure to be.

"There is a remarkable fact about the reaction between nitric oxide and stannous chloride, we have yet to mention. At a temperature of fully 100°, there is no action between nitric oxide and acid stannous chloride solution. The stannous chloride remains unchanged[1] for hours together, and neither nitrogen nor hydroxyamine is formed. The only thing we have noticed is always a trace of ammonia in experiments at 100°, and this, we are inclined to believe, is due to some other cause than this reaction alone. At 90°, the action is still exceedingly small, but as the temperature descends from about 80°, it becomes rapidly greater with the descent."

Dumreicher[2] contradicts Divers. He claims that at 100° nitric oxide and also hydroxylamine are reduced to ammonia by acidified stannous chloride. At room temperature, the yield of hydroxylamine is poor with acidified stannous chloride but is quantitative with tin and hydrochloric acid.

Gladstone and Tribe[3] found that the copper-zinc couple will reduce nitric oxide to ammonia.

Sabatier and Senderens[4] report that, with zinc turnings or iron filings, nitric oxide goes slowly, first to nitrous oxide and then to nitrogen. Addition of ferrous sulphate increases the solubility of the nitric oxide, and thereby increases the rate of reaction.

These same authors[5] have shown that nitric oxide reacts with dry metals at high temperatures. The stages in this reduction must be

$$NO \longrightarrow N_2O \longrightarrow N_2$$

Knorre and Arndt[6] developed a method of analysis for nitric oxide, in which this gas, together with an excess of hydrogen is passed through a platinum tube heated to bright redness. The product of reduction is nitrogen, but, if the combustion is carried out too rapidly, ammonia is formed also, just as in the case of nitrous oxide.

Chesneau[7] reports that a blue solution of chromous chloride reduces nitric oxide to hydroxylamine when the gas is run in rapidly, and to ammonia when it is run in slowly.

---

[1] Mr. Milligan suggests that this may be due chiefly to the sparing solubility of nitric oxide at the higher temperature.

[2] Monatshefte, 1, 724 (1880).

[3] J. Chem. Soc., 43, 346 (1883).

[4] Compt. rend., 120, 1158 (1895).

[5] Compt. rend., 114, 1429 (1892).

[6] Ber., 32, 2136 (1899).

[7] Compt. rend., 129, 100 (1899).

Kohlschütter[1] finds that nitric oxide is reduced to hydroxylamine in acid solutions and to ammonia in neutral solutions. This is in line with the fact[2] that, in general, increased acidity reduces the reduction potential of most reducing agents faster than it increases the oxidizing power of nitrogenous gases.

Freshly precipitated (and presumably neutral) ferrous oxide reduces nitric oxide to nitrogen.[3]

Adhikary[4] studied the reduction of nitric oxide by an excess of hydrogen in the presence of various metals. It was found that the yield of ammonia is greater when the metal is in a fine state of subdivision and is freshly reduced. Reduction occurs when the gases are passed over nickel at 300°, and after the reaction has started the temperature may be lowered to 120°. Gold, silver, or lead in the form of foil are almost inactive, but the freshly reduced metals in the form of powder cause the production of large quantities of ammonia. Gold acts best at 335°-345°, and silver at 430°. Zinc dust, reduced iron, and powdered tin give almost quantitative yields of ammonia, while magnesium, mercury, and aluminum are inactive. Antimony and bismuth when freshly reduced from their oxides also exert a catalytic action.

Sabatier and Senderens[5] finds that nitric oxide will reduce various metallic oxides and will itself be oxidized to nitrogen peroxide. Certain oxides, such as $PbO_2$, $Ag_2O$, and $MnO_2$, suspended in water, will oxidize nitric oxide to the metallic nitrite.

These same authors[6] report that nitrogen peroxide reacts more readily on metallic oxides and metals than does nitric oxide, and is a stronger oxidizing agent. The intermediate stages undoubtedly are

$$NO_2 \longrightarrow N_2O_3 \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2.$$

Divers[7] says that "nitric peroxide acts freely on metallic silver to form nitrate and nitric oxide, and has no action whatever on silver nitrite, and that silver nitrate heated with nitric oxide, even at temperatures well below 200°, interacts with it to form nitrite and nitric peroxide."

## The Reduction Products of Nitric Acid

In the development of a reduction scheme we assume that reductions due to hydrogen consist of the addition of one or more molecules of hydrogen to one molecule of the nitrogen compound to be reduced.

This assumption is difficult to prove because in many instances we may be dealing with a dynamic equilibrium between the compounds represented by the single and double formulae.

---

[1] Ber., 37, 3053 (1904).
[2] Nichols and Derbigny: J. Phys. Chem., 30, 491 (1926).
[3] Gay: Ann. Chim. Phys., (6) 5, 145 (1885).
[4] Z. anorg. Chem., 69, 209 (1910); Chem. News, 112, 163 (1915).
[5] Compt. rend., 114, 1476 (1892).
[6] Compt. rend., 115, 236 (1892); compare 114, 1429 (1892).
[7] Proc. Chem. Soc., 20, 58 (1904).

It has been proved by Nichols and Derbigny[1] that nitrous oxide goes into solution in water, with the formation of a substance having acid properties. I have proved the same to be true in the case of nitric oxide. This is in line with the ordinary conception of a reaction of a gas with a solution, as consisting of an intermediate solvent-gas compound which gives the reaction ordinarily attributed to the gas itself.

In this scheme vertical lines represent reduction and horizontal lines combination and decomposition with a gain or loss of water molecules. Fig. 1.

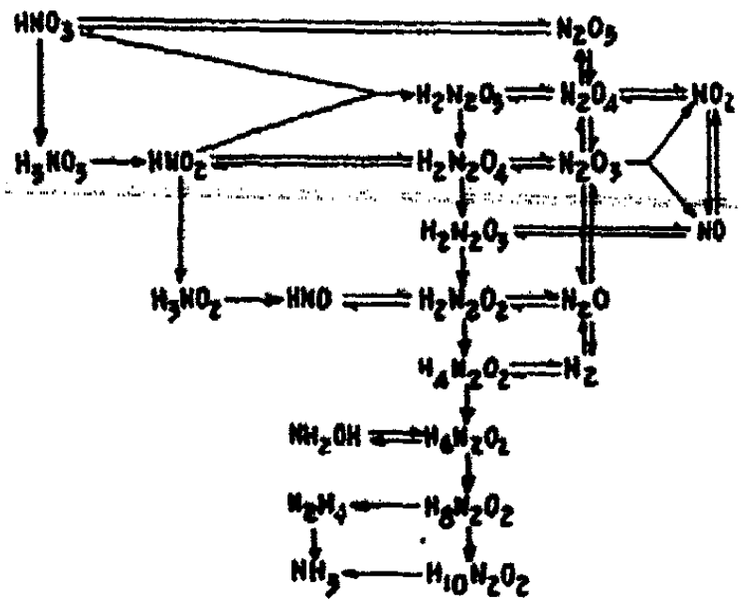



FIG. 1
Reduction Products of Nitric Acid

The justification for the decomposition

$$HNO_3 \rightleftarrows N_2O_5$$

is a method given by Mellor[2] for the preparation of nitric anhydride by distillation of concentrated nitric acid from phosphrous pentoxide.

The equilibrium

$$HNO_3 + HNO_2 \rightleftarrows H_2N_2O_3 \rightleftarrows 2\ NO_2 + H_2O$$

was discussed under nitrous acid.

The decomposition

$$N_2O_4 \rightleftarrows 2\ NO_2$$

is one of the classical examples of gas equilibria. It has been studied both experimentally and mathematically by a large number of investigators.[3]

The first reduction product of $H_2N_2O_5$ would be $H_4N_2O_5$, which could lose a molecule of water to form nitrous acid, for which we may write $H_2N_2O_4$ or $HNO_2$.

The equilibrium

$$NO + NO_2 \rightleftarrows N_2O_3$$

has been studied by Ramsay and Cundall,[4] and Dixon and Peterkin.[5] Nitrous anhydride ($N_2O_3$) dissolves in water with the formation of nitrous acid.

[1] J. Phys. Chem., **30**, 503 (1926).
[2] "Modern Inorganic Chemistry," 514 (1912).
[3] See Haber-Lamb, "Thermodynamics of Technical Gas Reactions," 149 (1908).
[4] J. Chem. Soc., **47**, 187, 672 (1885).
[5] J. Chem. Soc., **75**, 613 (1899).

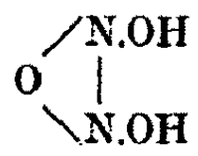
When nitrous acid undergoes reduction we have two cases to consider. The reduction of the double molecule gives us $H_4N_2O_4$ which may lose a molecule of water to form $H_2N_2O_3$. This substance can lose another molecule of water with the formation of two molecules of nitric oxide.

When nitric oxide goes into solution in water, conductivity measurements of the solution show a marked increase in conductivity over that of pure water. This proves the presence of a product which ionizes in water solution, and is a product of combination with water. If one molecule of water were in combination with one molecule of nitric oxide we have a substance whose imperical formula is $H_2N_2O_3$.

Angeli[1] prepared the sodium derivative of what he called nitrohydroxylamine ($NHOH.NO_2$) by treatment of a cold saturated solution of hydroxylamine hydrochloride with a concentrated alkaline solution of sodium ethoxide, and treatment after filtration with ethyl nitrate. The white salt separated immediately. Its formula is $Na_2N_2O_3$. Upon acidification this salt immediately decomposes with the formation of nitric oxide.

In a later paper Angeli and Angelico[2] described the preparation of various salts of the new substance which they now call nitrohydroxylamic aicd.

Thum[3] had found evidence of this acid four years earlier, but had been unable to isolate it. He called it azoxyhydroxyl and gave it the formula

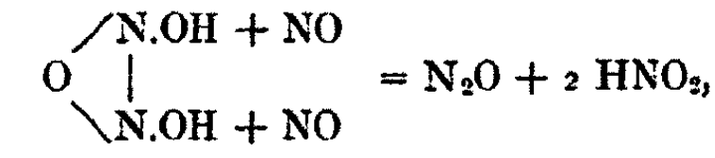


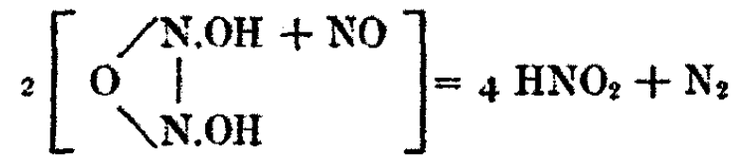
Angeli gave it this formula:

HO.N:NO.OH.

Zimmermann[4] finds that nitric oxide reacts with water to form nitrous acid and nitrous oxide.

Previous investigators[5] had found these products and nitrogen in addition. Those may be explained on the basis of Thum's formula:





If now, the single molecular form of nitrous acid undergoes reduction the first product will be $H_3NO_2$ which can lose water to give us HNO. This is the reactive form of hyponitrous acid designated by Divers. This can polmerize giving us $H_2N_2O_2$, the stable hyponitrous acid. The salts of this acid were

[1] Gazz., 26 II, 17 (1897).
[2] Gazz., 33 II, 245 (1903).
[3] Monatshefte, 14, 294 (1893).
[4] Monatshefte, 26, 277 (1893).
[5] Russell and Lapraik: J. Chem. Soc., 32, 35 (1877); Cooke: Chem. News, 58, 155 (1888).

first prepared by Divers.[1] Pure hyponitrous acid was first obtained by Hantzsch and Kaufmann.[2]

There has been much work on this acid. A bibliography of the literature up until 1899 may be found in a paper by Divers.[3] In this paper he deals at length with the acid, its salts, and properties. Free hyponitrous acid decomposes giving nitrous oxide and water.

$$H_2N_2O_2 = N_2O + H_2O$$

The reverse of this decomposition has been proved by Nichols and Derbigny.[4] These authors confirm Divers,[5] Berthelot and Maquenne,[6] and Thum[7] in giving hyponitrous acid the symetrical formula $(HNO)_2$.

Divers states that sodium amalgam will not reduce hyponitrous acid either to ammonia or hydroxylamine. This does not seem right, and should be checked.

The first reduction product of hyponitrous acid is $H_4N_2O_2$, which upon loss of two molecules of water becomes elementary nitrogen. Since it has been proved[8] that elementary nitrogen can be reduced electrolytically, we can reason by analogy with nitrous and nitric oxides, and say that nitrogen dissolves in water with the formation of a compound which can undergo electrolytic reduction.

Upon reduction the hypothetical acid $H_4N_2O_2$ will give $H_3N_2O_2$, a compound which loses water with the formation of hydroxylamine. That hydroxylamine is not a direct reduction product of nitric has been proved by Tafel[9] and confirmed by me.[10]

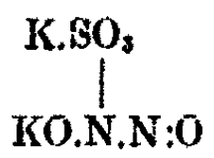
There is no need to postulate a direct reduction step for hydroxylamine. This would be difficult to prove and is unnecessary from the standpoint of our theory.

The first reduction product of the hypothetical compound $H_6N_2O_2$ is $H_4N_2O_2$, a product which upon loss of two molecules of water yields hydrazine. We know very little about this step in the reduction chain.

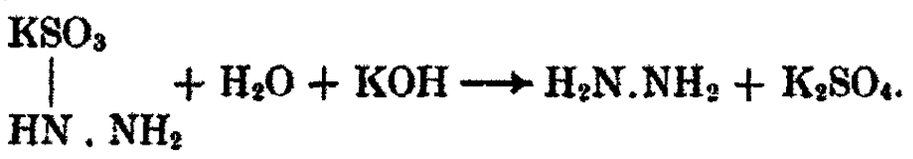
Hydrazine is formed by the reduction at low temperature of alkaline $K_2N_2SO_5$ ($K_2SO_3.2NO$) with sodium amalgam.[11] Practically no ammonia is formed until all the $K_2N_2SO_5$ is used up. Duden[12] confirms this, and adds that zinc dust and alkali may be used as the reducing agent. Raschig's formula is

---

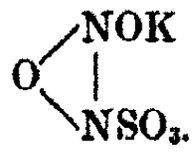
[1] J. Chem. Soc., **24**, 484 (1871).
[2] Ann., **292**, 317 (1896).
[3] J. Chem. Soc., **75**, 85 (1899).
[4] J. Phys. Chem. **30**, 491 (1926).
[5] J. Chem. Soc., **55**, 772 (1889).
[6] Compt. rend., **108**, 1286, 1305 (1889).
[7] Monatshefte, **14**, 294 (1893).
[8] See pages 1263, 1264.
[9] See page 1238.
[10] See page 1242.
[11] Divers and Haga: J. Chem. Soc., **69**. 1610 (1896).
[12] Ber., **27**, 3498 (1894).



which reduces to



Hantzsch[1] writes the formula



Nitramide, $NH_2NO_2$ also reduces to hydrazine,[2] though not quantitatively.

Francke[3] states that concentrated solutions of hydrazine sulphate react quantitatively with nitrous acid in the cold

$$N_2H_4 + HNO_2 \longrightarrow N_2O + NH_3 + H_2O$$

Girard and de Saporta[4] write this reaction $2\,NaNO_2 + N_2H_4 . H_2SO_4 \longrightarrow N_2 + H_2N_2O_2 + Na_2SO_4 + 2\,H_2O$. They also say that hydrazine sulphate reduces cupric oxide according to the equation:

$$4\,CuSO_4 + N_2H_4 . H_2SO_4 + 10\,NaOH \longrightarrow 2\,Cu_2O + N_2 + 5Na_2SO_4 + 8\,H_2O$$

Müller,[5] Flaschner,[6] and Tafel and Hahl[7] have determined the voltages required to reduce nitrous acid, hydroxylamine, and hydrazine.

Bancroft[8] comments upon hydrazine as follows:

"It was found by von Brackel[9] that hydrazine is obtained when a solution of sodium bisulphite, silver hyponitrite, and hydrochloric acid (the acid being equivalent to the silver) is reduced with zinc dust and glacial acetic acid in the cold. The hydrazine was not isolated as such, but a yellow precipitate of benzalazine was obtained on adding benzaldehyde. The presence of sulphite is apparently essential, just as the presence of sulphuric acid is desirable in the reduction of nitric acid to hydroxylamine. I should like to see the experiment tried of running nitric acid with and without nitrous acid slowly into a cold, concentrated solution of sulphurous acid."

The last step in the reduction chain is the reduction of the hypothetical product $H_8N_2O_2$ giving $H_{10}N_2O_2$ which decomposes into two molecules of ammonium hydroxide, or loses water with the formation of ammonia.

It is not claimed that these four hypothetical intermediates have the formulae given them, but they do exist either in this or a more or less hydrated form.

---

[1] Ber., 27, 3264 (1894).
[2] Thiele and Lachmann: Ber., 27, 1909 (1894); Ann. 288, 267 (1895).
[3] Ber., 38, 4102 (1905).
[4] Bull., (3) 31, 905 (1904).
[5] Z. anorg. Chem., 26, 1 (1901).
[6] Monatshefte, 28, 235 (1907).
[7] Z. anorg. Chem., 56, 375 (1908).
[8] J. Phys. Chem., 28, 491 (1924).
[9] Ber., 33, 2115 (1900).

The direct reduction of the gases is somewhat different, for here we are dealing either with dry metals or hydrogen together with a catalyst.

The decomposition of $N_2O_5$ into $N_2O_4$ and oxygen was studied by Daniels and Johnston.[1]

When a metal is oxidized by a nitrogenous gas, the reduction of the gas consists of a loss of one or more atoms of oxygen from the molecule. The work of Sabatier and Senderens[2] accounts for these direct reductions.

In the cases of reduction by hydrogen there must be a connecting link between the two direct chains.

## Summary

1. The gradual development of the theory for the reduction of nitric acid has been presented.

2. A general theory for the mechanism of the action of metals on nitric acid is given.

3. The veracity of this theory is proved by application to the data of a large number of investigators in addition to my own.

4. The theory is one that is generally applicable to studies of oxidation and reduction reactions.

5. "The action of metals on nitric acid may be considered as a special case of the electrolytic theory of corrosion. The factors governing the products obtained are: the specific reducing power of the metal which may be measured by the hydrogen overvoltage in a corresponding sulphuric acid solution; the catalytic action of the metal on the various reduction products; and the catalytic action of the metallic nitrate on the various reduction products." This tells us of our primary products, but we must keep the chemistry of our problem in mind, since the various intermediate products may react with nitric acid or among themselves, yielding products quite different from the primary ones.

6. A voltaic cell arrangement is devised whereby we can pick apart and analyze the various factors entering into any given case.

7. Many metals are shown to be identical in their chemical and electrochemical reactions, when the various disturbing factors are removed.

8. Evidence is presented that the real depolarizer in the action of metals on nitric acid is nitrosic acid ($H_2N_2O_5$).

9. The existing data on the action of various reducing agents in solution are shown to be explained by the theory.

10. The reduction of intermediate products is examined and the discrepancies accounted for.

11. A schematic representation of the reduction products of nitric acid is presented and an explanation given.

---

[1] J. Am. Chem. Soc., **43**, 53 (1921).

[2] See page 1264.

12. Further work on this subject will be carried out at Cornell University. Problems to be solved are: hydrazine; effect of sulphuric acid; reduction of nitric oxide and nitrogen peroxide; oxidation of ammonia and various intermediate products; and reduction of alkaline nitrates.

**Acknowledgment**

To Professor Wilder D. Bancroft, at whose suggestion this investigation was undertaken, the writer gratefully acknowledges his indebtedness for the direction of this research. I wish to thank also, Mr. H. F. Vieweg for the major portion of the work on nitrous acid. The work of Mr. Vieweg was done under a grant to Professor Bancroft, from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

*Cornell University,*
*July, 1926.*

# THE COLOUR CHANGE OF CONGO RED IN ACIDIFIED ACETONE-WATER SOLUTIONS

QUA-89

BY FRANK MAURICE CRAY

Hantzsch[1] and Scholtz[2] studied the colour change of Congo Red in presence of mineral acids and observed that the addition of organic solvents to a solution of Congo Red in water greatly influenced the sensitivity of this substance to acids.

The present research was based upon the observation that if acid is added to a solution of Congo Red in a solvent containing acetone and water under the conditions defined below, the colour gradually changes from red to blue and finally the blue form is precipitated from the solution.

The time elapsing between the addition of acid and the development of a definite stage in this colour change has been studied and has been found to be dependent upon the concentrations of the acid and Congo Red as well as the composition of the solvent and the temperature at which the experiments were carried out.

*Materials.*

The Congo Red, which was supplied specially for use as an indicator, was repurified from a mixture of acetone and water several times. Stock solutions deep blood red in colour were made up in water as required.

The acetone was redistilled and accepted only if its specific conductivity was less than $1.0 \times 10^{-7}$ reciprocal ohms at 20°C. while that of the water was less than $1.5 \times 10^{-6}$ reciprocal ohms at 20°C.

*Experimental.*

Congo Red and hydrochloric acid solutions were made up separately as required in the given acetone-water mixture in order to avoid errors due to variation in temperature resulting from the considerable heat effects on mixing acetone with water.

All solutions were made up to contain the specific volume of water in 100 volumes of the mixed solvent at 15°C.

5 cc. of the acetone-water solution of Congo Red were pipetted in each case into hard-glass tubes six inches long by ⅝ inch in diameter and a small hard-glass tube 3 inches long by ½ inch in diameter containing 5 cc. of the acid solution in acetone-water was carefully placed in each of these tubes, which were then closed by a waxed cork and sealed with paraffin wax. Generally four such tubes were prepared for each acid concentration and when experiments were repeated, the whole of the solutions were made up afresh.

[1] Ber., **48**, 158 (1914).
[2] Z. Elektrochem., **10**, 551 (1907).

The glass tubes fitted as described were kept in a glass thermostat at the required temperature within ±0.1°C. The small inner tubes were cut off at an angle of 45° so that when the tubes were inverted and shaken, the Congo Red and acid solutions were rapidly mixed. The time taken to the development of the first clear blue colour, a very marked step in the colour change was measured by means of a stop watch. Suitable standard tints were made up with Brom Thymol Blue and Brom Cresol Purple in a buffer solution of pH 7.2.

*Results.*

The experimental results are given in series which show: I. The influence of hydrogen ion concentration and composition of the solvent when the Congo Red concentration is constant; II. The effect of change in Congo Red concentration when the hydrogen ion concentration and composition of the solvent are kept constant.

The values for $\alpha$ the degree of dissociation of hydrochloric acid in the acetone water mixtures are taken from a paper by Brownson and Cray.[1]

SERIES I

The Influence of Hydrogen Ion Concentration and Composition of the Solvent when the Congo Red Concentration is constant

(a) Congo Red concentration in reaction tube:—$2.7 \times 10^{-5}$ gram mols per litre.

Temperature 25° C.

*10 volumes of water in 100 acetone water.*

| Conc. of HCl Mols/ Litre. | $\alpha$ From Conductivity Data | [H]· | T. Secs. |
|---|---|---|---|
| $0.204 \times 10^{-2}$ | .70 | $0.142 \times 10^{-2}$ | 7.5 |
| 0.163 | .73 | 0.119 | 11.5 |
| 0.122 | .775 | 0.094 | 23 |
| 0.112 | .79 | 0.088 | 33 |
| 0.102 | .80 | 0.082 | 44 |
| 0.092 | .82 | 0.075 | 61 |
| 0.081 | .83 | 0.067 | 104 |
| 0.071 | .84 | 0.060 | 152 |

*20 volumes of water in 100 acetone water.*

| Conc. of HCl Mols/ Litre. | $\alpha$ From Conductivity Data | [H]· | T Secs. |
|---|---|---|---|
| $2.98 \times 10^{-2}$ | .621 | $1.85 \times 10^{-2}$ | 9.5 |
| 2.76 | .630 | 1.74 | 13.5 |
| 2.55 | .640 | 1.63 | 19 |
| 2.34 | .65 | 1.52 | 26 |
| 2.13 | .661 | 1.41 | 36 |
| 1.92 | .674 | 1.29 | 57 |
| 1.70 | .687 | 1.17 | 121 |
| 1.49 | .702 | 1.05 | 260 |

*30 volumes of water in 100 acetone water.*

| Conc. of HCl Mols/ Litre. | $\alpha$ From Conductivity Data. | [H]· | T Secs. |
|---|---|---|---|
| $6.01 \times 10^{-2}$ | .70 | $4.21 \times 10^{-2}$ | 11 |
| 5.59 | .707 | 3.95 | 15 |
| 5.16 | .713 | 3.68 | 19 |
| 4.74 | .721 | 3.42 | 33 |
| 4.31 | .732 | 3.15 | 55 |
| 3.89 | .741 | 2.88 | 91 |
| 3.46 | .751 | 2.60 | 150 |

*35 volumes of water in 100 acetone water.*

| Conc. of HCl Mols/ Litre. | $\alpha$ From Conductivity Data. | [H]· | T Secs. |
|---|---|---|---|
| $7.30 \times 10^{-2}$ | .745 | $5.44 \times 10^{-2}$ | 7 |
| 6.25 | .758 | 4.74 | 10 |
| 5.73 | .766 | 4.39 | 13 |
| 5.21 | .772 | 4.02 | 21 |
| 4.69 | .782 | 3.67 | 34 |
| 4.17 | .791 | 3.30 | 61 |
| 3.65 | .802 | 2.93 | 135 |

[1] J. Chem. Soc., 127, 2923 (1925).

SERIES I (Continued)

*40 volumes of water in 100 acetone water.*

| Conc. of HCl. Mols/ Litre. | αFrom Conductivity data | [H]· | T Secs. |
|---|---|---|---|
| $5.37\times10^{-2}$ | .821 | $4.47\times10^{-2}$ | 10 |
| 5.16 | .824 | 4.25 | 13 |
| 4.95 | .826 | 4.09 | 16 |
| 4.52 | .832 | 3.76 | 22 |
| 4.10 | .838 | 3.44 | 33 |
| 3.68 | .844 | 3.11 | 51 |
| 3.46 | .848 | 2.93 | 73 |
| 3.25 | .852 | 2.77 | 112 |
| 3.04 | .856 | 2.60 | 180 |

*50 volumes of water in 100 acetone water.*

| Conc. of HCl. Mols/ Litre. | αFrom Conductivity data | [H]· | T Secs. |
|---|---|---|---|
| $3.0\times10^{-2}$ | .904 | $2.72\times10^{-2}$ | 9 |
| 2.79 | .907 | 2.53 | 13 |
| 2.58 | .910 | 2.35 | 19 |
| 2.36 | .913 | 2.15 | 36 |
| 2.15 | .917 | 1.97 | 60 |
| 1.93 | .921 | 1.78 | 116 |
| 1.83 | .923 | 1.69 | 150 |
| 1.72 | .925 | 1.59 | 220 |

*60 volumes of water in 100 acetone water.*

| Conc. of HCl Mols/ Litre. | αFrom Conductivity Data. | [H]· | T Secs. |
|---|---|---|---|
| $1.29\times10^{-2}$ | .953 | $1.23\times10^{-2}$ | 5 |
| 1.07 | .958 | 1.02 | 12.5 |
| 0.97 | .960 | 0.93 | 19 |
| 0.91 | .962 | 0.88 | 26 |
| 0.86 | .964 | 0.83 | 34.5 |
| 0.83 | .965 | 0.80 | 50 |
| 0.78 | .966 | 0.75 | 90 |
| 0.76 | .967 | 0.73 | 126 |

*70 volumes of water in 100 acetone water*

| Conc. of HCl Mols/ Litre. | αFrom Conductivity Data | [H]· | T Secs. |
|---|---|---|---|
| $0.39\times10^{-2}$ | .984 | $0.384\times10^{-2}$ | 10 |
| 0.335 | .986 | 0.330 | 16 |
| 0.31 | .987 | 0.306 | 22 |
| 0.28 | .988 | 0.277 | 28 |
| 0.26 | .989 | 0.257 | 36 |
| 0.23 | .9895 | 0.228 | 72 |
| 0.21 | .990 | 0.208 | 170 |

Experiments were not carried out in solvents containing over 70 volumes of water in 100 volumes of acetone water. Although a time reaction is still evident in the solvent containing 85 per cent of water, the first development of the clear blue colour is not sufficiently marked for accurate measurements. In pure water as is well known, Congo Red does not show a time reaction in colour change from red to blue in presence of acid although Luers[1] has shown that Congo Rubin does do so.

A similar series of results was obtained with twice this concentration of Congo Red, namely $5.4\times10^{-5}$ gram molecules per litre. These results were of the same type as those given above, consequently they are not given in detail. The hydrogen ion concentrations required in any solvent to bring about the colour change in a given time were approximately inversely proportional to the Congo Red concentrations.

(b) Congo Red concentration in reaction tube $2.7\times10^{-5}$ gram mols per litre. Temperature 20°C.

[1] Kolloid-Z., 26, 15 (1920).

A similar series of results was obtained at 20°C. as at 25°C. the relationship between hydrogen ion concentration and time being of the same type.

A table of results, interpolated for given time periods in selected cases is given below:

| Time (Secs) | 20 vols. of water in 100 of acetone water $[H]^{\cdot}$ | 35 vols. of water in 100 of acetone water $[H]^{\cdot}$ | 50 vols. of water in 100 of acetone water $[H]^{\cdot}$ |
|---|---|---|---|
| 10 | $1.88\times10^{-2}$ | $4.6\times10^{-2}$ | $2.42\times10^{-2}$ |
| 30 | $1.52\times10^{-2}$ | 3.69 | 2.02 |
| 50 | 1.37 | 3.34 | 1.85 |
| 80 | 1.27 | 3.05 | 1.69 |
| 100 | 1.24 | 2.94 | 1.625 |

### Series II

### The Effect of Change in Congo Red Concentration when the Hydrogen Ion Concentration and Composition of the Solvent are constant.

Solvent: 50 volumes of water in 100 volumes of acetone water

Temperature 25°C. $[H]^{\cdot} = 169\times10^{-2}$ gram ions per litre

| Congo Red gram mols/litre | Time (secs) |
|---|---|
| $5.4\times10^{-5}$ | 8 |
| 5.06 | 10 |
| 4.725 | 13 |
| 4.39 | 18 |
| 4.05 | 27 |
| 3.71 | 37 |
| 3.375 | 56 |
| 3.05 | 85 |
| 2.70 | 150 |

The results for other solvents were of the same type.

## Discussion

The colour changes of Congo Red and dyes of similar constitution such as Congo Rubin have been studied by a number of investigators chief among whom are Hantzsch[1] and Ostwald[2]. The views of these authors are given at length in their papers and only a short résumé of some of the principal points is possible here.

Hantzsch holds the view that the colour change from red to blue arises as a result of constitutional change and considers that the sodium salt is a true azo body while there exist two isomeric acids, one an azo compound red in colour and the other a quinonoid substance coloured blue. The existence of these isomeric acids is based principally upon the difference between the absorption spectra of red alcoholic solutions of the sodium salt to which small volumes of sulphuric acid have been added and water solutions containing the same amount of sulphuric acid but blue in colour. This evidence cannot be considered definitely conclusive by itself.

[1] Ber., 48, 158 (1914).

[2] Kolloidchem. Beihefte, 10, 179 (1919).

Ostwald on the other hand holds that the colour change of Congo Rubin which has a constitution similar to Congo Red is colloidal-chemical in character, variations in degree of dispersion playing the chief part. In support of this theory, he adduces evidence that the red water solutions of Congo Rubin change to blue violet not only on the addition of acids but also neutral salts and bases and further that the precipitating power of high valent cations follows in the same order as in the case of relatively charged inorganic colloids.

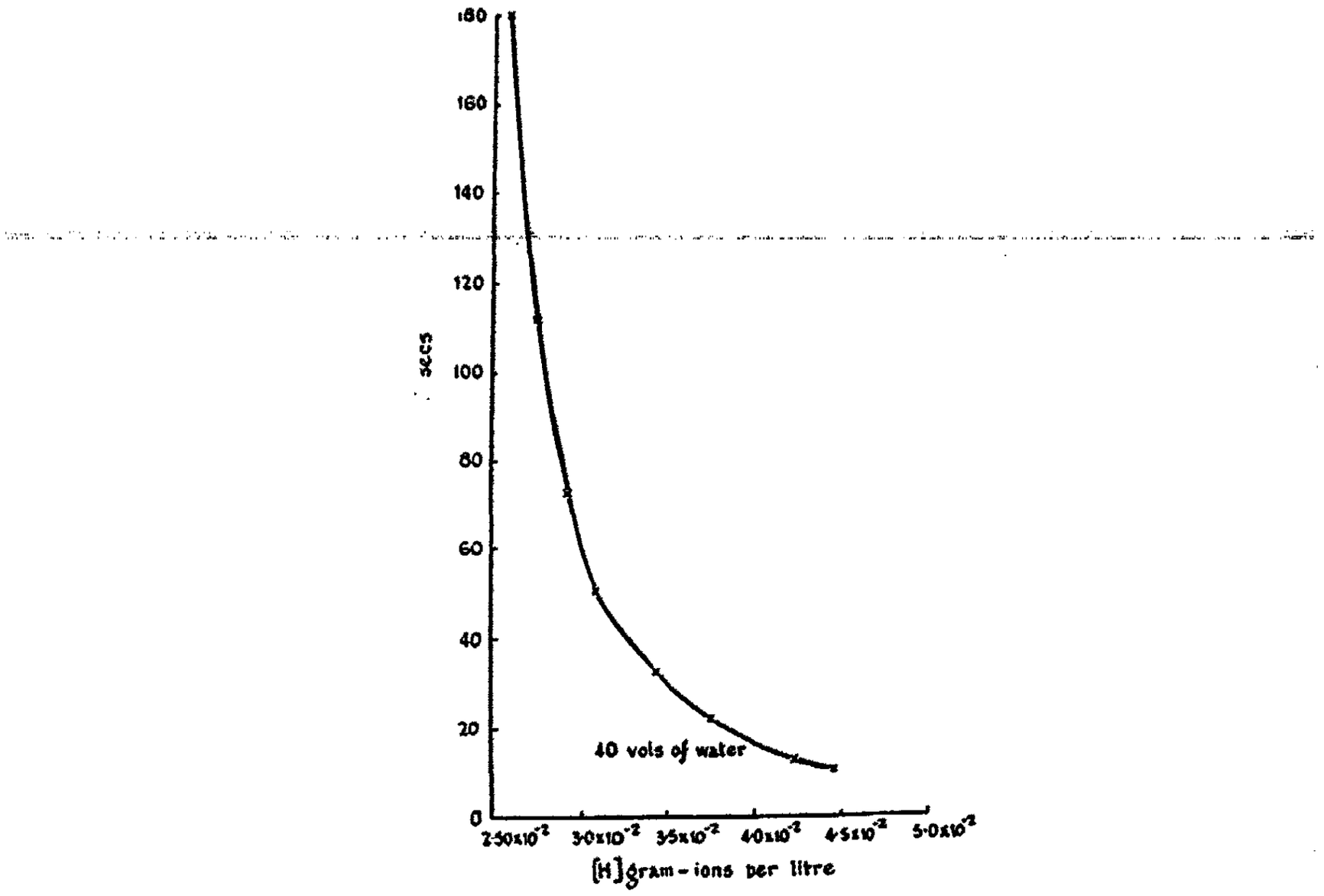



FIG. 1

Small quantities of protective colloids hinder this colour change by electrolytes and moreover Congo Rubin numbers can be found resembling gold numbers, the efficiencies of the protective colloids being in the same order in both cases.

The results of the present research do not allow a definite decision to be arrived at between these two theories but may nevertheless be of some interest.

The curves connecting the time taken to reach the definite blue stage in the colour change and the hydrogen ion concentration of the solution (Series I) show that at high hydrogen ion concentrations the time tends to reach a limiting value whilst at lower concentrations the curve tends to become asymptotic to a line parallel to the time axis, indicating that the colour change will not occur in any solvent unless the hydrogen ion concentration exceeds a certain value. A typical curve of this nature is shown in Fig. 1 for the solvent containing 40 volumes of water in 100 volumes of acetone-

water. Henry and Morris[1] have shown that the concentration coagulation time curves of gold sols in presence of various sodium salts are of the same type, there being a threshold value and also a region of rapid coagulation. Moreover, these authors show that plotting log concentration of coagulant against log time results in graphs which are either straight lines or lines of small curvature convex to the log t axis. Similar graphs were obtained from the results of this research.

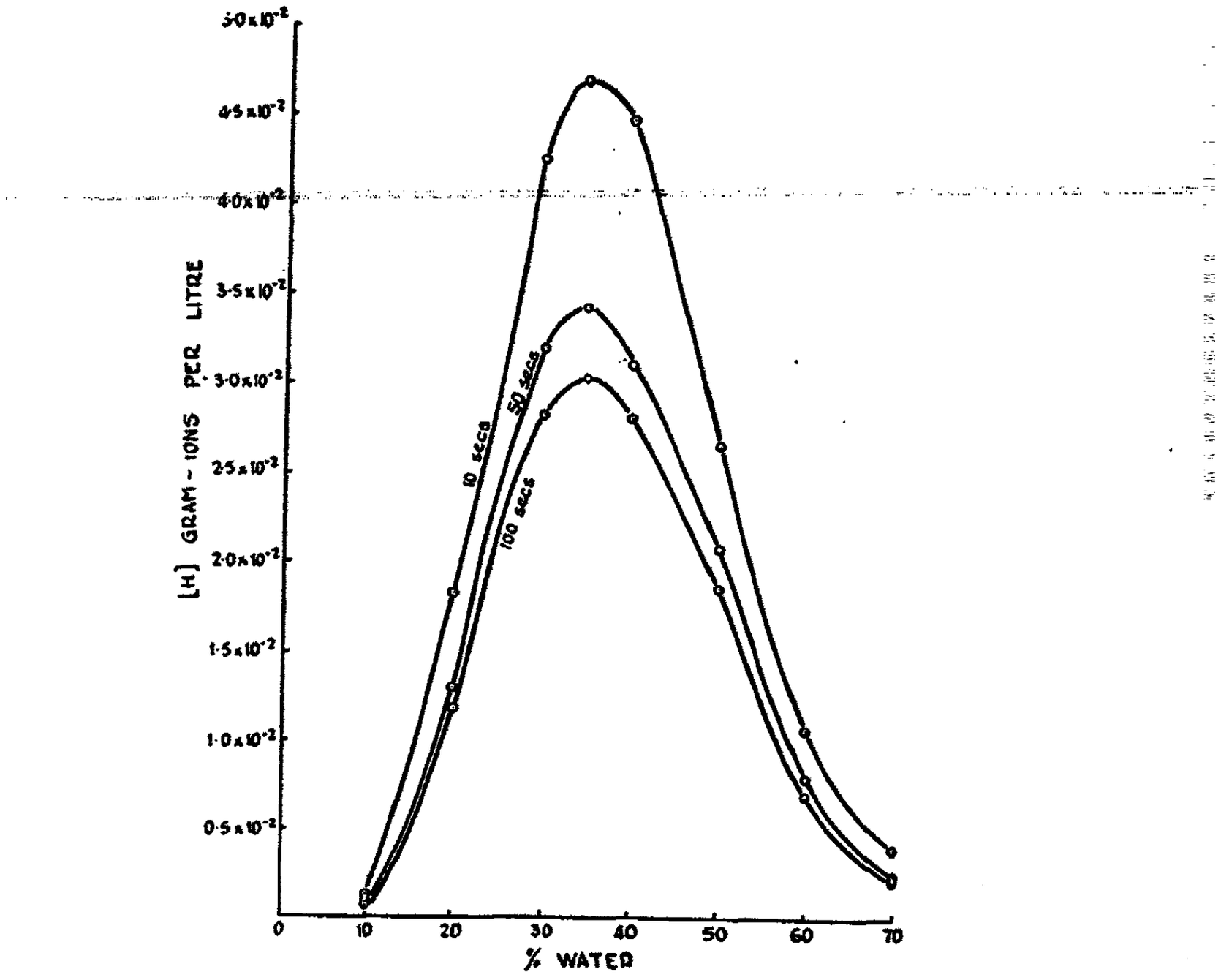



FIG. 2

The similarity between these curves and those for the coagulation of a gold sol tends to support the contention of Ostwald that changes in dispersion play the chief part in the colour changes of indicators of the type of Congo Red and Congo Rubin, the change being analogous to the colour changes of metal sols such as for example gold sols.

The curves relating hydrogen ion concentration and composition of the solvent for stated times of the colour change, when the Congo Red concentration is constant are shown in Fig. 2. The hydrogen ion concentration required

[1] Trans. Faraday Soc., **20**, 30 (1924).

for the colour change to take place in a given time is a maximum in the solvent containing 35 volumes of water in 100 volumes of acetone-water. Many organic substances are more soluble in mixtures of two solvents than in either separately. This change in solubility is sometimes accompanied by changes in solvation or degree of dispersion. Moreover, it is possible (Ostwald) for the solubility not to be abnormal although the substance shows for example a higher degree of dispersion in the mixed solvent than in either of the two components. The results of this research may be explained on the assumption that the degree of dispersion of Congo Red is greater in this solvent containing 35 volumes of water in 100 volumes of acetone-water than in the other acetone-water mixtures studied.

## Summary

The colour change of Congo Red in acidified acetone water solutions from red to blue takes place as a time effect, the velocity of the change depending upon the concentrations of the acid and of the Congo Red as well as the composition of the solvent and the temperature at which the experiments are carried out.

Comparisons drawn between this colour change and the coagulation of gold sols by electrolytes tend to support the contention of Ostwald that the colour change of Congo Red from red to blue is colloidal-chemical in nature and that variations in degree of dispersion are the principal cause of the colour change.

This time effect in the colour change of Congo Red in acidified acetone solutions was deonstrated at a Royal Society Soirée in 1922. The publication of the results has been delayed until the dissociation of hydrochloric acid in acetone-water mixture could be studied.

The author wishes to express his indebtedness to Dr. G. Rotter, C.B.E., and Dr. J. N. Pring, for their interest in this work which is published by permission of the Director of Artillery.

*Research Department,*
*Royal Arsenal,*
*Woolwich.*
*May 21, 1926.*

1275

# THE SYSTEM WATER—ACETIC ACID—TOLUENE: TRIANGULAR DIAGRAM AT 25°C., WITH DENSITIES AND VISCOSITIES OF THE LAYERS

BY ROWLAND MARCUS WOODMAN

During work on the distribution of a consolute liquid between two immiscible solvents, it was found necessary to have an accurately-determined diagram for a system containing a pair of partly miscible liquids. The present paper deals with the distribution of acetic acid, an easily-estimated liquid between water and toluene.[1]

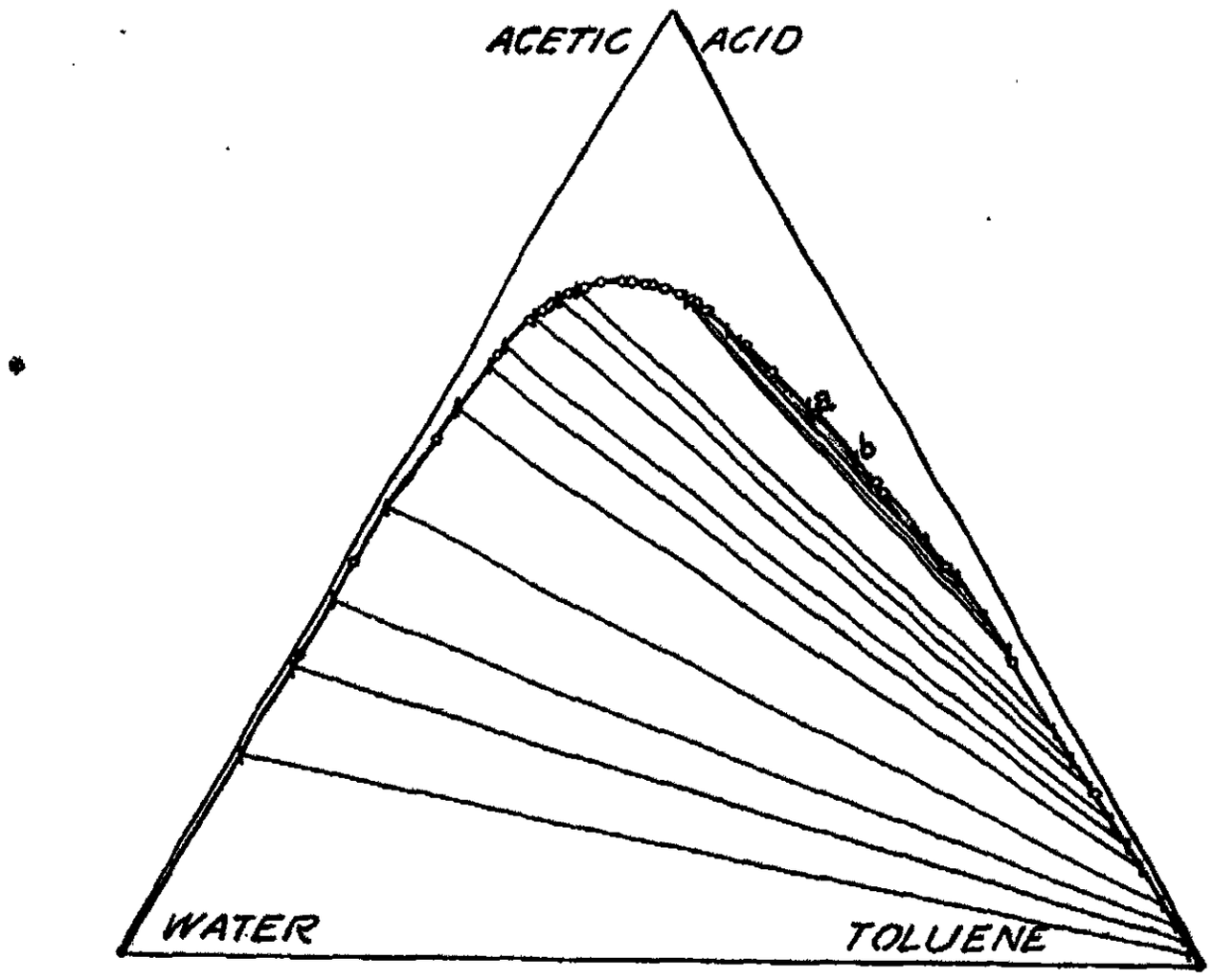



FIG. 1

The glacial acetic acid used ($D_{4^\circ}^{25^\circ} = 1.045$) was labelled "B. D. H., A. R.," and, by titrating a weighed portion, previously diluted, against n-NaOH in the presence of phenolphthalein,[2] the sample was found to contain 98.96 per

[1] Waddell (J. Phys. Chem., 2, 233 (1898)) has investigated the system water—acetic acid—benzene by a method similar to that used here. The system water—acetic acid—toluene has been partially investigated by Herz and Fischer (Ber., 37, 4746; 1904, 38, 1138 (1905) with the view of determining the distribution of the acid between the two immiscible solvents.

[2] Krauch: "Chemical Reagents," 3 (1919).

cent. by weight of acid. The water was that obtained as the middle fraction from the distillation of previously-purified water in a well-used glass distilling apparatus. The toluene ($D_{4^\circ}^{25^\circ} = 0.8598$), was purified in the usual manner.

The points outlining the curve (Table I, and circles, Fig. 1), were obtained by the following synthetic method: water and toluene were separately weighed into a tared flask and the mixture brought to 25° by immersion of the flask in the thermostat. Acetic acid was then titrated into the mixture from a standardised burette with a small drop (45 drops = 1 c.c.) until, on shaking, a turbidity only was apparent. The flask was now immersed in the thermostat again and acetic acid added drop by drop until homogeneity was obtained. This preliminary titration (usually occupying some hours and, therefore, liable to inaccuracy), was made the basis of a more rapid and accurate titration: the same amounts of water and toluene were weighed out as exactly as possible and all but a few drops of the acid rapidly added from the burette in one fraction of known temperature. The flask's contents were now warmed to 25° and the remaining drops of acid added singly. As one drop of acid was usually sufficient to differentiate between turbidity and non-turbidity, and as the titrations were arranged to be always over ten c. c. (13-110 c. c.), it was possible in every case to keep the error in titration well below 0.5 per cent. Knowing the specific gravities of acetic acid over the range of temperature 15°-25°, the weight percentages of toluene, water and acid in the final solutions obtained were calculated, Table I.

TABLE I

a = % water by weight
b = % toluene by weight

| a | b | a | b | a | b | a | b |
|---|---|---|---|---|---|---|---|
| 0.4721 | 81.3979 | 10.82 | 22.34 | 14.50 | 14.62 | 25.30 | 5.454 |
| 1.474 | 66.866 | 11.53 | 19.89 | 16.00 | 12.54 | 25.80 | 5.308 |
| 2.966 | 55.124 | 11.93 | 19.30 | 17.10 | 11.32 | 26.52 | 5.02 |
| 4.594 | 45.84 | 12.02 | 19.48 | 18.00 | 10.29 | 28.13 | 4.446 |
| 4.689 | 44.72 | 12.38 | 18.37 | 20.08 | 8.662 | 33.42 | 2.975 |
| 6.871 | 35.38 | 12.83 | 17.43 | 21.76 | 7.415 | 43.89 | 1.419 |
| 8.507 | 29.27 | 12.98 | 17.53 | 23.23 | 6.342 | 57.5967 | 0.6533 |
| 9.809 | 25.28 | 13.56 | 16.07 | 24.34 | 5.97 | 67.8344 | 0.2856 |

To complete the diagram it was necessary to fix the tie-lines: mixtures of the three liquids were made up in cylinders immersed in the thermostat, occasional shakes being given. After the lapse of a time sufficient to ensure equilibrium, quantities of the two layers were pipetted into tared, stoppered flasks and weighed.[1] The weight percentages of acetic acid in the two layers were then determined by titration, the results, Table II, being plotted as short lines on the equilibrium diagram (Fig. 1). The tie-lines were then obtained by joining the corresponding pairs of crosses.

[1] In sampling the lower layer any of the upper layer entrapped by passage of the pipette through, was expressed by closing the upper end of the pipette and warming the bulb by the hand; this procedure was found to work quite satisfactorily, and was followed also when measuring the densities of viscosities of the layers.

## Table II

a = ratio of gram-moles acetic acid in 1 litre of aqueous phase to gram-moles in 1 litre of toluene phase

| Aqueous Layer: | | | Toluene Layer: | | | |
|---|---|---|---|---|---|---|
| Wt. percent. of Acetic Acid | Density of Layer ($D_4^{25°}$) | Viscosity of Layer $\eta_{25°}$ | Wt. percent. of Acetic Acid | Density of Layer ($D_4^{25°}$) | Viscosity of Layer $\eta_{25°}$ | a |
| 0 | 0.9971 | 0.008928 | 0 | 0.8600 | 0.004967 | — |
| 21.38 | 1.025 | 0.01116 | 1.374 | 0.8614 | — | 18.51 |
| 30.87 | 1.035 | 0.01337 | 2.797 | 0.8630 | 0.005202 | 13.23 |
| 37.69 | 1.042 | 0.01470 | 4.072 | 0.8650 | 0.005201(?) | 11.15 |
| 47.50 | 1.050 | 0.01642 | 6.363 | 0.8676 | 0.005309 | 9.035 |
| 58.05 | 1.054 | 0.01875 | 10.35 | 0.8730 | 0.005298(?) | 6.774 |
| 62.53 | | | 12.98 | | | |
| 64.86 | 1.052 | 0.01980 | 14.98 | 0.8796 | 0.005441 | 5.178 |
| 67.70 | 1.049 | 0.01974 | 18.55 | 0.8847 | 0.005551 | 4.337 |
| 69.71 | 1.044 | 0.01940 | 21.50 | 0.8896 | 0.005615 | 3.805 |
| 70.55 | 1.039 | 0.01904 | 24.88 | 0.8952 | 0.005761 | 3.291 |
| 69.85 | 1.024 | 0.01677 | 32.96 | 0.9099 | 0.006362 | 2.384 |
| 69.40 | | | 36.13 | | | |
| 66.68 | 1.006 | 0.01469 | 40.64 | 0.9276 | 0.007263 | 1.779 |
| 65.31 | | | 44.41 | | | |
| 58.46 | 0.9757 | 0.01272 | 53.07 | 0.9588 | 0.01025 | 1.120 |

N. B. The corresponding weight percents. of water and toluene can be read off from the curve.

The diagram clearly shows that the critical point lies well over on the toluene side of the curve (between the points marked *a* and *b*), and thus, as the percentage of acetic acid in the aqueous layer passes through a maximum on approaching this point, some diffidence might be shown as to which side of the maximum to place several of the points corresponding to the aqueous phase, were it not for the fact that the percentage of acetic acid in the toluene layer must increase continuously in approaching the critical point.

The tie-lines on being produced converge to a point; this is quite different from the systems water-pyridine-benzene[1] and lead-tin-zinc,[2] where there are changes in the direction of slope of the ties. The critical point should obviously be the point of contact of the tangent to the curve drawn from this point of convergence.

The densities—measured by a small pyknometer—and the viscosities of the aqueous layers also pass through maxima, the values being much higher than for pure acetic acid at the same temperature; in the case of the toluene layers the densities and viscosities increase continuously as the layer ap-

[1] Woodman and Corbet: J. Chem. Soc., 127, 2461 (1925).
[2] Wright: Proc. Roy. Soc., 50, 372 (1892).

proaches in composition to that at the critical point:[1] It will be noticed that the properties and composition of the layers tend to become identical on approaching the critical point, as would be expected.

The ratio gram-moles (or grams) of acetic acid in a litre of aqueous phase to gram-moles (or grams) in a litre of toluene phase, continuously decreases as the total amount of acetic acid in the system increases. Little weight, however, can be attached to calculations of the partition coefficient in systems of this type by the method in vogue for partition of a solid between two immiscible liquids, because of the tendency of the two layers to approximate in composition as the relative amount of the consolute liquid is increased.

*School of Agriculture,*
*Cambridge,*
*England.*
*May 26, 1926.*

[1] In a few cases the densities and viscosities of the layers were not measured because of lack of liquid. The queried viscosities are, of course, very probably incorrect; but they are given for what they are worth, as they are possibly only 1 per cent. out at most; they were not repeated because of lack of the sample.

## NEW BOOKS

**Colloid Chemistry.** *Edited by Jerome Alexander. Vol. I. 23 × 16 cm; pp. 974. New York: Chemical Catalog Company, 1926. Price: $14.60* This is a miscellaneous collection of papers by miscellaneous authors. "Not only has no effort been made to select contributors whose ideas and opinions agree on all points; but, on the contrary, the proponents and exponents of diverse and even conflicting views have been asked to state their ideas freely and without reserve." This means interesting papers but considerable overlapping and relatively little co-ordination.

The papers and authors in this volume are: the submicroscopic structure of matter, Jerome Alexander; theory of the colloid state of matter, P. P. von Weimarn; the mesomorphic states of matter, G. Friedel; colloids as one-phase system, E. Buchner; the states of matter exemplified by a typical colloid—soap and the soap-boiling process, J. W. McBain; determination of size and mass of colloidal particles, E. F. Burton; measuring the electron and checking the kinetic theory by ultra-miscroscopic observations on minute droplets, R. A. Millikan; surface energy and surface tension, W. D. Harkins; cohesion and molecular forces, Sir William H. Bragg; surface tension of colloidal solutions and dimensions of certain organic molecules, P. Lecomte du Noüy; surface films as plastic solids, R. E. Wilson; molecular association, W. E. S. Turner; friction, surface energy, and lubrication, Sir William B. Hardy; the mechanism of coagulation, H. R. Kruyt; theory of the opalescence of homologous liquids and mixtures of liquids in the vicinity of the critical state, Albert Einstein; the scattering of light in one-phase systems, W. H. Martin; the effect of emulsoids on colored solutions, Hsien Wu and Daisy Yen Wu; aerosols, W. E. Gibbs; atmospheric nucleation, Carl Barus; colloid meteorology, W. J. Humphreys; colloidal water and ice, H. T. Barnes; astronomy, H. N. Russell; the planetesimal hypothesis, W. D. MacMillan; the thermal chemistry of colloids, F. L. Browne and J. H. Mathews; electric phenomena in colloid chemistry, Leonor Michaelis; the specific inductive capacity of substances in the colloidal state, Jacques Errera; the osmotic pressure of colloidal solutions, J. Duclaux; the effects of molecular dissymetry on some properties of matter, Irving Langmuir; physics, chemistry, and the colloidal state, W. Kopaccwski; adsorption and its significance, Herbert Freundlich; adsorption by precipitates, H. B. Weiser; some novel aspects of colloidal protection, Jerome Alexander; fibrous alumina, H. Wislicenus; the influence of colloids on the solubility of colloids, H. J. Creighton; solubility and size of particles, G. A. Hulett, attraction intensity and attraction pressure, J. Traube; quantitative investigations on the changes in strength of union with water exhibited by hydrates with crystallization water when their degree of dispersity is changed by mechanical means, Tokutaro Hagiwara; quantitative researches on dispersoid synthesis, Senji Utzino; difficultly soluble silver salts, their preparation and properties, A. Lottermoser; constitution of the dispersed micelle in platinum electrosols, A. de G. Rocosolano; pyrosols, Richard Lorenz; the adsorption of gases by metals, L. L. Bircumshaw; fluidity and plasticity, E. C. Bingham; consistency, W. H. Herschel; the viscosity of colloidal solutions, Emil Hatschek; the sol-gel transformation and the properties of jellies, S. C. Bradford; the problem of gel structure, D. J. Lloyd; diffusion in jellies, R. E. Liesegang; banded precipitates in porous media, S. C. Bradford; reactions in gels, H. N. Holmes; the crystallization of sulphur in rubber, H. A. Endres; ultramicroscopy, Max Poser; the immersion ultramicroscope, Richard Zsigmondy; ultrafiltration and electro-ultrafiltration, H. Bechhold; centrifugal and diffusion methods for the study of dispersity and hydration in sols, The Svedberg; subsidence in colloidal systems, E. E. Ayres, Jr.; sedimentation-analysis and its application to the physical chemistry of clays and precipitates, Sven Odén; the colloidal aspect of analytical chemistry, Henry Bassett; membrane filters and their uses, Richard Zsigmondy.

It is claimed by von Weimarn, p. 85, that crystals go through a colloidal stage of solution when they dissolve; but all he really shows is that a crystal may become very small just

before it is entirely dissolved, which is a very different matter. Buehner, p. 126, says that "the word phase is nowadays abused in colloid chemistry, and the impression is given that the notion phase might be of outstanding importance in this branch of science. I propose to show in this article that such is not the case, since it proves impossible to make out whether a colloid is composed of one or two phases: in fact, both conceptions are equally justified and no conclusive reasons have ever been given in favor of either of them."

McBain says, p. 139, that "soap jellies occur, which are perfectly transparent and which exactly resemble gelatine jellies, but in dilutions in which, through heating or addition of water or through supersaturation, curd fibers are completely absent. Such true jellies exhibit the high conductivity and osmotic activity characteristic of colloidal electrolytes. Like gelatine jellies they are not liquid crystals, but are isotropic and they do not give a radiograph. . . .

"Neat soap is the name given by the soap boiler to the upper liquid layer of concentrated soap which merely has to be cooled and cut into bars or stamped to serve as household or bar soap. . . . It of course alters in structure and physical characteristics on cooling, becoming soap and owing to crystallization of the least soluble soaps as curd fibers. . . . Neat soap is a liquid crystal, that is, a doubly refracting, plastic liquid. It is clear and transparent. Though often colored, no discontinuities are visible and a layer, in which the liquid crystal has the same orientation throughout, causes no distortion of objects seen through it. There are no particles or fibers to be seen in it, and the microscope shows that it is quite continuous so that the turbidity often exhibited when the specimen has been stirred, is seen by examination under crossed nicols to be caused by different orientation of the doubly refracting liquid in different portions of the same mass. In other words, neat soap is a single homogeneous phase of the same composition and structure throughout. This is in great contrast to the curd which the ultramicroscope and often even the naked eye shows to be a heterogeneous tangle of opaque white curd fibers enmeshing clear solution.

"Neat soap is plastic, in that small specimens do not flow under the influence of gravity, although large masses as in the soap pan have an almost level surface and flow readily through a pipe. At first sight neat soap might appear to be a jelly, but closer examination shows that it possesses very little of the elasticity characteristic of a jelly. For instance, a true soap jelly, which is likewise perfectly clear and tends to retain its shape, quivers when shaken, and a small piece if deformed springs back to its original shape, whereas the plastic anisotropic neat soap retains any shape given it. Furthermore, it may be mentioned that the true soap jellies, just like gelatine jellies, are isotropic or singly refracting when not under strain.

"When anhydrous soap is heated it first melts to form liquid crystals, and this anisotropic liquid exists for a further 100° of temperature before it 'melts' again to the clear isotropic liquid. Further, it can be admixed with water and even salt in various proportions without losing its homogeneity, and we can thus pass without discontinuity from the molten anhydrous soap to the soap boiler's neat soap and beyond. The whole of this form we therefore call neat soaps."

In a salt solution one problem is the thickness of the surface film which has a different concentration from the mass of the solution. Harkins decides, p. 242, that the films are approximately monomolecular. "In dilute solutions the water film apparently has the same thickness on solutions of lithium and sodium chlorides. In more concentrated solutions the thickness is smaller on lithium chloride solutions, but only because the activity of lithium is much greater. At least in dilute solutions the water film is thickest on calcium chloride solutions. The thickness of the water film decreases with the activity (effective concentration) and increases somewhat with an increase of charge on the ions provided the activity is not too different."

Harkins points out, p. 252, that the contact angle with glass is certainly zero for water, benzene, carbon tetrachloride, chloroform, ether, and ethylene disbromide, and that it is probably zero for most liquids.

According to R. E. Wilson, p. 277, "solutions which form plastic solid films give erroneously high values for their surface tensions by the du Noüy and presumably by other methods of measurement, because the yield value of the plastic solid film is added to the true reversible surface tension."

Hardy states, p. 299, that "water has a profoundly disturbing effect upon the lubricating properties of other substances. Its vapor will, for instance, almost wholly destroy the lubricating properties of an alcohol. On the other hand, water can be an excellent lubricant. It is such for ebonite, or for glass or steel when already covered with a film of a solid lubricant which does not dissolve in water. These apparently contrary properties were found to be reconcilable when the influence of water was followed in a number of cases. When water vapor is admitted to the chamber its influence on the friction of clean surfaces of glass, quartz, or steel is nil; but if the surfaces have already been lubricated by a primary film, water vapor *lowers friction if the lubricant is immiscible with water and raises friction if the contrary is true.* No exception to this simple rule was found.

"Up to a certain point the mode of action of the vapor is clear. Consider, as the simplest case, a surface coated with a primary film of a solid paraffin. Water vapor diminishes the friction of the surface of a block of solid paraffin,—the vapor condenses as an insensible primary film of water which has considerable lubricating power. . . . When, therefore, surfaces of glass or steel are coated with a layer of paraffin, water will reduce their friction even though the layer of paraffin be only a film of insensible thickness.

"We must, therefore, suppose that when water vapor condenses on to a primary film of paraffin on a solid, the value of $\mu$ is that given by *four* primary films, two median ones of water, two outer ones of paraffin, one on each solid face, and the conclusion reached is that four films lubricate better than two. This may be of the nature of a general law."

Price has suggested that "the destruction of Sodom and Gomorrah by a rain of brimstone and fire can be attributed to a charged mist of petroleum formed in the Caucasus by the outburst of an oil spring, and carried southward to the cities of the plain. There it reached the isoelectric point, flocculated, and was precipitated as rain and became ignited by lightning. Similar self-ignited oil-clouds are a familiar phenomenon in the Caucasus," p. 419.

"Probably the most interesting form of fog is the intense black fog which sometimes occurs during the very cold weather over the open surface of the St. Lawrence. Mists and winter fog are quite common over this river whenever the temperature goes below 11°F. The black fog occurs only at sub-zero temperatures and appears to be a heavy precipitation of semi-fluid globular particles which in their formation absorb completely the energy of the sunlight. It is preceded by a white fog, which, early in the morning may rise to heights of 1200 feet in long streamers. With the rising of the sun the white fog subsides and the color changes to a sulphur yellow like burning saw-dust, and then rapidly to deep opaque black at the bottom. This shuts out completely all view of the water, of objects on the surface, and of the opposite shore. In Fig. 2 I show a photograph taken last winter of one of the thickest black fogs ever known on the river. Fig. 2 was taken at 9 a. m. just after the sun had driven the fog down, and shows the black blanket over the entire water surface between the edges of the border ice fields.

"On rowing out into this fog the temperature was much higher than the surrounding air and the blanket felt quite warm to the face, proving what an effective protection this fog is to the loss of heat from the water. The white fog can be readily seen to consist of plates and minute particles which are deposited along the shore on the grass and trees and give rise to some very beautiful sights," (Barnes, p. 439).

Bradford states, p. 762, that "small additions of alcohol to warm one percent gelatine solutions, which are not saturated above about 26° or 27°, increase the large amounts of salt solutions required to salt out the gelatine. But, when more than a certain quantity of alcohol has been added, the solutions become opalescent and very small amounts of salts are sufficient to cause precipitation. The explanation is, probably, that the solubility of gelatine in water is first increased and then diminished by the addition of alcohol." It is probable that some important fact has been omitted in this statement.

Miss Lloyd calls attention, p. 775, to the fact that "some interesting work is reported by Callow (1925) on the velocity of ice crystallization through gelatine gels supercooled to —3°. In such gels seeded with an ice crystal, the ice face advances slowly through the gel along definite tracks, at a rate depending on the concentration of the gelatine and of any electrolytes present. If such a frozen gel is thawed, recooled, and again seeded with the crystal, separation of ice now takes place at an enormous rate, apparently along the tracks previously made. These facts suggest that the first separation of ice had irreversibly ruptured some rigid structure in the gel."

Liesegang points out that the presence of a jelly may change the apparent course of a reaction, p. 786. "When an acid acts upon a mixture of powdered calcium carbonate and calcium phosphate, calcium carbonate is dissolved preferentially. The residue therefore contains relatively more calcium phosphate. For this reason Levy declared the acid theory of rachitis and osteomalacia to be erroneous, because, on analyzing these pathological bones, he found the usual proportion between calcium carbonate and calcium phosphate, *i. e.*, no relative enrichment of the latter. But when both substances are distributed in a jelly, they are *both* dissolved by an inwardly diffusing acid as far as it intrudes. On the other side of this limit the previous proportions remain unchanged. Thus the progress of the reaction is essentially changed, and the objection of Levy against the acid theory is without foundation, though it was so acceptable to orthodox chemists, that for many years one hardly dared to advance a theory of these diseases."

Liesegang offers no explanation of this and apparently considers it a peculiarity of a jelly. What it probably means is that the acid, when diffusing in, dissolves the calcium carbonate preferentially but then dissolves the calcium phosphate because there is no more calcium carbonate at that point. It is a case of a localized excess of acid. If this is right, one should get the same results by packing a mixture of calcium phosphate and carbonate into a narrow glass tube, filling the glass tube with water, and allowing acid to diffuse in from the bottom. This would give the same physical conditions without any jelly material.

Some interesting facts are given in Bassett's article on "The Colloidal Aspect of Analytical Chemistry." "Some interchange between adsorbed material and material in solution will always occur. The tendency will always be for an ion which is readily adsorbed to replace one which is less strongly adsorbed. The following case, due to Charriov, is of some analytical interest. Alumina precipitated by ammonia from a solution containing chromate is yellow owing to adsorbed chromate which cannot be removed by prolonged washing with boiling water, or with water containing ammonium nitrate, chloride, or acetate. When, however, the alumina is precipitated with ammonium carbonate, instead of hydroxide, or if it is precipitated with the latter and subsequently washed with a five percent solution of ammonium carbonate, it is obtained quite white and free from chromate. Carbonate ion has displaced chromate ion," p. 920.

"The difficulty caused by marked adsorption of a readily adsorbed ion can sometimes be overcome by a modification of the adsorbent. Thus, if phosphoric acid has to be determined after separation of tin, a low result is obtained if the tin is removed as stannic sulphide owing to marked adsorption by the latter. Stannous sulphide, however, does not adsorb phosphoric acid appreciably, so that if the tin is reduced by means of zinc and removed by stannous sulphide estimation of phosphoric acid in the filtrate gives correct results. According to Anger and Odinot stannic sulphide carries down cobalt and nickel from a hydrochloric acid solution whereas stannous sulphide does not," p. 921.

"Effects due to the colloid character of the filter paper (or indeed of other filtering materials) are sometimes not properly appreciated. The filter paper fibers are negative colloids, and when a precipitate which has resulted from the coagulation of a positive colloid is filtered through the paper, a sort of double decomposition occurs with attachment of the particles of the positive colloid to the negative filter paper. If the individual particles are sufficiently small this occurs in the pores of the paper, completely blocking them up and making filtration extremely slow. This sort of thing happens with aluminium hydroxide as usually precipitated, and with zinc sulphide when precipitated from alkaline solution and indeed is liable to happen with any similar positive colloid.

"Owing to their large surface, and their colloid character, the fibers readily adsorb dissolved substances from solution and also water. This adsorption is perhaps mainly due to the simple surface action, but it is partly of the more profound kind which occurs when a sol is neutralized by an electrolyte. It follows that a filter paper may not only remove soluble constituents from a solution being passed through it, but it may be extremely difficult to wash these out again. Errors can obviously be caused in this way. The weight of precipitate obtained after drying or ignition may be too great, while values found for constituents subsequently estimated in the filtrate may be too low. In extreme cases traces of substances may be entirely removed from solution by filter papers and so escape detection, though in suitable cases their removal by such means may be made the basis of a method for separating and estimating them. In cases where filter papers are used which are not of the ashless variety, disturbances may be caused by replacement of the inorganic constituents of the paper, which are probably present in the adsorbed condition, by other substances, derived from the solution being filtered. The correction subsequently applied for the ash of the filter may then be wide of the mark," p. 923.

"The adsorption effects noticed with ordinary impure adsorbents are frequently complicated by the impurities present. Thus with ordinary charcoal the ash constituents play an important role. The same also applied to filter paper. According to Kolthoff the adsorption of acid by filter paper is almost entirely determined by the ash and due to chemical interaction between the acid and the mineral matter. Ash free paper or cotton wool hardly adsorb any acid. Indeed from the experiments of Masters the tendency seems to be for it to adsorb the base from neutral salts and leave the acid.

"In a somewhat similar way the adsorption effects observed with glass wool seem to be largely determined by the alkaline character of this material. Asbestos which has been carefully purified by treatment with acid practically does not adsorb positive ions whereas ordinary impure asbestos does and cannot safely be used as a filtering medium," p. 925.

"Scheringa found that ferric hydroxide always carried down zinc when precipitated by caustic soda—even if the zinc salt be added after the caustic soda. Precipitation with cold 25 percent ammonia solution gave a complete separation, however, if ammonia of the same strength was used to wash the precipitate.

"The well-known fact that many hydroxide precipitates gradually become less reactive, and less readily soluble in acids, may well be due in part to some such process as that outlined for copper hydroxide, though not proceeding to such a degree of dehydration as in that case. There seems little doubt at any rate that it is connected with some loss of water either from the sol particles or from the gel.

"A similar change seems to be the cause of the instability of the solutions of many hydroxides (*e. g.*, that of aluminium) in caustic soda, or in ammonia (*e. g.*, chromium hydroxide) or even in acids (*e. g.*, the slow hydrolysis of ferric chloride solutions) although the type of crystalloidal compound initially present in the solution is quite different in the three cases. If the concentration and proportion of caustic alkali, ammonia or acid are not excessive, the metallic hydroxide molecules formed by hydrolysis gradually unite to form highly disperse sol particles which in time coalesce, undergo some dehydration, and ultimately separate in a relatively dense and unreactive condition. According to Fricke and Windhausen no dehydration occurs but only an increase in the size of particles when chromium hydroxide separates from caustic potash solutions," p. 929.

"The sulphides of analytical Groups II and IV present several features which recall those found among hydroxide precipitates. They are so insoluble that their precipitation is essentially a colloidal process and they adsorb large quantities of water. This tends to result in bulky gels built up of aggregates of very small particles. The water content of the precipitates is variable and loosely held, which accounts for the difference in views as to whether they are hydrated sulphides or hydrosulphides or even partly hydroxides and hydrosulphides. Possibly all these compounds may be present in different cases and under different circumstances. The tendency to lose water—and perhaps $H_2S$ too—seems to be even more marked among the sulphides than among the hydroxides, and with this is connected the remarkable difficulty with which the sulphides of cobalt, nickel and, to a less

extent, zinc and other metals dissolve in acids although very little acid will prevent their formation in the first instance. Amphoteric neutralization similar to that discussed in the case of the hydroxides may well take place with the sulphides too and be partly responsible for the readiness with which some of the Group II sulphides, notably that of copper, carry down from acid solution sulphides of Group IV metals such as zinc," p. 931.

"The blue starch-iodine complex is an example of the use of colored adsorption products as indicators of the end point in titration. "Other interesting examples have been described by Fajans and Hassel, who found that silver halide sols cause characteristic color changes in very weak solutions of the alkali slats of fluorescein and its halogen substitution products when excess of silver ion is present. So long as halogen ions are present in the solution particles of silver halides tend to be negatively charged owing to adsorption of halogen ions. When more silver ion has been added than is required to combine with all the halogen ion, reversal of sign of the silver halide particles occurs owing to adsorption of silver ion. The positive sol particles so formed then adsorb the dye anion. This causes a color change, which under appropriate conditions may be sharp enough to show correctly the end point of the titration. Chlorides can be so titrated in presence of fluorescein, the concentration of which should be about 1/300000 molar. A reddish color shows the end point in this case. 1/30000 molareosin can serve as an indicator in the titration of iodides, the end point being shown by the appearance of a violet color. In a mixture of iodide and chloride, titration in presence of eosin will give the iodide alone, while the sum of the two halogen ions can be obtained with fluorescein as indicator," p. 935.

The book contains an enormous amount of very interesting material and a painfully large number of almost worthless articles. It will be of value to the advanced student. It is of interest to everybody as a literary document, as showing, for instance, that there still are people who consider colloidal solutions as one-phase systems. The editor has appended a number of foot-notes of his own. These are not helpful and should be omitted in the volumes to come.

*Wilder D. Bancroft*

**The Fats.** *By J. B. Leathes and H. S. Raper. Second edition. 25 × 16 cm; pp. vii+242. London and New York: Longmans, Green and Co., 1925. Price: $4.50.* The chapters are entitled: the substances that enter into the composition of fats; extraction and estimation of fat; determination of the character and properties of fats; the origin and occurrence of fats in nature; the digestion and absorption of fats; the fat in the blood during absorption of fat; the discharge of reserve fat into the blood; the transfer of fat from the blood to organs; the oxidation of fat; the part played by fats in the life of the cell.

"There is a large group of substances widely distributed through the animal and vegetable kingdoms which have one property in common, that they contain in their chemical constitution and are mainly composed of the radicals of fatty acids, principally and generally only the higher ones. These compounds with but few well-attested exceptions form a group by themselves that does not overlap the borders of the other groups of substances, the proteins and carbohydrates, which together with them constitute the material in which the phenomena of life are manifested. They are at least as sharply defined a group as either of these, and they hardly can be said to have less physiological significance. And yet there is no one comprehensive name to include them all. The term fat has a precisely defined chemical meaning which restricts its application to a certain number only of the substances of this group, and yet many of these substances that are in the strict chemical sense fats have on account of their physical properties to be spoken of as oils, while some are generally known as waxes: of the compounds, on the other hand, that are not in the strict sense fats, some have had assigned to them the term 'wax,' a term for which also a chemical definition has been devised that does not correspond to the ordinary meaning of the word, while for a large class, the physiological importance of which is daily coming more into evidence, no better general name has been proposed than 'lipoids,' which is at once a cloak for ignorance and an indefinable limbo into which any one can thrust anything of which he knows little or nothing, including often what is not a compound of any fatty acid at all," p. 1.

The hydrolytic dissociation of soaps is prevented by the addition of alcohols. "Hence the rule that in titrating fatty acids with aqueous alkalies, alcohol should always be present at the end of the titration in a concentration of about fifty percent," p. 10.

"The glycerides of fatty acids occur in animals stored in the connective tissue cells of adipose tissue which is found principally in the subcutaneous tissue, the bone marrow, beneath certain parts of the peritoneal, pericardial and pleural serous membranes, and in the interstitial tissue of the voluntary muscules. In this adipose tissue fat the glycerides are as a rule to a small extent esters of stearic, to a larger extent of palmitic, and most of all of oleic acid. In certain animals the glycerides of other fatty acids occur. In lard the liquid fatty acids have properties (iodine value, *vide infra*) which indicate that ten percent of the acids entering into the composition of this fat are of the linoleic series (Twitchell). In the fat of the horse and the hare there is similar evidence for the presence of glycerides of other acids. It is further remarkable that, in certain species, the fat of animals kept in captivity differs from that of those living wild. The evidence that points to the presence of linoleic acid esters in the fat of the domesticated pig points to there being more of such esters in the fat of the wild boar. And the same difference is particularly well marked in the rabbit (iodine value of fatty acids from tame rabbit 64, from wild rabbit 101), and the duck (iodine value of fat of tame duck 58, of wild duck 85).

"On the other hand, this difference does not appear to hold for the cat, and the character of the fat of the chamois and deer living in freedom (iodine value 25 to 30) does not justify generalisations from the facts mentioned," p. 37.

"The changes undergone by fats and oils when they become rancid are probably initiated or favoured by enzymes and hydrolyse the glycerides. The free fatty acids are then oxidised by the oxygen of the air in the presence of traces of moisture. But the part played by enzymes and also by the action of light is a subject of some dispute. The changes consist in (1) the appearance of hydroxyl acids and (2) of lower volatile fatty acids, their esters or aldehydes; (3) the hydrolysis of the fat; and (4) the disappearance of the liberated glycerol.

"The more saturated acids the fat contains, the less liable is it to become rancid; cacao butter, for instance, is rarely found to undergo this change. The presence in a fat of other substances on which bacteria can grow increases the probability of rancidity; butter, for instance, is particularly prone to the change. But a sterile fat may nevertheless become rancid; and as Duclaux showed, the growth of bacteria in an impure fat, though it may promote a tendency to rancidity, is not the cause of the change. The taste of rancid fat is probably due to the formation of oenanthal and pelargonal from palmitoleic and oleic acids," p. 43.

"The formation of fat being a process of fundamental importance to animals and plants, it does not seem unlikely that the process in its essentials may be the same in both. This proof of the rôle of carbohydrates in the animal process strengthens, therefore, the less direct results which have been obtained with plants, which, it may be recalled, also indicate that, in the vegetable kindgom, carbohydrates form the starting point in the synthesis of fats.

"The carbohydrates and fats differ so widely in their chemical characters and composition that it is unlikely that the whole of the processes of transformation of the former into the latter would be easily demonstrated experimentally. It is not surprising, therefore, that direct evidence of a transformation of carbohydrate into fat has so far not been obtained in any isolated organ. Leathes and Hildesheim (1904 and 1908), however, have shown definitely that the liver participates in the process and certainly in its later stages," p. 168.

"Before passing to the discussion of the origin of glycerol one other matter awaits consideration, namely, the possible formation of fat from amino acids. Since certain of the naturally occurring amino acids have been shown to be capable of transformation into glucose in diabetic animals, it is reasonable to suppose that they may also be converted into fatty acids because glucose is capable of this change. Nevertheless, as indicated earlier in this chapter, protein, which is built up from amino-acids, has, so far, not been proved to give rise to fat formation in the body. The reason is probably to seek in two directions.

Firstly, only a certain number of the amino acids present in the protein molecule have been shown to be convertible into glucose, and then not always quantitatively; only three out of the five carbon atoms of glutamic acid, for instance, are so converted. Thus only a portion of the protein taken as food could be made into carbohydrate, and become available for fat formation even when all the conditions were favourable for this change. Secondly, the 'balance sheet' method has its limitations. Animals will not endure unlimited amounts of protein, and the quantities which would be required to provide for the claims of growth, the liberation of energy, and an excess from which the formation of fat would be awaited, are sufficient to upset the ordinary processes of nutrition, and so thwart the experiment. There is every reason to believe on chemical grounds that fat may be formed from certain of the amino acids, namely, those which give rise to glucose formation in diabetic animals, but the biological is beset with experimental difficulties," p. 116.

"When animals or plants store carbohydrates as a reserve they are laid down as glycogen or starch respectively. Only these two substances are made use of. Glycogen prepared from different animal tissues and from different species of animals is always the same substance so far as chemical investigation has shown. The same is true of starch. It is remarkable, therefore, that when fats are stored in the plant or animal, not one substance only, but a great variety of substances is found. This variety is due to differences in structure of the three fatty acid molecules, which are united to glycerol to form the naturally occurring triglycerides. The greatest variation is caused by differences in the degree of saturation of the constituent fatty acids, but differences in their molecular weight, due to the number of carbon atoms, is also a contributing factor. In a few instances, also, the fatty acids may contain hydroxyl groups. This diversity of composition gives rise to corresponding variations in physical properties, such as viscosity, solidifying and melting point. There is reason to believe that all the fats found in nature are fluid at the temperature at which they are normally formed in the animal or plant. The fats found in cold-blooded animals, or in plants growing in temperate or cold climates, are therefore always unsaturated to a considerable extent, since the unsaturated acids form triglycerides with low melting points. On the other hand, the saturated fats occurring in nature are only found to any marked extent in warm-blooded animals or in tropical plants, since the presence of saturated fatty acids, especially those containing 16 or 18 carbon atoms, gives rise to fats which are solid at the ordinary temperature. In the case of animals these differences are probably largely conditioned by the nature of the fat present in their food, but with plants they must be ascribed to variations in the synthetic processes by which the fats are produced," p. 118.

"The fact that during fat absorption, staining methods fail to reveal the presence of fat in the epithelial cell border does not necessarily mean that fat is not present there. Ample evidence is available to prove that fat may be present in cells in considerable amount and yet be unstainable, possibly because of its high degree of dispersion in the protoplasm (Fischer and Hooker, 1916). In almost any cellular tissue, liver, for example, the usual fat-staining methods may fail to show the presence of fat and yet chemical analysis will reveal a considerable amount. Similarly, a solution of oleic acid in egg albumin can be prepared which will not stain with osmic acid. Histological evidence does not help much therefore in a discussion as to the mode of fat absorption," p. 129.

"It is of interest to inquire why fat must be hydrolysed prior to absorption and then resynthesised again when it has passed into the epithelial cells of the mucosa. It is obvious that this would prevent the absorption of substances such as petroleum, which are like fats, but unsatisfactory for supplying the body's need of energy, and are, therefore, rejected. This may be the only reason, but it is possible that fat may undergo some modification during absorption, so that the fatty acids resulting from the hydrolysis of the fat in the food are recombined into glycerides, but not exactly in the same way, so that a fat different from that in the food results. There is some evidence that this takes place, and this may, therefore, be a second reason why hydrolysis must precede absorption," p. 132.

"Fats absorbed from the intestine by lacteals is conveyed by the thoracic duct to veins at the base of the neck, and, therefore, like that portion whatever it may amount to which enters the blood capillaries directly, is conveyed by the blood to the various organs. The

difference between the two routes means that fat absorbed by the blood will go through the liver before it reaches other tissues, and that which goes by the thoracic duct will be distributed equally to all parts. The readiness with which the liver in certain circumstances takes up fat may make the lacteal route advantageous when fat is to be laid by in adipose tissue," p. 143.

"The way in which the reserve of fat is put into circulation and conveyed to the organs where its energy is to be liberated is very little understood. From the consideration of the facts mentioned, a starving man must be able to draw on fat stored in his adipose tissue to the extent of something like 200 grms. a day, or perhaps 200 mgrms. a minute during the waking hours. His blood, or the blood of normal men (Bloor's average from twelve) contains the amount of fatty acids corresponding to 200 mgrms. of fat in almost exactly 5c c.c. or perhaps one-hundredth part of the whole circulating blood. In one minute therefore the transport of fat in such conditions, when by hypothesis 90 percent of the energy is derived from fat mobilised from adipose tissue, represents a turnover of something like one percent of the total amount of fatty acid present in one form or another in the whole blood. It is necessary to visualise this, because otherwise there is a temptation to think that it should be very easy to demonstrate any extensive physiological mobilisation of reserve fat by analysis of the amount of fat in a sample of blood taken from any accessible vein. The temptation may be escaped, moreover, also by the reflection that a physiological mobilisation of fat is presumably brought about by some reaction due or corresponding to the avidity of working cells for fat—the faster the fat is thrown into the blood, the faster it will be removed by hungry cells. If the adjustment is delicate it would be logical to expect the amount of fat in the mixed blood to be unchanged; if it is not, then at some moments the amount of fat must be above, but at others below the normal value, and there is nothing to indicate how the desired figures are to be obtained. It is indeed remarkable how often they have been," p. 154.

"Animals use fat primarily as a source of energy. This does not mean that fat is only of importance to the animal as a source of energy, for, as pointed out in the following chapter, fatty acids in one form of combination or another are indispensable constituents of animals and when the quantity in the body is reduced by inanition below a certain minimal figure, death ensues. It is, however, true to state that the greater part of the fat which is taken daily as food is utilised for the liberation of energy as heat and work. Were this fat simply stored, animals would gain in weight very rapidly and in a short space of time resemble bladders of lard. This self-evident truth, that the bulk of the fat taken by an animal is oxidised and not stored up is supported by evidence gained from a study of the gaseous exchange on different diets," p. 175.

"André Mayer and his fellow-workers then have done much to substantiate the conception of cell protoplasm that Hoppe Seyler, and Hermann, indicated many years ago. Protoplasm is not merely an old word for a solution of proteins; nor are the phenomena of life manifested merely in a colloidal solution of proteins in which certain electrolytes and certain reserve food-stuffs play merely subsiduary parts. Protoplasm is a complex equilibrated system in which, side by side, with colloidal solutions of proteins, fatty components together with cholesterol, though quantitatively less in amount, play a rôle which it is impossible to say is less essential than theirs.

"André Mayer, moreover, thinks that this system has for each type of cell a composition characteristic for that type, and that the proportion in which the components occur in the protoplasm determines its behaviour. His estimations of water, total solids, total fatty acids, phosphorus associated with fatty acids and cholesterol in the different organs, are an attempt to define the characteristics of the protoplasm of these organs. If only he could include determinations of the amino acid groupings in their proteins, their chemical pattern and molecular structure, his attempt would bring us nearer the truth; but, with these, he is, in these studies, not concerned. The relation which he finds, however, between the 'lipocytic coefficient,' and the amount of water held by the living cells of each organ, is an interesting illustration of his thesis. The lipocytic coefficient, the proportion that is between cholesterol and fatty acids, is higher in the corpuscles than in the serum, in the serum

than in the lung, and, after the lung has decreasing values in the kidney, the liver and the muscles (Terroine and Weill, 1913). He finds that the amount of water held by these tissues in proportion to their solids, and also the amount of water they take up when immersed in pure water, varies inversely with the amount of fatty acids, and directly with the amount of cholesterol they contain. In the muscles, which contain a variable amount of reserve fat that is not built up into the protoplasmic fabric, differing in this respect from the other organs, the amount of water taken up varies directly with the cholesterol, and inversely with the amount of phosphorus associated with fatty acids. When the proportion of cholesterol to fatty acid changes in starvation, the amount of water taken up by the tissue changes in the same sense. The red blood corpuscles of different species are haemolysed by different degrees of dilution of the serum. Those most sensitive to lowered osmotic pressure are those that have the highest lipocytic coefficient, that contain less fatty acids, or more cholesterol, those, that is, that imbibe water most rapidly. The assumption of water by a protoplasmic system is always, according to Mayer's generalisation, limited by its fatty component, and the limiting action of this is checked and counteracted by the cholesterol associated with it," p. 204.

"A unicellular organism that floats in water retains its contents, products of the digestion of its food, salts and others, from diffusing into the surrounding water. A red blood corpuscle retains its haemoglobin and allows none of it to escape in the plasma, in which this substance is easily soluble; it also retains certain salts in very different concentrations from those in which they occur in the plasma. If the plasma is diluted so as to alter the molecular concentration outside the corpuscle, water passes into the latter, but its contents do not pass out until so much water has passed in that the corpuscle appears to burst like an overdistended sac and its contents escape. Both these types of cell we say are bounded by a membrane which is impermeable to substances contained in the cell. But it is not impermeable to all substances alike; for if the plasma be diluted not with water but with a solution of urea or of ammonium chloride isotonic with the plasma, although there is no difference of osmotic pressure set up on the two sides of the surface of the corpuscle the urea and ammonium chloride, unlike sodium chloride, can pass into the corpuscle and will tend to attain the same concentration within it as without; but in doing so, in order to preserve osmotic equilibrium, they will be accompanied by water, so that the result is the same in the end as if the plasma had been diluted with pure water. We have, therefore, to say that the membrane bounding the corpuscle is specifically permeable to some and specifically impermeable to other molecules or ions. Moreover, there is evidence that these properties in many types of cells are subject to variation; on excitation, under the action of anaesthetics or of certain disturbances of a balanced proportion of oppositely endowed ions, Ca and Na, for instance, changes in the permeability of the surface layer may momentarily, or it may be lastingly, take place. The high resistance to the passage of electric currents exhibited by the corpuscles or by tissues composed of living cells, although these cells contain electrolytes, is another illustration of the restrictions imposed, in the resting condition of the cells, on the movements of ions within them.

"Such phenomena imply retaining membranes composed of some material which is not dispersed in the liquid protoplasm but invests it in a coherent continuous layer; the membrane cannot be seen, it must be a mere surface film, but penetrable by water though not by the substances found in the protoplasm," p. 207.

*Wilder D. Bancroft*

# ON THE REACTION MECHANISM OF THE CATALYTIC OXIDATION OF AMMONIA

BY SHUN-ICHI UCHIDA

## 1. Introduction

If we pass a stream of ammonia-air mixture of definite composition through a thin layer of catalyst, (platinum, mixed oxides of iron and bismuth, etc.), kept at a constant temperature, with various velocities, and plot the yield of nitric oxide against the "time of contact" as abscissa, we obtain a maximum yield corresponding to a definite "time of contact." This occurrence of a maximum is of considerable interest from the standpoint of chemical kinetics. Its usual explanation is that nitric oxide is itself a highly unstable compound, and if we allow the reacting gases to remain in contact with catalyst too long, the system will go to the most stable one of nitrogen and water, while for a too short contact, the ammonia will not have time to react with oxygen, and between these two extremes we must obtain an optimum yield of nitric oxide. But, the exact nature of reactions with which the system passes over to the stable system is altogether unsettled. Some writers give

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O, \qquad (1)$$

although we are not inclined to think such a direct leap of the initial system to the most stable is actually taking place side by side with

$$4NH_3 + 5O_2 = 4NO + 6H_2O \qquad (2)$$

and, moreover, the two reactions, (1) and (2), occurring simultaneously, can never give a maximum in the yield of nitric oxide.

The most plausible explanation is to assume the decomposition of the nitric oxide once formed. This can be effected by one of the following two alternative reactions i. e.,

$$4NH_3 + 6NO = 5N_2 + 6H_2O \qquad (3)$$

and

$$2NO = N_2 + O_2. \qquad (4)$$

According to the experiments of the present writer (unpublished) as well as those of Baxter and Hickey[1] the reaction (3) is a very slow one even in the presence of catalysts and, besides, if we assume that the activities of catalysts are definite and constant for each of (2) and (3), their combined effect also cannot give rise to a maximum.

The only possible alternative which can explain the existence of a maximum in the NO-yield is to consider the reaction to be a consecutive one consisting of the following two reactions:

(2) $4NH_3 + 5O_2 = 4NO + 6H_2O,$

(4) $2NO = N_2 + O_2.$

and (4) $2NO = N_2 + O_2.$

[1] G. P. Baxter and C. H. Hickey: J. Am. Chem. Soc., 27, 300 (1905).

As to the latter reaction, (4), some explanation seems necessary. Most of the writers on this subject overlook this reaction simply because its reaction velocity was slow, and the work of K. Jellinek is invariably cited. But the only existing determinations of this reaction velocity by this author[1] were for homogeneous gas phase and cannot be applied in the present case. Jellinek himself failed to obtain a homogeneous decomposition when he used platinum reaction vessels, particularly at lower temperatures, for even at 689°C platinum acted as an eminent catalyst for NO decomposition. Rideal[2] and Scott[3] pointed out this reaction as one of the possible causes of nitrogen loss in the oxidation of ammonia, but their accounts in this respect are only qualitative and insufficient.

In the course of the study on ammonia oxidation catalysts the present writer has constructed quite a reliable apparatus which enabled him to get some insight into the reaction mechanism.

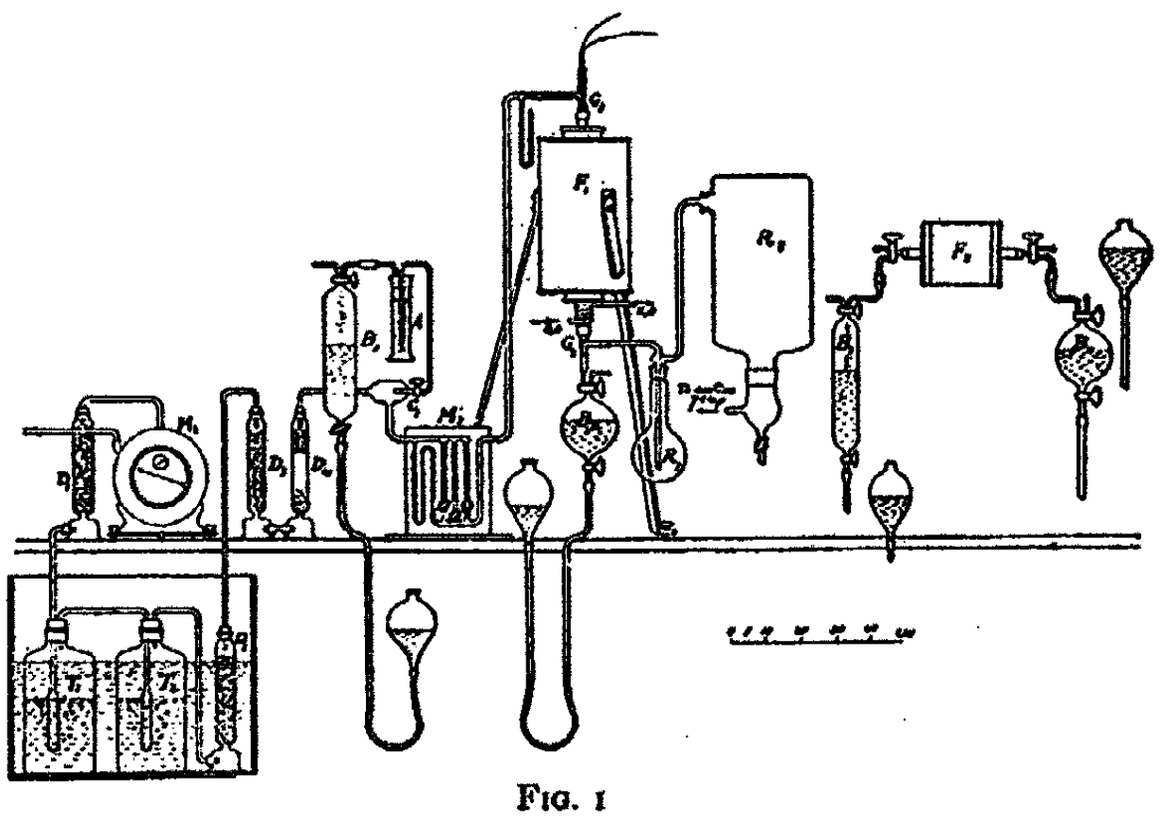


FIG. 1

## 2. Description of the Apparatus and the Method of Calculation

By means of a suction pump at the end of the train, (Fig. 1), air is drawn in through a gasmeter, $M_1$, and an ammonia solution of proper strength kept in a thermostat, and is then dried by caustic soda and soda lime, ($D_3$ and $D_4$). The velocity of flow is measured by a capillary flowmeter, $M_2$. A porcelain tube placed in an electric resistance furnace, $F_1$, is glazed inside and outside, and contains a layer of double sheets of platinum gauze, or about 1.5 cc of granular catalyst as the case may be, at about two thirds from the top. A small part of the mixed gases is taken in through A (containing 0.2N $H_2SO_4$) into $B_1$ where the volume of air is read off, and, together with the titration value of the contents in A, the ammonia percentage is calculated. $B_2$ is a

[1] K. Jellinek: Z. anorg. Chem., 49, 249 (1906).
[2] E. K. Rideal: J. Royal Soc. Arts, 69, 638 (1921).
[3] W. W. Scott: Ind. Eng. Chem., 16, 81 (1924).

sampling flask of about 2000 cc capacity, which is at first filled with water, and, lowering the levelling bottle, the sample gas is taken in slowly. The sampling device, $G_2$, consists of two concentric tubes, the outer one serves to conduct the main part of the oxidized gases to the pump through pressure reservoirs, $R_1$ and $R_2$, and the inner tube, which is about 2 mm in diameter, reaches about 10 cm inside the furnace so as to draw the sample before condensation has taken place. When enough gas is taken, which amounts usually to 800 to 1200 cc, $B_2$ is detached from $G_2$ and is shaken violently for about five minutes so as to absorb all of the nitric oxide as nitric acid, which is titrated afterwards with 0.2N NaOH with sodium alizarin sulphonate as indicator. The residual gas consists of a large amount of nitrogen and a small amount of oxygen. The latter is absorbed by heated copper in a furnace, $F_2$, and the free nitrogen gas is read off.

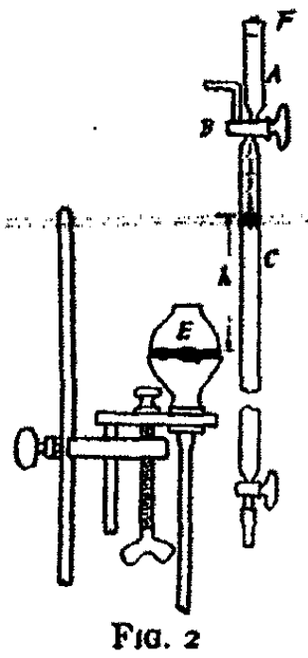


FIG. 2

In order to calculate the yield of nitric oxide, a preliminary value has been calculated under the assumption that the whole of the residual nitrogen gas comes from air. The true value of yield has been obtained by adding to the preliminary value a correction term, which takes into account the elementary nitrogen due to the unfruitful decomposition of ammonia. This correction term is calculated from the ammonia percentage and the preliminary value.

### 3. Catalysis and the Time of Contact

One of the most important requirements in connection with the experimentation is that the catalysts must be constant in their activity throughout the whole series of experiments. In this respect, both of the two kinds of catalysts here used were quite satisfactory. One of them was the mixed oxides of iron and bismuth (3.8% $Bi_2O_3$) with the grain size of 1.5 to 2.0 mm, prepared by precipitating with ammonia from a dilute mixed solution of nitrates and by drying in an electric oven below 120°C; and the other was double sheets of platinum gauze made of wire of 0.065 to 0.070 mm in diameter and had 1369 meshes per square centimeter.

The "time of contact" is here expressed as the number obtained by dividing the free space of catalyst layer by the velocity in volume of the mixed gases per second reduced to 0°C and 760 mm. With the platinum catalyst the free space is readily obtained from the diameter of wire and the weight of the gauze per square centimeter. In the case of oxide catalyst, the ratio, $\alpha$, of the free space to the apparent volume of the catalyst, that is, catalyst volume plus free space, has been determined, from which the corresponding free space of the catalyst layer is calculated.

Fig. 2 represents a rough sketch of the apparatus used for the determination of free space ratio. The diameter of the part A is the same as that of the porcelain tube used and the total volume of this part is about 10 cc. It has a well ground stopper, F. The burette, C, has a capacity of 30 cc with 0.1 cc graduations. To determine $\alpha$, A is filled at first with the granular catalyst

to be used, and the pressure inside A is made equal to the atmospheric pressure by adjusting the three way cock, B. Then, C is connected with A and the mercury reservoir E is lowered so as to set up a certain reduced pressure h, and the expanded volume of A into C is read. The similar procedure is repeated with vacant A and we get v with the same pressure difference h. $\alpha$ can easily be shown to be represented by

$$\alpha = v'/v,$$

where v′ is the volume expansion with catalyst. Due care must be taken against adsorption phenomena, but, using air, the above catalyst gave very concordant results with various values of h at room temperature. The number, 0.70, was obtained as the mean.

### 4. Experiments with Platinum Gauze

Platinum gauze acted very constantly as is often reported by various writers. Table I shows the results obtained. The temperature was measured at the upper surface of the gauze, with which the tip of the porcelain protection tube of the thermocouple was brought in contact.

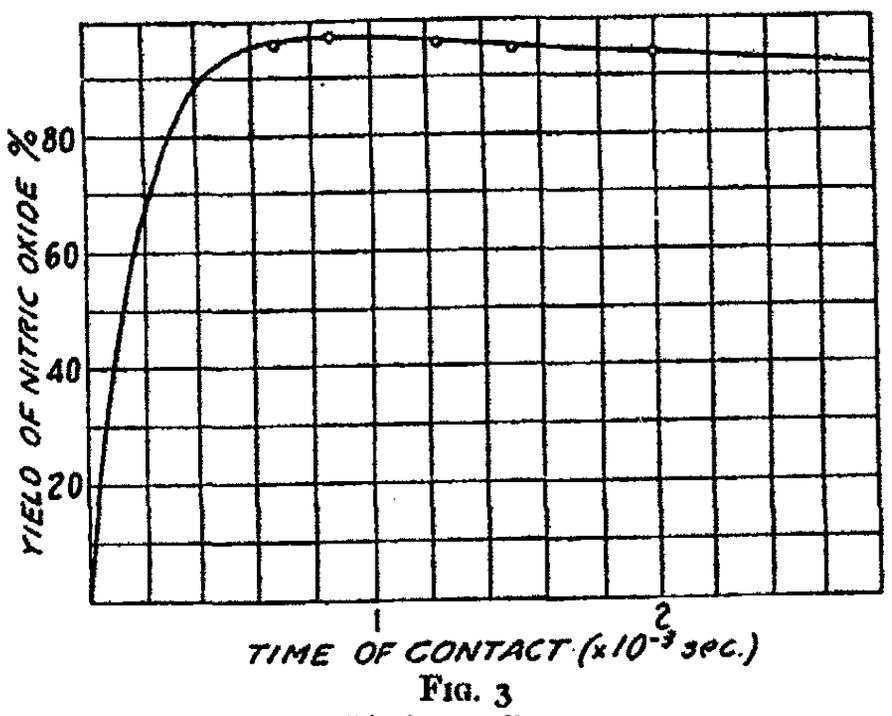



Fig. 3
Platinum Gauze

Owing to the high gas velocity, the heat of reaction liberated at the platinum surface was enormous and made the temperature measurement very difficult. The first column shows the ammonia concentration obtained by titration. The second column shows the volume of the mixed gases that have passed the catalyst in one minute at 0°C and 760 mm mercury. The next column gives the gas velocity in terms of time of contact in sec. The fourth column gives the yield of NO, and the means are given in the next column. Every group of determinations was obtained with renewal of the porcelain tube and the glass sampling device, because, if the same ones were used too long, the rates of oxidation began to fall off gradually and at the same time small quantities of metallic sublimates were observed on the hot end of the sampling tube and the lower inside of the porcelain tube. These sublimates were difficult of solution in aqua regia, and most probably they are platinum.

TABLE I (Fig. 3)
Temperature: 581 ± 4°C

| $NH_3$ conc. (%) | Vel. of mixed gases per min. cc 0° 760 mm. | Time of cont. sec. | Rate of oxidat. (%) | |
|---|---|---|---|---|
| 8.87 | 1200 | 0.00200 | 93.1 | |
| 8.95 | " | " | 95.0 | 94.3 |
| 8.82 | " | " | 94.9 | |
| 8.68 | 1620 | 0.00150 | 95.3 | |
| 8.64 | " | " | 95.0 | 95.2 |
| 8.57 | 1950 | 0.00124 | 96.7 | |
| 8.53 | " | " | 96.6 | 96.4 |
| 8.57 | " | " | 95.9 | |
| 9.03 | 2800 | 0.00087 | 97.2 | |
| 9.09 | " | " | 97.3 | 97.3 |
| 8.82 | 3590 | 0.00068 | 96.3 | * |
| 8.87 | " | " | 95.9 | 96.1 |
| 8.70 | " | " | 96.1 | |

*In the last three a trace of unoxidized ammonia was detected.

## 5. Experiments with Fe-Bi Catalyst

This catalyst, also, acted very constantly after it had passed a period of amelioration as Table II shows:

TABLE II
Time of contact: 0.041 sec., Temp.: 590°C

| Time from beginning hour | min. | Amm. conc. % | NO-Yield % | Time from beginning hour | min. | Amm. conc. % | NO-Yield % |
|---|---|---|---|---|---|---|---|
| 6 | 56 | 8.76 | 96.9 | 38 | 9 | 8.53 | 95.5 |
| 8 | 6 | 8.83 | 94.6 | 40 | 44 | 8.48 | 95.2 |
| 9 | 0 | 8.81 | 95.2 | 42 | 32 | 8.39 | 95.1 |
| 11 | 37 | 8.68 | 96.1 | 44 | 34 | 8.44 | 94.9 |
| 12 | 49 | 8.70 | 96.5 | 47 | 47 | 8.35 | 93.6 |
| 13 | 49 | 8.70 | 96.3 | 49 | 11 | 8.51 | 96.6 |
| 15 | 24 | 8.71 | 95.4 | 51 | 9 | 8.67 | 94.6 |
| 16 | 59 | 8.67 | 98.5 | 52 | 57 | 8.63 | 95.6 |
| 18 | 37 | 8.80 | 96.7 | 57 | 18 | 8.50 | 93.3 |
| 20 | 2 | 8.73 | 97.0 | 59 | 15 | 8.47 | 94.4 |
| 21 | 45 | 8.72 | 97.1 | 61 | 37 | 8.99 | 95.9 |
| 25 | 50 | 8.80 | 95.6 | 65 | 22 | 9.05 | 96.8 |
| 27 | 36 | 8.88 | 93.9 | 67 | 43 | 8.70 | 94.7 |
| 29 | 49 | 8.56 | 95.7 | 69 | 34 | 8.70 | 94.5 |
| 31 | 29 | 8.65 | 94.6 | 71 | 21 | 8.65 | 95.1 |
| 32 | 58 | 8.50 | 95.4 | 73 | 25 | 8.58 | 95.4 |
| 36 | 35 | 8.56 | 95.0 | | | | |

Table III shows the rates of oxidation at various times of contact. Here, the concentration of ammonia has become occasionally more than 9.50%, but, from another series of experiments it has been known that this does not affect the rates of oxidation more than one percent.

TABLE III

Temperature: 578 ±3°C

| $NH_3$ conc. % | Velocity of mixed gases per min. (cc. 0°C, 760 mm.) | Time of contact in sec. | Rate of oxidat. | |
|---|---|---|---|---|
| 9.39 | 520 | 0.094 | 91.6 | |
| 9.43 | " | " | 90.5 | 90.2 |
| 9.55 | " | " | 90.0 | |
| 9.58 | " | " | 88.2 | |
| 8.87 | 680 | 0.073 | 91.8 | |
| 8.92 | " | " | 92.4 | 92.1 |
| 9.03 | " | " | 92.2 | |
| 9.09 | 1200 | 0.041 | 96.3 | |
| 8.78 | " | " | 93.0 | |
| 8.74 | ' | " | 95.5 | 95.2 |
| 8.75 | " | " | 96.0 | |
| 8.90 | 1940 | 0.025 | 99.2 | |
| 8.70 | " | " | 99.9 | |
| 8.65 | " | " | 99.7 | 99.2 |
| 8.90 | " | " | 97.5 | |
| 8.98 | " | " | 99.7 | |
| 9.53 | 2460 | 0.020 | 95.3 | 96.5 |
| 9.48 | " | " | 97.6 | |
| 9.00 | 3070 | 0.016 | 91.3 | * |
| 8.92 | " | " | 92.4 | |
| 8.94 | " | " | 90.7 | 91.6 |
| 8.80 | " | " | 92.1 | |

*In the last four runs ca. 0.4% unoxidized ammonia was detected.

## 6. Interpretations of the Experimental Results

If we assume that the catalytic oxidation of ammonia is a consecutive reaction consisting of the two reactions:

$$(2) \qquad 4NH_3 + 5O_2 = 4NO + 6H_2O,$$
$$(4) \qquad 2NO = N_2 + O_2;$$

and that the catalyst has different catalytic power towards these two—the velocity constants being denoted by $k_1$ and $k_2$ respectively—and also that these two reactions are unimolecular, $k_1$ with respect to ammonia, $k_2$ with respect to NO as is often the case with heterogeneous catalysis, the yield of nitric oxide can be expressed by:

$$\eta = \frac{k_1}{k_2 - k_1}\left[e^{-k_1 t} - e^{-k_2 t}\right] \qquad (5)$$

where $\eta$ is the yield of nitric oxide and t is the time of contact of the reactant gases with the catalyst.

Now, if we know the values of $\eta$ at times of contact, t, 2t and 3t, we can, by a simple computation,[1] calculate the numerical values of $k_1$ and $k_2$.

TABLE IV. (Fig. 3).

Platinum gauze, $k_1 = 5725\ (sec)^{-1}$; $k_2 = 31.4\ (sec)^{-1}$; $k_1/k_2 = 182.5$

| Time of contact $10^{-3}$ sec. | Rate of oxidation calc. from (5) | (%) obs. |
|---|---|---|
| 0.1 | 43.5 | |
| 0.2 | 66.9 | |
| 0.4 | 89.1 | |
| 0.5 | 93.2 | |
| 0.68 | 96.4 | 96.1 |
| 0.8 | 97.0 | |
| 0.87 | 97.2 | 97.3 |
| 0.92 | 97.2 | |
| 1.00 | 97.1 | |
| 1.24 | 96.6 | 96.4 |
| 1.50 | 95.9 | 95.2 |
| 2.00 | 94.4 | 94.3 |
| 3.00 | 91.5 | |

TABLE V. (Fig. 4.)

Fe-Bi catalyst, $k_1 = 204.5\ (sec)^{-1}$; $k_2 = 1.17\ (sec)^{-1}$; $k_1/k_2 = 175$

| Time of contact $10^{-3}$ sec. | Rate of oxidation calc. from (5) | (%) obs. |
|---|---|---|
| 0.1 | 18.6 | |
| 0.5 | 63.8 | |
| 0.7 | 75.7 | |
| 1.0 | 86.4 | |
| 1.5 | 94.1 | |
| 1.6 | 95.0 | 91.6 |
| 2.0 | 96.6 | 96.5 |
| 2.5 | 97.1 | 99.2 |
| 3.0 | 97.0 | |
| 4.1 | 95.9 | 95.2 |
| 5.0 | 94.9 | |
| 7.0 | 92.7 | |
| 7.3 | 92.3 | 92.1 |
| 9.1 | 90.4 | 90.2 |
| 10.0 | 89.5 | |

[1] The writer obtained these three values of $\eta$ from graphical interpolation. As to the procedure see F. Thiersch: Z. physik. Chem., III, 175 (1924); Rutherford: "Radioactive Transformations" p. 48 (1919).

As can be seen from Tables IV and V, the rate of oxidation or the yield of nitric oxide calculated on the above assumption reproduces the observed value in a striking way, although the values corresponding to very short time of contact are found a little too low. This can be explained as follows:

In the presence of water vapor and oxygen, ammonia and nitric oxide react readily to form nitrogen gas and water according to

$$4NH_3 + 2N_2O_3 = 4N_2 + 6H_2O. \qquad (6)$$

When the time of contact is too short, a part of the ammonia passes through the catalyst layer without undergoing oxidation and react with the oxide gases before being drawn out from the sampling cock.

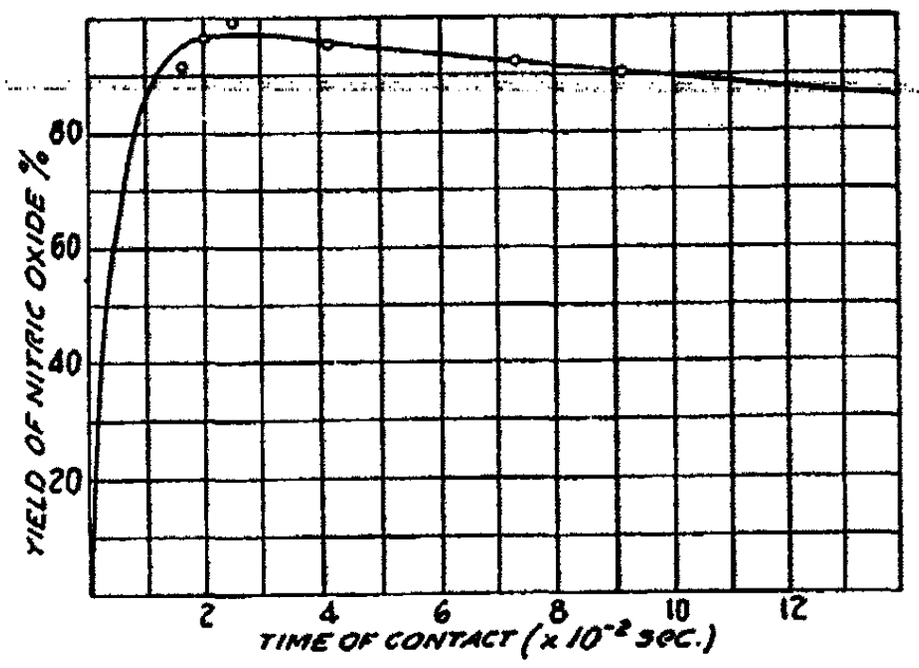



FIG. 4
Fe—Bi Oxides

As is well known, the maximum yield of the intermediate product of a consecutive reaction is represented by:

$$\eta_m = \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_1-k_1}} = \theta^{\frac{1}{1-\theta}}; \qquad (7)$$

where $\theta = k_1/k_2$, so that the maximum yield $\eta_m$ is a function of $\theta$ only and is not influenced by the absolute values of either $k_1$ or $k_2$. The time of contact corresponding to $\eta_m$ can be calculated from

$$t_m = \frac{\ln\left(\frac{k_1}{k_2}\right)}{k_1-k_2}. \qquad (8)$$

In Table VI, $\eta_m$ and $t_m$ for platinum and base metal catalysts calculated from (7) and (8) are shown together with experimentally obtained values. They are concordant within experimental error.

TABLE VI

| | Maximum yield of NO | | Optimum time of contact | |
|---|---|---|---|---|
| | calc. (%) | obs. (%) | calc. (sec.) | obs. (sec.) |
| Platinum gauze | 97.2 | 97.3 | $0.92.10^{-3}$ | $0.87.10^{-3}$ |
| Fe-Bi oxides | 97.1 | 99.2 | $2.54.10^{-2}$ | $2.5.10^{-2}$ |

## 7. Summary

1. With powerful catalysts such as fine platinum gauze or Fe-Bi mixed oxides, we can neglect the reaction

$$(3) \qquad {}_4NH + 6NO = {}_5N_2 + 6H_2O$$

and consider the whole reaction to be the result of the two reactions

$$(2) \qquad {}_4NH_3 + 5O_2 = {}_4NO + 6H_2O$$

and

$$(4) \qquad {}_2NO = N_2 + O_2$$

occurring consecutively, which explains the occurrence of a maximum in the NO-yield versus time of contact curve with satisfaction.

2. The maximum yield of nitric oxide is governed by the ratio of $k_1$ to $k_2$, the velocity constants (unimolecular) of reactions (2) and (4), and not by their absolute values. The reaction (2) is extremely rapid, $k_1$ being one hundred and eighty times as large as $k_2$ in cases here reported, and reaction (3) has not time to take place to any perceptible extent.

3. Platinum of the catalyst evaporates slowly but distinctly at such a low temperature as 580°C. This is not due to the scaling off of the activated surface as examined microscopically. The loss of platinum which Landis[1] has reported must be due to the same phenomenon.

In conclusion, the writer wishes to express his sincere thanks to Dr. F. Kodera, director, through whose kind permission this paper is published and also to Prof. M. Katayama and Prof. N. Kameyama who have favored him with valuable suggestions.

*Government Nitrogen Research Institute,*
*Meguro, Tokyo, Japan.*
*May 26, 1926.*

[1] W. S. Landis: Trans. Am. Electrochem. Soc., 35, 283 (1919).

# THE ADSORPTION OF IONS BY METALLIC MERCURY*

BY JACOB ELLIS ROSENBERG AND GEBHARD STEGEMAN

An investigation relative to the feasibility of estimating the sulfate content of a solution by electrometric measurements, produced some unusual results which led to a subsequent investigation of the cause of the unexpected phenomena. Briefly, the first mentioned investigation represented an attempt to measure the variation in the potential of a lead electrode in a solution containing sulfate ion when a soluble lead salt was added to the solution. It was expected that the precipitation of the lead sulfate formed would prevent any large increase in the concentration of the lead ion until the sulfate ion had practically disappeared.

The potential measurements were not at all concordant and seemed to be particularly affected by agitation, especially in the presence of the precipitated lead sulfate.

A variation in potential of 0.07 volt was frequently produced by vigorous agitation of the solution. The position of the electrode in the solution also appeared to have a noticeable influence on the potential. A variation of as much as 0.02 volt being registered, depending on whether the electrode was placed in the bottom of the vessel in contact with an excess of lead sulfate, or at the top of the solution where little solid salt was present.

These phenomena are not subject to a complete interpretation on the basis of the Nernst Theory of Electromotive Force.

According to Gibbs[1] the boundary surface between two phases may be considered to be a phase in itself which has properties different from each of the other two. The potential of an electrode in a solution may be due to a potential difference between the metal and the boundary phase and a further difference between the boundary phase and the solution. Geymant[2] has made a suggestion to this effect. If this is the case it may be expected that the difference in potential between the metal and the boundary phase is by far the greater value.

If we assume the existence of a boundary phase and its probable function in determining the potential of an electrode in a solution, it is possible to account for some of the phenomena mentioned. Agitation would disturb this boundary phase to some extent and would certainly disturb the solution adjacent to it. Since the boundary phase undoubtedly contains a higher concentration of solute than the solution itself, agitation will tend to prevent the formation of this boundary phase with its maximum concentration of solute and a consequent difference of potential must result. The change in potential of the lead electrode on being raised to the top of saturated solution

*An abstract of a thesis presented to the Faculty of the Graduate School of the University of Pittsburgh by Jacob Ellis Rosenberg in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[1] Trans. Conn. Acad., 3, 439, (1876).
[2] Z. physik. Chem., 108, 387-405 (1924).

of lead sulfate containing an excess of solid lead sulfate, is ascribed to the fact that the salt adsorbs lead ions from the boundary phase, thus decreasing the concentration of lead ions which are effective in determining the potential of the electrode. Since the higher potential was attained when the solid salt was in intimate contact with the electrode, the reduction in concentration of lead ions in the boundary phase due to adsorption by the salt would produce the effect noted.

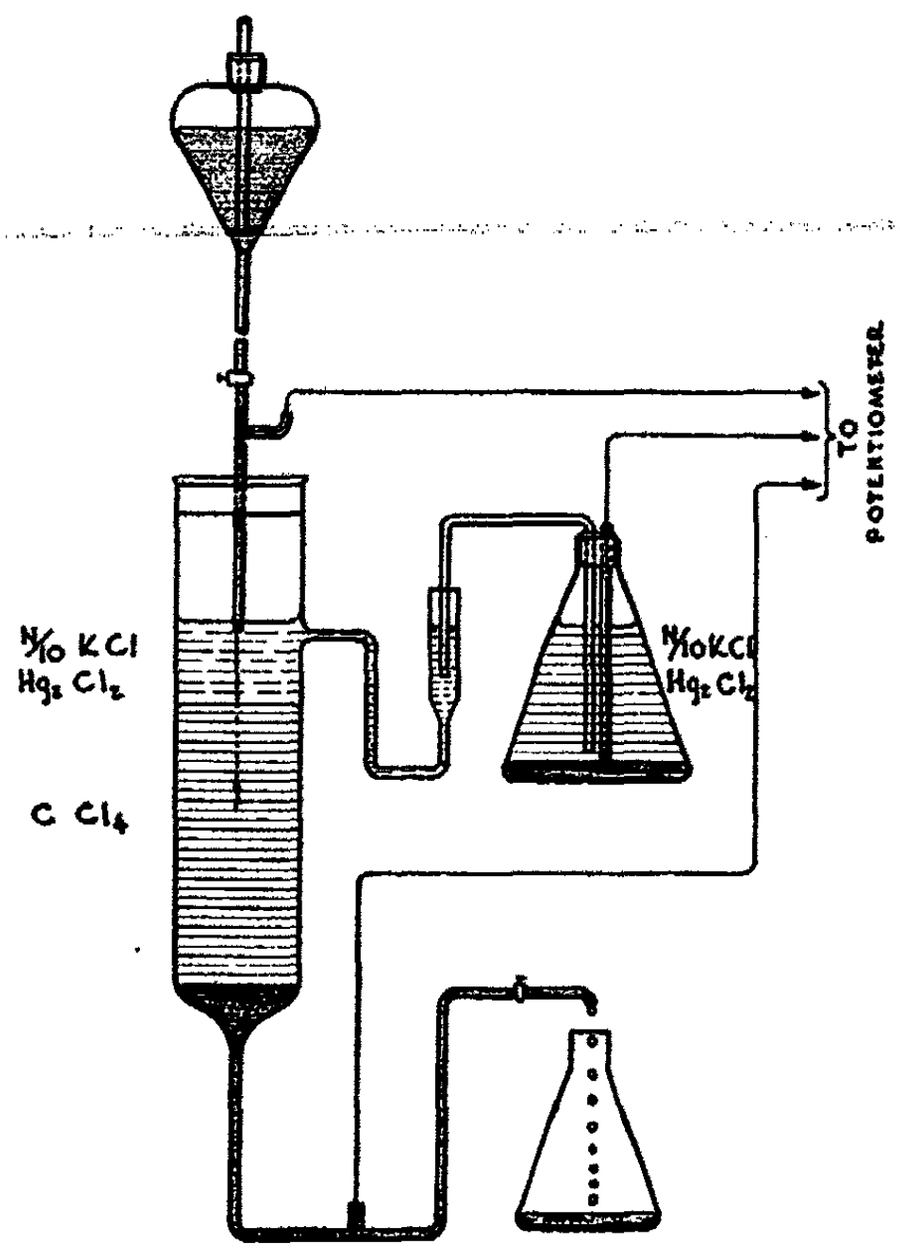



FIG. 1
Diagram of Apparatus

Whatever the ultimate explanation may be, these few phenomena have suggested that the adsorption of ions by metallic surfaces may be of considerable influence in the production of potential differences.

The adsorption of ions by a metallic surface must be a function of time, and it was thought that the time involved might be sufficient to permit a measurement to be made. The method of measurement chosen was designed to permit a mercury surface to remain in contact with a solution of one of its salts for a time, so short that maximum adsorption could not have taken place. The potential of this mercury was then measured against a mercury

surface which had been in contact with the same solution for a sufficient time to have reached the equilibrium concentration. Reference to Fig. 1 will make the method employed obvious.

*Procedure.* An attempt was made to perform the measurements tabulated at constant temperature. It was discovered, however, that the variation in the potential due to other errors inherent in the method of measurement, was such as to exceed that which might be produced by any slight temperature change which would be experienced. The variation in temperature did not however exceed $25° \pm 1°$ C.

The measurements recorded consisted in turning on the stop-cock to the open position and measuring the potential of the mercury stream against the standard electrode. The point of discontinuity in the mercury stream was found to be very constant, and the actual length of the stream which was exposed to the solution in question was determined by means of a cathetometer. In calculating the time of contact listed in the various tables the effective height of the mercury column was determined as follows: The mercury was allowed to flow freely from the tube immersed in the solution until the flow stopped. Due to capillarity a certain amount of mercury remained in the tube. The length of this column of mercury was deducted from the total length of the mercury column and the resulting value was used as the effective length of the mercury column.

*Materials used.*

*Mercury.* Mercury was distilled according to the method of Hulett until no potential differences were apparent between successive distillates in contact with N/10 KCl saturated with calomel.

*Potassium Chloride.* The potassium chloride used was obtained from a reliable manufacturer. It was recrystallized three times from pure water and dried at 150°C.

*Hydrochloric Acid.* The N/10 hydrochloric acid was prepared from a constant boiling mixture of pure hydrochloric acid.

*Calomel.* This salt was prepared by the electrical method recommended by Lipscomb and Hulett.[1] This mercury used was that described above. The usual precautions for the preparation of solutions in which this calomel was used were carefully observed.

*Variation in the Time of Contact.*

(a). *Effect of Variation in Velocity of the Mercury Stream.* The values given in Table I represent the potentials obtained by variation in the velocity of the flowing mercury stream. The velocity was calculated by the formula $v = \sqrt{2hg}$ where v is the velocity, h the height and g the gravitational constant. No account was taken in these measurements of the distance travelled in the solution before the mercury stream became discontinuous. The outlet tube was in all cases below the surface of the solution.

[1] J. Am. Chem. Soc., 38, 21 (1916).

TABLE I

| Height of Hg in cm. | Velocity $= \sqrt{2hg}$ $\frac{cm}{sec.}$ | $\frac{N}{10}$ calomel electrode-Hg volts |
|---|---|---|
| 251.7 | 702.4 | .340 |
| 185.0 | 602.1 | .305 |
| 124.1 | 493.2 | .301 |
| 70.2 | 370.9 | .255 |
| 47.2 | 304.2 | .224 |
| 30.2 | 243.3 | .211 |

A similar set of data were obtained with another tip which gave a longer stream before becoming discontinuous.

TABLE II

| Height of Hg in cm. | Velocity $= \sqrt{2hg}$ $\frac{cm}{sec.}$ | $\frac{N}{10}$ calomel electrode-Hg volts |
|---|---|---|
| 251.7 | 702.4 | .308 |
| 179. | 592.3 | .260 |
| 130. | 504.8 | .165 |
| 106.7 | 457.3 | .121 |
| 43.5 | 292.0 | .080 |

These data are significant in that they show that the greater the velocity, the larger is the difference in potential between the flowing and the stationary electrode. It should be mentioned here that the length of the stream in contact with the solution before it becomes discontinuous is a function of the velocity; the maximum velocity giving a stream of minimum length.

(b) Table III represents a series of measurements taken with a constant velocity of the mercury stream. The variation in the time of contact was produced by raising the tip of the outlet tube above the solution. Since the length of the mercury stream before it becomes discontinuous is a function of the velocity, a very short time of contact could be obtained. The point at which the stream became discontinuous was noted by means of a cathetometer as well as the height of the solution. The difference obviously represents the distance traveled in the solution. Due to the disturbance of the surface by the mercury stream, the distance traveled in the solu'ion may not be exactly the correct one so obtained, but a series of measurements with a variation in the distance of the tip above the solution would at least be comparable. The time of contact was obtained by dividing the velocity by the distance traveled.

TABLE III

| Height of Hg in cm. | Distance traveled in cm. | Velocity in cm. per sec. | Time of contact in sec. | E.M.F. |
|---|---|---|---|---|
| 258.5 | .04 | 711.8 | $.56\times10^{-4}$ | 0.479 |
| 258.5 | .09 | 711.8 | $1.26\times10^{-4}$ | 0.452 |
| 258.5 | .15 | 711.8 | $2.11\times10^{-4}$ | 0.435 |
| 258.5 | .32 | 711.8 | $4.49\times10^{-4}$ | 0.413 |
| 258.5 | .40 | 711.8 | $5.62\times10^{-4}$ | 0.375 |
| 258.5 | .49 | 711.8 | $6.88\times10^{-4}$ | 0.363 |
| 258.5 | .51 | 711.8 | $7.16\times10^{-4}$ | 0.361 |

(c) *Use of an Inert Liquid.* In an attempt to reduce the time of contact of the mercury stream with the solution, a series of experiments was carried out in which the mercury stream impinged on a glass plate after passing through a certain length of solution. It was anticipated that the mercury stream might in this way be made discontinuous at any desired point. The results were disappointing, however, since the time of contact of the mercury stream with the solution was actually increased. The mercury stream merely flattened out on the glass plate, thereby increasing the time of contact instead of reducing it. To obviate this difficulty a layer of carbon tetrachloride was placed in the bottom of the vessel, with the solution of calomel resting above it. The tip of the mercury discharge tube was then lowered into the solution of calomel and set at a distance from the layer of carbon tetrachloride, sufficiently close so that the mercury stream would not become discontinuous in the solution of calomel. In this way the time of contact could be reduced without removing the mercury discharge tube from the solution. The distance between the discharge tube and the carbon tetrachloride was measured by means of the cathetometer. There was some disturbance of the carbon tetrachloride layer by the stream of mercury, but the results were better than anticipated. Tabie IV gives the results obtained.

TABLE IV

| Height of Hg in cm. | Distance traveled in cm. | Velocity in cm. per sec. | Time of contact in sec. | E.M.F. |
|---|---|---|---|---|
| 229 | .28 | 670 | $4.18\times10^{-4}$ | 0.394 |
| 208 | .26 | 639.2 | $4.07\times10^{-4}$ | 0.390 |
| 159 | .29 | 558 | $5.20\times10^{-4}$ | 0.378 |
| 137 | .32 | 518 | $6.18\times10^{-4}$ | 0.371 |
| 116 | .36 | 477 | $7.55\times10^{-4}$ | 0.362 |
| 200 | .40 | 443 | $9.03\times10^{-4}$ | 0.353 |
| 82 | .39 | 401 | $9.73\times10^{-4}$ | 0.345 |
| 66 | .44 | 360 | $12.23\times10^{-4}$ | 0.335 |
| 41 | .46 | 283.5 | $16.23\times10^{-4}$ | 0.324 |
| 35 | .49 | 262 | $18.71\times10^{-4}$ | 0.306 |

A comparison of the values found in Tables III and IV indicates a reasonable agreement between the time of contact and the E. M. F. produced by the two methods of measurement.

(d) Table V contains the results of a series of measurements obtained when N/10 HCl calomel was substituted for N/10 KCl calomel. These measurements were carried out in the same way as those indicated in Table IV, with the exception that height of the mercury column was constant at 254.9 cms.

TABLE V

| Height of Hg in cm. | Distance traveled in cm. | Velocity in cms. per sec. | E.M.F. |
|---|---|---|---|
| 254.9 | .02 | $.284 \times 10^{-4}$ | .493 |
| 254.9 | .11 | $1.56 \times 10^{-4}$ | .442 |
| 254.9 | .20 | $2.84 \times 10^{-4}$ | .417 |
| 254.9 | .27 | $3.84 \times 10^{-4}$ | .394 |
| 254.9 | .64 | $9.11 \times 10^{-4}$ | .361 |
| 254.9 | .79 | $11.2 \times 10^{-4}$ | .330 |
| 254.9 | 1.09 | $15.5 \times 10^{-4}$ | .315 |
| 254.9 | 2.46 | $35.0 \times 10^{-4}$ | .276 |

Comparison of these values with those found in Table IV shows a reasonable agreement only, but it must be emphasized that the estimation of the distance traveled by the mercury stream while in contact with the solution of mercury ions is a difficult matter with the arrangement used.

(e) Another series of measurements was made in which the time of contact of the mercury with the solution was varied by raising the discharge tube above the solution. Since the distance traveled by the mercury stream before it becomes discontinuous is a function of the velocity, the time of contact could be made vanishingly small by raising the tube to the right height so that the stream became discontinuous just at the moment of contact. The results follow.

TABLE VI

| Distance above the solution in cm. | Velocity cm/sec | E.M.F. |
|---|---|---|
| .35 | 711.8 | 0.359 |
| .91 | 711.8 | 0.369 |
| 1.46 | 711.8 | 0.386 |
| 2.31 | 711.8 | 0.418 |
| 3.08 | 711.8 | 0.530 |
| >3.08 | 711.8 | no contact |

TABLE VII

| Distance above the solution in cm. | Velocity $\frac{\text{cm}}{\text{sec}}$ | E.M.F. |
|---|---|---|
| .40 | 711.8 | 0.350 |
| .55 | 711.8 | 0.375 |
| .98 | 711.8 | 0.440 |
| 1.40 | 711.8 | 0.523 |
| 1.50 | 711.8 | 0.532 |
| 1.60 | 711.8 | 0.533 |
| >1.60 | 711.8 | no contact |

The results shown in Tables VI and VII were obtained by using two discharge tips of different sizes which produced streams of mercury which showed a discontinuity at different points. It is significant that the maximum potential obtained was the same in each case, indicating that the time of contact had become vanishingly small.

*E. M. F. of mercury in solutions containing no mercury ion.* A series of measurements was made in which mercury was allowed to flow into a N/10 KCl solution containing no mercury ion, which had been freed of air by bubbling hydrogen gas through the solution for eighteen hours. The results follow.

Mean of five measurements E.M.F.

(1) N/10 calomel electrode—Hg flowing rapidly into N/10 KCl = 0.541

(2) N/10 calomel electrode—Hg stationary in N/10 KCl = 0.724

(3) N/10 calomel electrode—Hg (disturbed surface) in N/10 KCl = 0.637 — 0.603

(4) N/10 calomel electrode—Hg flowing slowly into N/10 KCl = 0.540

These results appear to be significant in that the maximum E. M. F. shown for the mercury flowing into a solution containing zero concentration of mercury ions is approximately the same as that obtained by those measurements where the time of contact was vanishingly small. The value 0.724 volts for a stationary mercury electrode in contact with N/10 KCl is accounted for on the assumption that in the absence of mercury ions the metal acts as a hydrogen electrode. The E. M. F. of the N/10 calomel electrode against a hydrogen electrode in a N/10 KCl solution should be 0.7548 volts at 25° C, but the discrepancy between the observed and calculated value is not surprising considering the fact that mercury is not a suitable substance for use as a hydrogen electrode. It has also been established that mercury is not particularly effective as a catalytic agent, so the rate of adsorption on its surface must be relatively small. It is possible, therefore, to offer a plausible explanation for the apparent lack of adsorption of hydrogen ion on the surface of the flowing mercury. Only after a considerable time does a stationary mercury surface acquire the potential of the hydrogen electrode. In experiment (3) there is apparently only a partial saturation of the mercury surface by hydrogen ions, due to the fact that the surface of the mercury was continually being disturbed.

*The Effect of Larger Mercury Ion Concentration.* The measurements previously described were made with solutions of small mercury ion concentration. In a solution in which the mercury ion concentration is large the adsorption should be very rapid. Because of the rapidity of the adsorption, it would be expected that smaller differences of potential would exist between the flowing mercury and stationary mercury, using the same effective height of mercury column, than were observed in a more dilute solution.

A saturated solution of mercurous nitrate was prepared by shaking the solid salt with water and mercury. A saturated solution of ammonium nitrate

was placed between the calomel electrode and the mercurous nitrate solution in the vessel. In the vessel near the tip of the mercury dropper was placed a platinum spiral which had been electrolytically coated with mercury. This was used to measure the potential of a stationary mercury electrode in the solution. A preliminary comparison of a large stationary mercury surface and the spiral in the same solution, indicated no difference in potential between the two. The same effective height of mercury column (258.5 cm) was used as in the other measurements on more dilute solutions. The mercury stream in contact with the solution was about two centimeters in length.

Table VIII gives the results of a series of measurements in which the electrolyte was a saturated solution of mercurous nitrate whose concentration was gradually reduced by dilution with water. In the case of the more dilute solutions represented in the measurements numbered 6 to 9 inclusive the concentration of the mercury ions was reduced by the addition of N/10 KCl solution.

TABLE VIII

| Expt. | $Hg - Hg_2(NO_3)_2 - N/10$ Calomel stationary mercury E.M.F. | $Hg - Hg_2(NO_3)_2 - N/10$ calomel flowering mercury E.M.F. | Difference |
|---|---|---|---|
| 1 | 0.4075 | 0.4046 | .0029 |
| 2 | 0.3847 | 0.3758 | .0089 |
| 3 | 0.3684 | 0.3086 | .0598 |
| 4 | 0.3496 | 0.1562 | .1934 |
| 5 | 0.3214 | 0.0851 | .2363 |
| 6 | 0.0931 | −0.2058 | .2989 |
| 7 | 0.0610 | −.02532 | .3142 |
| 8 | 0.0426 | −0.2840 | .3266 |
| 9 | 0.000 | −0.340 | .340 |

In all cases the flowing electrode was negative to the stationary one in the same solution. Since the time of contact of the flowing mercury with the solution was in all cases the same, the smaller differences in potential between the flowing and stationary electrodes in solutions of high mercury ion concentration, are easily accounted for on the basis of the rapidity of the adsorption, as this would obviously be a function of the concentration of the ion adsorbed.

## Discussion of Results

It appears to be a logical contention from a survey of the measurements indicated in the various tables, that the potential of the flowing mercury measured against the stationary mercury, each in contact with the same solution, must be due to differences in the concentration of mercury ions on the surfaces involved. Since the concentration of mercury ions on the flowing electrode must certainly be less than that on the stationary surface which has had sufficient time to adsorb the equilibrium quantity of ions, the flowing electrode would be in all cases less positive. This was found to be the case.

Referring to Palmaer's first work on the dropping electrode[1] it is found that the difference in potential of the flowing and stationary electrode amounts to 0.365 volts, the flowing electrode being the less positive of the two. Near the dropping electrode was a stationary mercury surface whose potential was measured against a reference electrode. In a solution of $Hg_2Cl_2$ in N/100 $KNO_3$ the dropping of the mercury caused the electrode near the dropper to become negative to the electrode in the unchanged solution. The maximum difference was 0.153 volts. Measuring the potential of the dropping electrode against the reference electrode Palmaer obtained a value of 0.518 volts. He recorded only this one measurement with the flowing electrode. He explained this difference of 0.365 volts between the stationary and the dropping electrode as being due to the decrease in the concentration of mercury ions near the tip of the dropper by the dropping mercury.

If this explanation be correct, then no difference between the flowing and stationary mercury would be observed when the stream was first started and any difference in potential observed later should increase with time. In the investigation herein described, the same potential was observed whether it was measured as soon as the stream was started or after several minutes of flowing. Palmaer's explanation would also not account for the change in potential with the length of the stream of mercury. These results can, however, be readily accounted for by assuming that there is an adsorption of mercury ions by the electrode surface. From the data listed in Tables VI and VII it is found that when the time of contact was vanishingly small the maximum potential obtained was approximately 0.533 volts. This approximates closely the value of 0.518 volts obtained by Palmaer and it is unlikely that his solution in the vicinity of the dropping electrode had zero concentration of mercury ions. Accordingly, his value should be less than 0.533 volts. The potentials obtained by dropping mercury into a solution of KCl containing zero concentration of mercury ion indicate that the maximum potential, which should have been obtained if the time of contact could have been reduced to zero in the case of the experiments listed in Tables VI and VII would be approximately 0.540 volts.

The experimental data listed in the various tables have led to the following conclusions with regard to the potential of a flowing mercury electrode.

I. The potential varies with the velocity of the flow; the greater the velocity, the more negative is the flowing mercury to the stationary mercury.

II. The potential varies with the length of the stream in contact with the solution containing mercury ions; the shorter the length of the stream, the more negative is the flowing mercury.

III. The potential of the flowing mercury electrode against a stationary mercury electrode in a N/10 KCl or N/10 HCl solution saturated with calomel approaches −0.53 volts as a minimum; or the maximum potential of the combination:

$$Hg(\text{stationary}) - N/10\,KCl - Hg_2Cl_2 - Hg(\text{flowing}) = 0.53 \text{ volts}$$

[1] Z. physik. Chem., 25, 265 (1898).

In order to explain the behavior of the flowing mercury electrode, the following generalizations are made regarding a mercury electrode in a solution containing mercury ions:

1. Mercury ions are adsorbed at the surface of the mercury electrode.
2. An appreciable time is required for the adsorption to reach the maximum value.
3. The single electrode potential of the mercury electrode depends directly on the concentration of mercury ions at the surface of the electrode and not on the concentration of the solution. The concentration of the solution determines the concentration of ions at the electrode surface, but the concentration in the bulk of the solution does not directly affect the potential.
4. The difference in potential between a stationary and a flowing electrode in the same solution is due to the time requirement of the absorption. The flowing electrode has a smaller concentration of ions on its surface and is, therefore, less positive.
5. The potential of a given electrode is determined by the concentration of the most noble metal ion at its surface.

A consideration of the results of this investigation indicates that the absorption of ions by a metallic surface may have some influence in producing the well-known phenomenon of overvoltage. It is the intention of the authors to discuss this influence in a subsequent paper.

# THE SOLUBILITY RELATIONS OF NAPHTHALENE*

BY H. LEE WARD

In a very important series of papers Hildebrand[1] and his collaborators have produced much evidence to show that the deviations from the ideal solubility laws may be ascribed to differences in the internal pressures of the solvent and solute and to polarity. Hildebrand and Jenks have developed a method for the evaluation of solubility data and applied it to the solubilities of naphthalene, iodine and rhombic sulphur. The method consists in plotting the logarithm of the mol fraction of the substance separating as the solid phase against the reciprocal of the absolute temperature. In case an ideal solution is formed in a given solvent, the resulting curve is a straight line, whose slope (S) is given by the expression $S = L_f/4.58$ where $L_f$ is the molal heat of fusion of the solid. If the molal heat of fusion varies with the temperature, there is a corresponding deviation from the straight-line relationship, but as a first approximation, it can be neglected. For non-ideal solutions of substances of not very different pressures or no very pronounced polarities, the curves approach straight lines.

Mortimer[2] has applied the above method to the quantitative determination of solubility curves on the assumptions (a) that the logarithm of the mol fraction versus the reciprocal of the absolute temperature curves are straight lines passing through a point on the 1/T axis corresponding to the absolute melting point of the solid phase and (b) that the deviations of the slopes of such straight lines from the ideal slope, $S = L_f/4.58$ are due to internal pressure differences of solvent and solute. From a series of such curves he determines the internal pressures of various pure substances relative to naphthalene. From these in turn he calculates the solubility of the various compounds in one another, even applying the method to the case of polar solvents.

Since the above conclusions are so important in the theory of solutions and are, in addition, of so much practical value, especially to the organic chemist, it seems highly desirable to make a systematic investigation of the exact form of the log N versus 1/T curve for various typical solutes in a number of solvents of differing internal pressures and polarities. In the present paper an attempt has been made to accomplish this for the solubility of naphthalene. The choice was made because both Hildebrand and Mortimer have used the literature measurements for this substance as an example, and these are rarely complete enough to determine the exact details of the curves. Also, the napthhalene derivatives form a series of compounds with varying

*Contribution from the Department of Chemistry, Washington University.

[1] Hildebrand: J. Am. Chem. Soc., **38**, 1452 (1916); **39**, 2297 (1917); **41**, 1067 (1919); **43**, 500 (1921); Hildebrand and Jenks: **42**, 2180 (1920); **43**, 2172 (1921): Taylor and Hildebrand: **45**, 682 (1923); Hildebrand, Hogness and Taylor: **45**, 2828 (1923). See also Hildebrand: "Solubility," Am. Chem. Soc. Monographs (1924).

[2] Mortimer: J. Am. Chem. Soc., **44**, 1416 (1922); **45**, 633 (1923).

internal pressures and polarities, and of convenient melting points for determination of the complete solubility curves. It is hoped in later papers to give the results of such measurements.

Solubility measurements for naphthalene in benzene, chlorbenzene and carbon tetrachloride have been made by Schröder[1] employing the synthetic method. The procedure was to heat weighed quantities of solvent and solute in a sealed tube, rotated in a water bath, and observe the temperature at which the crystals had nearly disappeared. The tube was then slowly cooled until the crystals were seen to increase both in size and number. The mean temperature between these two values, observed with very slow rates of heating was taken as the solubility point. The accuracy of the determination was given as 0.5° at the higher naphthalene concentrations and 1.0° at the lower. Temperatures were not stated closer than 0.5°. The materials were carefully purified and their melting or boiling points noted. The results obtained agree as closely with the author's observations as could be expected from the accuracy claimed by Schröder. The average deviation in the mol fraction shown by the two sets of data is 0.0034. When reduced to a percentage basis the average difference is 0.7% and the maximum less than two percent.

Speyers[2] has measured the solubility of naphthalene in methyl, ethyl and propyl alcohols and in chloroform and toluene. His method is to saturate the solution at a fixed temperature and to analyze by specific gravity measurements. He does not specify the procedure by which this latter determination is carried out, but, in some specific gravity measurements for another purpose, states there might be an uncertainty of three units in the third decimal place in certain cases though the usual error was in the fourth place. Moreover, no attempt was made to purify the naphthalene and its melting point is not given. The solubilities for toluene do not lie on a smooth curve when plotted by the method of Hildebrand and are very much greater than the corresponding solubilities for benzene as determined by Schröder and the author. Since the internal pressures of toluene and benzene are so nearly alike, approximately the same molecular solubilities should be expected. There seems to be little doubt that Speyer's values for toluene are considerably in error. His determinations for methyl alcohol show somewhat higher solubilities than those here reported but except for the lowest mol fraction of naphthalene the differences are not very great.

Étard[3] reports the solubilities of naphthalene in hexane, carbon disulphide, and carbon tetrachloride. He does not state the method used or the purity of his materials. His values for hexane agree fairly well with those of the author except at the highest and lowest temperatures. The lower points when plotted by Hildebrand's method do not lie on the same curve as the rest and those at the highest temperatures would seem to show great deviations from the ideal law with large mol fractions of naphthalene, which is very doubtful.

[1] Schröder: Z. physik. Chem., 11, 449 (1893).
[2] Speyers: Am. J. Sci., (4) 14, 294 (1902).
[3] Étard: Bull., (3) 9, 82 (1893).

The solubility of naphthalene in nitrobenzene has been measured by Kremann,[1] employing the synthetic method. The results are in fair agreement with those here reported except for two points where the variation amounts to about two and a half percent.

*Experimental.* The procedure chosen for the solubility determinations was the well known synthetic method of Alexejew,[2] which consists in rotating a sealed tube containing definite quantities of solvent and solute in a bath and noting the temperature at which all of the solid phase disappears. The apparatus employed was very similar to that described by Schröder, except that an electric motor with a variable speed control was used for stirring in the place of a water motor, and the beaker employed for a bath had a capacity of four liters to secure better temperature regulation. The synthetic method offers the advantage that the analysis of the saturated solution is not necessary; a procedure which is rather undertain in the case of most organic substances. In addition, determinations may be readily carried out at temperatures above the boiling point of the solvent.

The principal difficulty in the method is to be certain that equilibrium is reached at the temperature at which the last of the solid phase disappears, which temperature will hereafter be designated the solubility point. In order to minimize the uncertainty, the temperature was always raised until all of the solid phase went into solution and the tube was then cooled as rapidly as possible while rotating or shaking. This procedure produced crystals which were of small size and very uniform. The bath was then heated slowly and a few degrees below the solubility point, the rate was adjusted so that the temperature did not rise more than a tenth of a tenth of a degree per minute. The temperature was taken when but a very few small crystals remained. Frequently the attainment of equilibrium was checked by still slower rates of heating and the points obtained were not more than a tenth of a degree lower.

In order to ascertain the error possible in the failure to attain equilibrium, a tube was selected at random which had previously shown a solubility point of 28.7°. The solvent was benzene. This sample was heated until all the naphthalene went into solution and then rapidly cooled to secure small crystals of uniform size. It was then heated to 28.8° at the usual rate, at which point no perceptible naphthalene was left undissolved. On very slow cooling crystals suddenly appeared at 27.3°. The amount coming out at that temperature was considerable and the individual crystals quite large. The same procedure was repeated by heating to 28.7° and this time the crystals appeared at 27.6° the phenomena being essentially as before. On heating to 28.6°, on the contrary, some crystals still remained though the amount was very small. On slowly cooling to 28.5° a perceptible increase in the number of crystals was noticed and at 28.4° this was absolutely unmistakable. Since in the first two cases the supercooling phenomenon was so evident, it is believed that there was not enough naphthalene remaining undissolved at 28.7° to act

[1] Kremann: Monatsheft, 25, 1246 (1904).
[2] Alexejew: Wied. Ann. 28, 305 (1886).

as a nucleus for crystallization. The amount necessary for this must, of course, be rather small. The solubility point, therefore, seems to be lower than 28.7°. As the growth of crystals was very marked at 28.4° and perceptible at 28.5° the true solubility point is probably 28.6° or 1/10 degree lower than that previously determined.

In order to fix the maximum error which might be made with very rapid heating rates, the tube containing a large amount of crystals was introduced into the bath at 27° and the heating carried out with the full flame of a burner. All crystals had disappeared at 29.1° in less than two minutes after introducing the tube. It would seem to be very difficult to make an error of half a degree when the solid phase is produced by sudden cooling.

On the basis of the above and other determinations it is believed that the error due to equilibrium not being established at the time the temperature is read, should never exceed 0.2° except possibly in the case of very slightly soluble substances. This error could be very materially reduced by very slow methods of heating employing thermostatic control. The ultimate accuracy of the method should be limited only by the amount of the solid phase visible to the eye, or perhaps, by the increased solubility of fine crystals over the coarse ones usually present in the analytical procedure. Schröder estimates that half of a milligram of an organic substance should be visible and this seems a reasonable figure. The increase of solubility for small crystals of organic substances does not seem to have been investigated but since their number is comparatively small in this procedure, it would probably be inconsiderable. It is the author's opinion that the synthetic method can be made more accurate than the analytical for all organic substances except for the few cases in which an accurate analytical method is known.

The thermometers employed were compared with primary standards which had been certified by the Bureau of Standards and which were used for standardization purposes only. The error in checking should not exceed a tenth of a degree and the inaccuracy of the solubility point should, therefore, not be greater than three tenths of a degree.

The tubes used in the determinations were of very thin walls. They were first filled with the solid phase, then drawn down to about five mm. at the center of the constriction and the required quantity of liquid solvent introduced. After sealing, the tubes were again weighed in order to ascertain the small loss of solvent which usually took place in the sealing process.

*Preparation of Materials.* Naphthalene was prepared by repeated recrystallization from methyl alcohol of C. P. naphthalene. The final material showed a freezing point of 80.05°-80.1° when measured on a large sample in a test tube. Some residues from the above process gave a freezing point but 0.05° lower, but were not used. The freezing point of the purest material agreed very well with the point of 80.1° obtained at the Bureau of Standards.

The benzene used in the preliminary curve was prepared by shaking technical material repeatedly with concentrated sulphuric acid to remove thiophene, and subsequent fractional distillation. The corrected boiling point was 80.0°-80.1° and the freezing point 5.4°. The material employed for the final curve was prepared by the method of Richards and Shipley[1] and the recrystallization was carried on until the freezing point showed no further rise as measured with a Beckmann thermometer. The material was kept over sodium wire and was distilled just before use. The melting point was 5.5°.

Toluene of the "Analyzed" grade was twice redistilled through a fractionating column and showed a corrected boiling point of 110.8° to 110.9°.

Commercial, water-white, chlorbenzene was three times fractionated through a Hempel column. In the last distillation nearly all the material distilled over a range of 0.03°. The middle portion showing a corrected boiling point of 132.0° ±0.1 was used in the determinations.

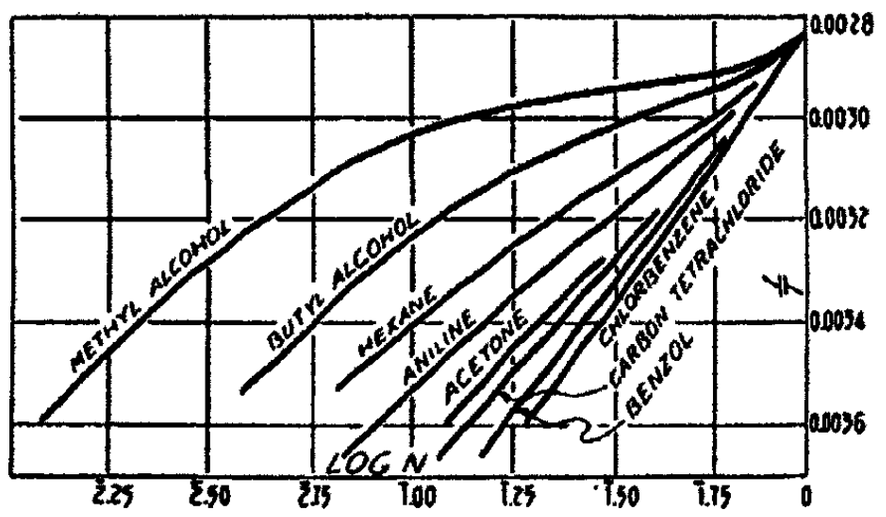



FIG. 1. Solubility Relationships of Napthalene.

Absolute, commercial methyl alcohol, with an odor very similar to that of pure ethyl alcohol, was distilled through a fractionating column. Almost all the material distilled within 0.1°. The main fraction was redistilled over sodium and the middle fraction of the distillate used for the measurements. Boiling point 64.7° corrected.

Normal butyl alcohol from the fermentation process was four times distilled through a Hempel column, employing metallic sodium as a dehydrating agent for the third distillation. Range during the last distillation 117.4° to 117.95° corrected. The fraction taken boiled from 117.6° to 117.8°.

Carbon tetrachloride was twice distilled and showed a corrected boiling point of 76.70° to 76.75°.

Technical aniline was twice distilled, the product boiled at 184.0°-184.1° under normal pressure, and showed but a slight color.

[1] Richards and Shipley: J. Am. Chem. Soc.,36,1825 (1914).

The nitrobenzene was once distilled and showed a range of not more than 0.1°. Boiling point 210.7°, corrected.

Acetic acid was prepared by the recrystallization of the C. P. glacial acid and showed a melting point of 16.5°.

The acetone was purified by means of calcium chloride and sodium amalgam, as described by Frankforter and Cohen,[1] and on distillation showed a corrected boiling point of 56.1°.

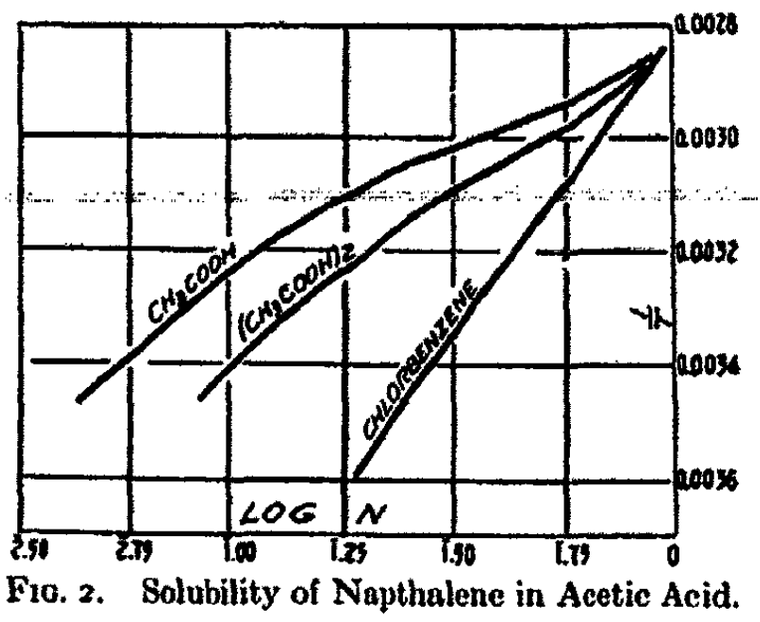



FIG. 2. Solubility of Napthalene in Acetic Acid.

The hexane first used was prepared by the distillation of a pre-war sample, which had been obtained from petroleum. The fraction employed had a boiling point of 68.0°-68.9° corrected, and probably contained small amounts of isohexanes and polymethylenes. A sample of synthetic, normal hexane, furnished by the Eastman Kodak Company, was distilled and the bulk of the material came over at 68.8°-69.0°, corrected. This fraction showed essentially the same solubility for naphthalene as the former one.

*Experimental Results.* The experimentally determined solubilities appear in Tables I to XI. From these data the mol fraction of naphthalene was calculated and plotted against the reciprocal of the absolute solubility temperature. The resulting curves, except those for toluene, acetic acid and nitro benzene, appear in Fig. 1. The curves for toluene and nitro-benzene are almost identical with that for benzene and the curve for acetic acid appears in Fig. 2. The experimental points lie much too nearly on the curves to be represented on the small scale used in the diagram. Even on the working plot, eighteen by forty inches, the deviations were in most cases very slight. The values for the logarithm of the mol fraction at points corresponding to the temperatures in Table XII were read off from the large scale plot and the values for the solubilities in terms of mol fractions of naphthalene appear in the table.

[1] Frankforter and Cohen: J. Am. Chem. Soc., 36, 1103 (1914).

TABLE I

Solubility of Naphthalene in Benzene

Preliminary Curve

| Grams Naphthalene | Grams Benzene | Solubility Point | Mol Fraction Naphthalene |
|---|---|---|---|
| 3.000 | 0.832 | 61.2° | 0.688 |
| 3.000 | 1.660 | 48.8 | 0.524 |
| 2.000 | 1.676 | 39.6 | 0.421 |
| 2.000 | 2.555 | 29.1 | 0.323 |
| 1.000 | 1.674 | 21.7 | 0.267 |
| 1.000 | 2.135 | 15.0 | 0.222 |
| 1.000 | 2.925 | 6.1 | 0.173 |

Final Curve

| | | | |
|---|---|---|---|
| 3.000 | 0.368 | 70.3 | 0.833 |
| 3.000 | 0.688 | 63.7 | 0.727 |
| 3.000 | 0.847 | 60.7 | 0.683 |
| 3.000 | 1.435 | 51.7 | 0.561 |
| 3.000 | 1.720 | 47.9 | 0.516 |
| 2.000 | 1.733 | 38.6 | 0.413 |
| 2.000 | 2.054 | 34.3 | 0.372 |
| 2.000 | 2.180 | 32.7 | 0.359 |
| 2.000 | 2.433 | 30.1 | 0.333 |
| 2.000 | 2.561 | 28.7 | 0.322 |
| 1.000 | 1.717 | 20.9 | 0.2617 |
| 1.000 | 2.182 | 13.9 | 0.2182 |
| 1.000 | 2.568 | 9.5 | 0.1917 |
| 1.340 | 3.484 | 9.0 | 0.1900 |
| 1.000 | 3.050 | 4.5 | 0.1664 |
| 1.090 | 3.480 | 3.2 | 0.1602 |
| 1.015 | 3.477 | 1.0 | 0.1510 |
| 1.000 | 3.424 | 1.1 | 0.1510 |

TABLE II

Solubility of Naphthalene in Toluene

| Grams Naphthalene | Grams Toluene | Solubility Point | Mol Fraction Naphthalene |
|---|---|---|---|
| 3.000 | 0.771 | 67.4° | 0.737 |
| 3.000 | 1.668 | 52.1 | 0.561 |
| 2.000 | 1.658 | 43.9 | 0.465 |
| 2.000 | 2.449 | 34.8 | 0.370 |
| 1.000 | 2.340 | 17.3 | 0.235 |
| 1.000 | 3.209 | 8.2 | 0.183 |

TABLE III

Solubility of Naphthalene in Chlorbenzene

| Grams Naphthalene | Grams Chlorbenzene | Solubility Point | Mol Fraction Naphthalene |
|---|---|---|---|
| 3.000 | 1.047 | 62.6° | 0.716 |
| 3.000 | 2.242 | 49.0 | 0.540 |
| 2.000 | 1.956 | 42.8 | 0.473 |
| 2.000 | 3.280 | 29.4 | 0.349 |
| 1.000 | 2.126 | 22.1 | 0.292 |
| 1.000 | 3.346 | 8.8 | 0.208 |
| 1.000 | 3.865 | 4.2 | 0.185 |

TABLE IV

Solubility of Naphthalene in Methyl Alcohol

| Grams Naphthalene | Grams Methyl alcohol | Solubility Point | Mol Fraction Naphthalene |
|---|---|---|---|
| 3.000 | 0.165 | 74.3° | 0.820 |
| 3.000 | 0.195 | 73.9 | 0.794 |
| 3.000 | 0.275 | 72.8 | 0.732 |
| 3.000 | 0.377 | 71.7 | 0.666 |
| 3.000 | 0.760 | 69.5 | 0.497 |
| 2.000 | 0.794 | 68.4 | 0.387 |
| 1.000 | 0.733 | 65.7 | 0.255 |
| 1.000 | 1.506 | 60.8 | 0.1425 |
| 1.000 | 2.192 | 56.7 | 0.1024 |
| 0.500 | 2.297 | 43.9 | 0.0516 |
| 0.500 | 3.079 | 37.4 | 0.0390 |
| 0.300 | 2.180 | 33.6 | 0.0333 |
| 0.300 | 2.866 | 26.3 | 0.0255 |
| 0.200 | 3.046 | 13.5 | 0.0163 |
| 0.100 | 2.310 | 0.8 | 0.0107 |

TABLE V

Solubility of Naphthalene in Normal Butyl Alcohol

| Grams Naphthalene | Grams Butyl Alcohol | Solubility Point | Mol Fraction Naphthalene |
|---|---|---|---|
| 3.000 | 0.184 | 76.0° | 0.905 |
| 3.000 | 0.338 | 73.9 | 0.837 |
| 3.000 | 0.543 | 71.7 | 0.762 |
| 3.000 | 0.746 | 70.1 | 0.700 |
| 2.000 | 0.743 | 68.1 | 0.609 |
| 1.000 | 0.760 | 63.2 | 0.432 |
| 1.000 | 1.520 | 56.9 | 0.276 |
| 1.000 | 2.159 | 52.3 | 0.211 |
| 0.500 | 1.550 | 46.5 | 0.1575 |
| 0.500 | 2.743 | 35.6 | 0.0953 |
| 0.400 | 2.593 | 31.6 | 0.0817 |
| 0.300 | 2.622 | 24.3 | 0.0621 |
| 0.200 | 1.897 | 22.0 | 0.0576 |
| 0.200 | 2.746 | 11.7 | 0.0405 |

TABLE VI

Solubility of Naphthalene in Carbon Tetrachloride

| Grams Naphthalene | Grams Carbon Tetrachloride | Solubility Point | Mol Fraction Naphthalene |
|---|---|---|---|
| 3.000 | 0.596 | 72.4° | 0.858 |
| 3.000 | 1.327 | 64.8 | 0.731 |
| 2.000 | 1.403 | 58.3 | 0.631 |
| 1.000 | 1.330 | 46.9 | 0.475 |
| 1.000 | 1.884 | 39.5 | 0.389 |
| 1.000 | 3.054 | 28.2 | 0.282 |
| 1.000 | 4.326 | 19.5 | 0.217 |
| 1.000 | 5.569 | 13.0 | 0.178 |
| 0.650 | 4.677 | 6.0 | 0.143 |
| 0.536 | 4.743 | 0.4 | 0.1195 |

## TABLE VII

### Solubility of Naphthalene in Aniline

| Grams Naphthalene | Grams Aniline | Solubility Point | Mol Fraction Naphthalene |
|---|---|---|---|
| 3.000 | 0.296 | 74.4° | 0.881 |
| 3.000 | 0.881 | 65.4 | 0.713 |
| 2.000 | 0.868 | 60.8 | 0.626 |
| 1.000 | 0.891 | 50.8 | 0.449 |
| 1.000 | 1.896 | 37.4 | 0.277 |
| 1.000 | 2.767 | 29.9 | 0.208 |
| 0.500 | 2.000 | 22.0 | 0.1537 |
| 0.500 | 2.968 | 12.9 | 0.1090 |
| 0.500 | 3.227 | 10.6 | 0.1012 |
| 0.400 | 3.896 | 0.6 | 0.0695 |

## TABLE VIII

### Solubility of Naphthalene in Nitrobenzene

| Grams Naphthalene | Grams Nitrobenzene | Solubility Point | Mol Fraction Naphthalene |
|---|---|---|---|
| 3.000 | 0.501 | 71.8° | 0.852 |
| 3.000 | 0.957 | 65.3 | 0.751 |
| 2.000 | 0.913 | 60.2 | 0.678 |
| 1.000 | 1.008 | 45.3 | 0.488 |
| 1.000 | 2.355 | 24.0 | 0.290 |
| 1.000 | 3.414 | 13.8 | 0.2195 |
| 0.710 | 3.548 | 2.9 | 0.1612 |

## TABLE IX

### Solubility of Naphthalene in Acetic Acid

| Grams Naphthalene | Grams Acetic Acid | Solubility Point | Mol Fraction Naphthalene for $CH_3COOH$ | Mol Fraction Naphthalene for $(CH_3COOH)_2$ |
|---|---|---|---|---|
| 3.000 | 0.313 | 75.1° | 0.818 | 0.900 |
| 3.000 | 1.010 | 68.3 | 0.582 | 0.737 |
| 2.000 | 1.028 | 64.9 | 0.477 | 0.646 |
| 1.000 | 0.907 | 59.6 | 0.341 | 0.508 |
| 1.000 | 1.929 | 50.4 | 0.1955 | 0.327 |
| 1.000 | 2.678 | 45.2 | 0.149 | 0.260 |
| 0.500 | 2.065 | 36.5 | 0.1016 | 0.185 |
| 0.500 | 2.978 | 29.0 | 0.0730 | 0.136 |
| 0.400 | 3.043 | 23.5 | 0.0580 | 0.1097 |
| 0.300 | 3.082 | 15.6 | 0.0437 | 0.0836 |

## Table X

### Solubility of Naphthalene in Hexane

| Grams Naphthalene | Grams Hexane | Solubility Point | Mol Fraction Naphthalene |
|---|---|---|---|
| 3.000 | 0.367 | 72.5° | 0.847 |
| 2.000 | 0.382 | 69.4 | 0.779 |
| 3.000 | 0.587 | 69.1 | 0.775 |
| 2.000 | 0.694 | 64.6 | 0.660 |
| 1.000 | 0.457 | 62.3 | 0.595 |
| 1.000 | 0.650* | 58.4 | 0.508 |
| 1.000 | 0.675 | 57.9 | 0.499 |
| 1.000 | 0.947 | 53.7 | 0.415 |
| 1.000 | 1.308 | 49.5 | 0.339 |
| 1.000 | 1.314* | 49.6 | 0.3385 |
| 0.800 | 1.338 | 45.8 | 0.287 |
| 0.650 | 1.335 | 42.3 | 0.2465 |
| 0.500 | 1.318 | 38.0 | 0.2031 |
| 0.500 | 1.449 | 36.1 | 0.1883 |
| 0.500 | 1.776 | 32.2 | 0.1591 |
| 0.500 | 1.935 | 30.8 | 0.148 |
| 0.300 | 1.296* | 28.5 | 0.1346 |
| 0.300 | 1.327 | 27.7 | 0.1318 |
| 0.300 | 1.914 | 19.5 | 0.0954 |
| 0.250 | 1.953* | 14.8 | 0.0792 |
| 0.200 | 2.035 | 8.7 | 0.0620 |

*Synthetic, normal hexane employed.

## Table XI

### Solubility of Naphthalene in Acetone

| Grams Naphthalene | Grams Acetone | Solubility Point | Mol Fraction Naphthalene |
|---|---|---|---|
| 3.000 | 0.324 | 69.5° | 0.805 |
| 3.000 | 0.406 | 67.2 | 0.770 |
| 3.000 | 0.604 | 62.7 | 0.693 |
| 3.000 | 0.823 | 58.5 | 0.623 |
| 2.000 | 0.773 | 52.9 | 0.540 |
| 3.000 | 1.568 | 47.2 | 0.465 |
| 2.000 | 1.570 | 39.3 | 0.366 |
| 1.000 | 0.785 | 39.3 | 0.366 |
| 1.000 | 1.059 | 32.6 | 0.300 |
| 1.000 | 1.541 | 24.2 | 0.227 |
| 1.000 | 2.305 | 14.3 | 0.1642 |
| 1.000 | 3.124 | 6.3 | 0.1266 |

TABLE XII

Solubility of Naphthalene in Various Solvents at Rounded Temperatures, expressed in Mol Fraction Naphthalene

| Temperature | Chlor-Benzene | Nitro Benzene | Benzene | Toluene | Carbon tetra-chloride | Acetone | Aniline | Hexane | Acetic Acid* | Butyl alcohol | Methyl alcohol |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 75° | 0.912 | 0.910 | 0.910 | 0.910 | 0.904 | 0.904 | 0.902 | 0.902 | 0.895 | 0.875 | 0.849 |
| 70 | 0.830 | 0.828 | 0.828 | 0.826 | 0.817 | 0.817 | 0.802 | 0.794 | 0.778 | 0.692 | 0.543 |
| 65 | 0.753 | 0.746 | 0.746 | 0.745 | 0.733 | 0.731 | 0.705 | 0.670 | 0.652 | 0.490 | 0.229 |
| 60 | 0.682 | 0.673 | 0.673 | 0.671 | 0.658 | 0.650 | 0.610 | 0.547 | 0.520 | 0.347 | 0.133 |
| 55 | 0.617 | 0.605 | 0.603 | 0.600 | 0.586 | 0.573 | 0.516 | 0.440 | 0.405 | 0.244 | 0.0912 |
| 50 | 0.555 | 0.542 | 0.540 | 0.537 | 0.515 | 0.501 | 0.437 | 0.348 | 0.319 | 0.186 | 0.0692 |
| 45 | 0.498 | 0.484 | 0.481 | 0.476 | 0.453 | 0.436 | 0.366 | 0.277 | 0.259 | 0.146 | 0.0545 |
| 40 | 0.444 | 0.432 | 0.428 | 0.422 | 0.395 | 0.378 | 0.306 | 0.222 | 0.210 | 0.116 | 0.0437 |
| 35 | 0.395 | 0.383 | 0.378 | 0.373 | 0.344 | 0.321 | 0.254 | 0.178 | 0.173 | 0.093 | 0.0352 |
| 30 | 0.352 | 0.339 | 0.333 | 0.329 | 0.299 | 0.274 | 0.209 | 0.144 | 0.142 | 0.0766 | 0.0290 |
| 25 | 0.313 | 0.298 | 0.292 | 0.289 | 0.257 | 0.233 | 0.172 | 0.119 | 0.116 | 0.0637 | 0.0241 |
| 20 | 0.277 | 0.262 | 0.257 | 0.254 | 0.221 | 0.197 | 0.143 | 0.0973 | 0.0973 | 0.0537 | 0.0203 |
| 15 | 0.243 | 0.229 | 0.225 | 0.222 | 0.188 | 0.166 | 0.119 | 0.0798 | 0.0819 | 0.0454 | 0.0171 |
| 10 | 0.215 | 0.199 | 0.195 | 0.192 | 0.161 | 0.142 | 0.0984 | 0.0650 | 0.0700 | 0.0386 | 0.0145 |
| 5 | 0.189 | 0.171 | 0.169 | | 0.137 | 0.122 | 0.0817 | | | | 0.0123 |
| 0 | | | 0.147 | | 0.117 | | 0.0684 | | | | 0.0104 |

*Acetic acid calculated as $(CH_3COOH)_2$

*Discussion of Results.* For a determination of the exact form of the ideal solubility curve for naphthalene on the basis of Raoult's Law, there is required (a) an accurate determination of the latent heat of fusion of naphthalene at its melting point and (b) a knowledge of the specific heats of solid naphthalene and of the supercooled liquid at temperatures between 0° and 80°. Since naphthalene does not supercool to any extent, it would probably be difficult to determine the heat capacity of the liquid below the melting point. Hildebrand[1] using the data of Bogojawlenski,[2] has calculated the ideal molecular solubility of naphthalene on the assumption that the difference between the solid and supercooled liquid is independent of the temperature between 80° and 25°. Since the data for the solid were given at low temperatures a rather long extrapolation to the melting point was necessary. Also, the value for the specific heat of the liquid was given only at the melting point. The results of Battelli, as given in Landolt's Tables, seem to show that the difference in specific heats of solid and liquid decreases with decreasing temperature, while the difference at the higher temperatures is greater than that found by Bogojawlenski. In view of the uncertainty of the data, it is doubtless best to neglect the variation in the heat of fusion of naphthalene over the range from 0° to 80°. It would seem, however, that the correction is in the direction of slightly increased solubility.

On the assumption that the latent heat of fusion is independent of the temperature, the modified Raoult expression

$$\log N = \frac{-L_F}{4.58}\left(\frac{1}{T} - \frac{1}{T_m}\right)$$

shows that the log N versus 1/T curve is a straight line whose origin is determined by the melting point of the naphthalene and whose slope is $\frac{-L_F}{4.58}$ where $L_F$ is the molal heat of fusion. The value of $L_f$ of Bogojawlenski would give a slope of 970 while the mean of the three other, earlier determined values, cited in Landolt's Tables would give 995. Since the upper section of the chlorbenzene-naphthalene curve has a slope of 970, a value toward which all the other curves tend in dilute solution, the value obtained by Bogojawlenski seems the more probable.

Since the writing of this paper the results of Andrews, Lynn, and Johnston[3] have appeared giving data with respect to the heats of fusion and specific heats of numerous organic compounds, among them naphthalene. The value of the molal heat of fusion is found to be 4540 calories which is in substantial agreement with the earlier data cited in Landolt's Tables and would give a slope for the ideal solubility curve of naphthalene of 995 instead of the 970 obtained from the data of Bogojawlenski and that found for the system naphthalene-chlorbenzene as found by the author. The difference between

[1] "Solubility," 37 (1924).
[2] Bogojawlenski: Chem. Zent., 5, 92, 945 (1905).
[3] Andrews, Lynn and Johnston: J. Am. Chem. Soc., 48, 1274 (1926).

the molal heat capacities of liquid and solid is given as 1.2 calories at the melting point, which would indicate that the molal heat of fusion does not vary much with the temperature at this point, thus giving a very nearly straight log N versus 1/T curve. At the lower temperatures, however, the heat content of the solid varies rather rapidly with the temperature and if the heat content curve of solid and liquid are extrapolated to the absolute zero, the former is greater thus indicating that heat is given out in the melting which is quite improbable. Since there is considerable question as to how far the extrapolation of the heat content of the liquid may be carried, it is doubtful if the data are sufficient to calculate the exact form of the solubility curve for naphthalene.

Since sufficiently accurate data are not at hand for the fixing of the exact form of the ideal solubility curve, the system naphthalene-chlorbenzene will be considered as ideal, at least as low as 25°, where the deviation from the straight line relationship for the log N versus 1/T curve begins. The mol fraction naphthalene in a saturated solution at this temperature is 0.32. Over this range the activity of naphthalene in a chlorbenzene solution is proportional to the mol fraction. It is possible, that at lower temperatures and smaller mol fractions of naphthalene, Raoult's law does not hold, but in any case the deviations must be small.

All the curves shown in Fig. 1 are of the same type, with a slight modification in the case of chlorbenzene. This type is the reversed S form described by Mortimer.[1] Such a curve might well be produced if the deviations from Raoult's law were functions of two variables which tended to act in opposite directions. If this is the case for the above systems, it is probable that both causes are continuously operative throughout the entire curve. It is evident from an inspection of the diagram, that the curves for all solutions which are very rich in naphthalene approach the ideal curve. It cannot be decided from the data presented whether the solution is ideal at certain finite concentrations of solvent or whether it approaches such a condition only as a limiting case when the mol fraction of naphthalene approaches one.

At somewhat lower naphthalene concentrations it is apparent that a factor is most strongly operative which causes positive deviations from Raoult's law and solubilities less than the ideal. The amount of such deviations, as would be predicted from Hildebrand's theory, increases with increasing differences in internal pressure and the relative positions of the curves are exactly as would be expected on the basis of this theory. The curvature in this region is very marked in the case of substances which differ considerably from naphthalene in internal pressure.

There follows a region in which the log N versus 1/T curves are relatively straight. In the case of the curves for methyl and butyl alcohols, which show large deviations from Raoult's law, the observed points at no time lie on a perfectly straight line, but in some of the other curves the deviations from the straight line relationship are within the limits of experimental error over a

[1] Mortimer: J. Am. Chem. Soc., **44**, 1416 (1922); **45**, 633 (1923).

considerable range. It is probable that this phenomenon is due to a balancing of the two factors. The limits within which the approximately linear relationship holds appear in Table XII. For nitrobenzene, benzene and toluene, the accuracy of the data does not permit the determination of the upper limit. For the other substances it may be stated that the straight line relationship begins at a mol fraction of between 0.60 and 0.70 of naphthalene and continues to a mol fraction of between 0.20 and 0.30. These figures are, of course, only approximations but they indicate the range over which the straight-line relationship may reasonably be expected to hold.

Owing to the fact that the upper section of most of the log N versus 1/T curves is not straight, it is evident that the prolongation of the relatively straight portion will not intersect the 1/T axis at a value corresponding to the melting point of naphthalene. Moreover, the direction of curvature is such as to bring the intersection at a lower temperature. The temperatures of these intersections appear in the last column on Table XIII. Since the log N versus 1/T curve must of necessity terminate at the melting point it is evident that only the curve for chlorbenzene is straight clear to that point. There must be a deviation from this linear relationship in the case of nitrobenzene, benzene and toluene although it is impossible to determine the exact point at which such deviation begins. These facts lend considerable support to the idea that naphthalene and chlorbenzene form an almost ideal solution. In case the reversed S type of curve should be general, it would be possible to determine the ideal solubility curve with considerable accuracy by the above procedure. The slope of this curve would also give a value for the latent heat of fusion of the solid.

Even though the log N versus 1/T curve is a straight line over a considerable range, it is evident that the complete solubility curve cannot be exactly determined from a single solubility determination and the melting point, or from the slope of the linear portion of the curve and the melting point. In case naphthalene and the solvent do not differ too much in internal pressure the slope of the linear portion of the curve is given rather accurately by the method of Mortimer,[1] as shown in Table XIV. Since in the above case the intercept on the 1/T axis lies but slightly below the melting point, there is no great error in fixing the solubility curve. When, however, the internal pressures are very different, the calculated slope by no means agrees with the experimental as appears in Table XIV. The agreement, as appears in column five of the table, is somewhat closer when the experimental slope is determined by passing a line through the center of the straight portion of the curve and the point on the 1/T axis corresponding to the melting point. Such a procedure gives at best only a vague idea as to the general shape of the curve and that only at temperatures not far from the melting point of the solute.[2]

[1] Mortimer: J. Am. Chem. Soc., **44**, 1416 (1922); **45**, 633 (1923).

[2] See also Hildebrand: "Solubility," 159 (1924)

TABLE XIII

Range in which the Log N versus 1/T Curve for Naphthalene is Linear

| Solvent | Upper Limit Concentration in Mol Fraction Naphthalene | Temperature | Lower Limit Concentration in Mol Fraction Naphthalene | Temperature | Temperature of Intercept on 1/T Axis. |
|---|---|---|---|---|---|
| Chlorbenzene | 1.00 | 80.1° | 0.32 | 25° | 80.1 |
| Nitrobenzene | ? | ? | ? | ? | 79.9 |
| Benzene | ? | ? | 0.23 | 16° | 79.7 |
| Toluene | ? | ? | 0.23 | 16° | 79.7 |
| Carbon tetrachloride | 0.59 | 55° | 0.18 | 13° | 78.0 |
| Acetone | 0.52 | 51° | 0.18 | 17° | 77.1 |
| Aniline | 0.65 | 62° | 0.19 | 28° | 74.6 |
| Hexane | 0.66 | 65° | 0.26 | 43° | 74.6 |
| Butyl Alcohol | 0.68 | 69° | 0.26 | 56° | 75.1 |
| Methyl Alcohol | 0.63 | 71° | 0.23 | 65° | 74.0 |

TABLE XIV

Calculated and Observed Slopes of Linear Portion of Log N versus 1/T Curves

| Solvent | Internal Pressure Relative to Naphthalene | Calculated slope | Observed slope | Modified slope |
|---|---|---|---|---|
| Hexane | 0.56 | 1740 | 2050 | 1690 |
| Carbon tetrachloride | 0.84 | 1150 | 1160 | |
| Toluene | 0.93 | 1040 | 1030 | |
| Benzene | 0.94 | 1030 | 1020 | |
| Chlorbenzene | 0.98 | 990 | 970 | |
| Nitro benzene | 1.07 | 1040 | 1010 | |
| Acetone | 1.32 | 1280 | 1280 | 1220 |
| Aniline | 1.46 | 1420 | 1560 | 1400 |
| Methyl Alcohol | 3.35 | 3250 | 8600 | 4200 |

In all cases, except possibly for nitrobenzene, there is at the lowest temperatures employed a deviation from the approximately linear relationship in the direction of increased solubility. In no case except for chlorbenzene does the solubility attained exceed the ideal but the slope of the benzene and toluene curves at the lower temperatures reported is less than the ideal, indicating that the solubility might equal or exceed the ideal if the measurements were carried still lower. This doubtless accounts for the fact that Washburn and Read[1] are able to calculate the eutectic temperature of the naphthalene benzene system with such accuracy, $-3.56°$ instead of the observed value of $-3.48°$. They have also used the earlier and somewhat higher value for the latent heat of fusion and, therefore, obtain a slightly lower value for the ideal solubility than that employed in this paper. In the other cases than those noted above the slope of the lower section of the curves is greater than the

[1] Washburn and Read: Proc. Nat. Acad. Sci., 1, 191 (1915).

ideal. It is very noticeable that the curves for solvents which differ most from the ideal show the greatest changes in slope in this region and there is some evidence, though not conclusive, that the polar solvents show a somewhat greater change than the non polar ones which differ in internal pressure from naphthalene by about the same amount.

When the mol fraction of naphthalene for mixtures with acetic acid is calculated on the basis of the usual formula for the latter, the resulting curve approaches the 1/T axis at a very different angle from the ideal as is seen in the upper curve of Fig. 2. If, however, double the usual molecular weight is assigned to the acid, the resulting curve is perfectly normal. It is not represented in Fig. 1, since during a great part of its course it nearly coincides with that for hexane. It is well known that acetic acid polymerizes in benzene to form $(CH_3COOH)_2$ but the fact that this polymerization persists to such high temperatures as 80° in other non-polar solvents, is rather remarkable. The phenomenon is probably connected with the fact that the acetic acid contains two strongly polar groups, the hydroxyl and carbonyl. It would be possible for such substances to form ring compounds of much less polarity than that possessed by the original molecule, especially when present in a non-polar environment.

It seems clear that, for the solubilities of naphthalene, at least two influences cause deviations from Raoult's law. The one acts chiefly at concentrations approaching pure naphthalene in such a way as to cause positive deviations and decreased solubilities while the other acts at low naphthalene concentrations and tends to neutralize the former effect. The first influence may be ascribed, as is done by Hildebrand, to differences of internal pressure of solvent and solute. The second is, perhaps, due to polarity effects, though other factors may also be active. Further investigations, particularly with more strongly polar solutes than naphthalene, are now in progress to decide this question.

*Summary and Conclusions.* 1. The solubilities of naphthalene in eleven different solvents of widely varying properties have been measured by means of the synthetic method. The range of temperature covered was between 0° and 80°.

2. The system naphthalene-chlorbenzene forms as nearly an ideal solution as can be determined from the data at present available.

3. It is evident from a plot of the logarithm of the mol fraction against the reciprocal of the absolute temperature, that all of the curves belong to a common type, the reversed S form of Mortimer.

4. This type seems to be due to the effect of at least two factors which tend to cause deviations from Raoult's law. The factor which is most important at high naphthalene concentrations acts to produce positive deviations from the law and solubilities less than the ideal. It is undoubtedly due to differences in internal pressure of solvent and solute as postulated by Hildebrand. At the lower naphthalene concentrations another factor enters and

tends to partially neutralize the first but does not, within the range of temperatures studied, cause a solubility greater than the ideal except possibly in the case of chlorbenzene.

5. A method has been suggested, in case the above relationship should prove to be general, for the determination of the ideal solubility curve of a solute and its latent heat of fusion.

6. The complete solubility curve cannot be determined from the slope of the logarithmic curve and the melting point of the pure solute, unless the solvent has very nearly the same internal pressure as the solute.

7. Acetic acid polymerizes to form double molecules in naphthalene at the melting point of the latter.

The author is indebted to Dr. J. H. Hildebrand of the University of California for several valuable suggestions for the presentation of the material contained in this paper.

1334
316 - 540

# THE RATE OF OXIDATION OF LINSEED OIL*

BY WILLIAM ROGERS, JR. AND HUGH STOTT TAYLOR

Considering the technical importance of the drying of oils, it is surprising that accurate quantitative study of their rates of oxidation has only recently been made. The early experiments were undertaken in order to fix the composition of linseed oil from a study of the oxidation products. Although Cloez[1] observed and studied the volatile products of oxidation; he used the increase in weight of a linseed oil film as a measure of the rate of oxidation. He showed the accelerating effect of different coloured light, technical driers, and partially oxidized oil on this rate. Plotting the change in weight against time, he obtained curves which developed slowly, rose steeply to a maximum, and then fell back to a level of constant weight. Coffey[2] points out that Mulder in 1867 recognized the formation of volatile products of oxidation in this reaction. Yet subsequent workers neglected to allow for the effect of their formation when determining the amount of oxygen taken up by the oil.

Bauer and Hazura[3] allowed a film of oil, containing lead oxide, to dry on glass plates and then analyzed the film. This is permissible in a study of the solid products of oxidation, and is adaptable to a qualitative estimation of the composition of the original oil, but a quantitative statement concerning this composition is hardly possible by this method.

In order to obtain a method for comparing the rates of drying of variously treated oils and the efficiency of commercial driers, Kissling[4] showed the reaction was purely chemical and independent of bacteria, and used the increase in weight of a film of the oil to indicate the rate of oxidation. His data showed the formation of volatile products. He was aware of this fact[5] but was satisfied that his test gave comparable results[6]. Using the time required by an oil film to dry as the criterion for the rate of oxidation, the dryness was determined by touching the film, Amsel[7] offers a method for detecting the presence of adulterants in linseed oil. In a subsequent paper[8] he used this method to study the drying efficiencies of different driers. That such methods would lead to unsatisfactory results was inevitable. The controversy which followed between Kissling[9], Amsel,[10] Lippert,[11] and Weger[12] is a testimony to the inaccuracy of their methods.

*Contribution from the Laboratory of Physical Chemistry, Princeton University.

[1] Compt. rend., 61, 236, 321, 981 (1865).
[2] J. Chem. Soc., 119, 1152 (1921).
[3] Z. angew. Chem., 1, 455 (1888).
[4] Z. angew. Chem., 4, 395 (1891).
[5] Z. angew. Chem., 8, 44 (1895).
[6] Z. angew. Chem., 11, 361 (1898).
[7] Z. angew. Chem., 8, 73 (1895).
[8] Z. angew. Chem., 8, 262 (1895).
[9] Z. angew. Chem., 4, 395 (1891); 8, 44 (1895); 11, 361, 613 (1898).
[10] Z. angew. Chem., 9, 429 (1896); 10, 303, 344, 369 (1897).
[11] Z. angew. Chem., 10, 306 (1897); 11, 412 (1898); 13, 133 (1900); 16, 365 (1903).
[12] Z. angew. Chem., 9, 531 (1896); 10, 401, 542, 560 (1897); 11, 49c, 507, 614 (1898); J. Soc. Chem. Ind., 17, 257, 360 (1898).

Weger showed the wide discrepancy between Kissling's results which used the time at which the film attained maximum weight as the criterion for dryness, and his own results which relied on the actual hardening of the film. This he attributed to the fact that maximum weight did not necessarily coincide with the point at which the film dried; and also showed that four factors, (a) Variation in temperature, (b) Variation of light intensity, (c) Changes in humidity, (d) Variability in the air currents, produce great differences in the time using either method. He came to the conclusion that only those results obtained by running the reactions simultaneously and side by side were comparable. This is true qualitatively but for any knowledge of the process a controllable and quantitative method for studying the oxidation is necessary. The discussion brought out two interesting points, (a) metallic driers must be soluble in the oil to give accelerated drying,[1] (b) The above variables must be controlled to give comparable results.

With these facts in mind, Genthe[2] devised a method which did give reproducible results and marked the first determination of the true rate of oxidation. He supported the oil on filter paper which eliminated the effects due to a thick film, and suspended this paper in a flask closed by a ground-glass stopper through which a manometer tube passed. Solid potassium hydroxide served to absorb the moisture in the flask and also to absorb the volatile products of oxidation. Thus he could always duplicate the temperature by immersing the flask in a thermostat, shut out the light by use of brown glass vessels, and eliminate the effect of moisture. The advisability of these precautions is shown by the reproducibility of his results. This offers a course of procedure which gives chemically significant and comparable results.

He noted that it was necessary to clean his pipettes and vessels with cleaning solution after each run in order to duplicate his results. This is an indication of the effect of small concentrations of catalyst; and is borne out by our results which show marked acceleration with only 0.0003 per cent of cobalt as cobalt linoleate to catalyse the reaction. The percentage is calculated as percentage of metal. With Uviol glass vessels he found that the ultra-violet light from a mercury vapour lamp caused the same degree of oxidation in one day which the dark reaction reached in fifty-five days. Weger (loc. cit.) had previously shown that direct sunlight gave a hard film, using manganese salts as driers, in one half the time required in diffused light. One very important observation is shown from his curves which represent the reactions using air and pure oxygen, i. e. raising the oxygen pressure from 150 mm. to 760 mm. The raw linseed oil is oxidized at only a slightly greater rate in pure oxygen at room temperature than in air, while the catalysed reaction is not accelerated at all by the use of pure oxygen. At 95° C pure oxygen does not alter the rate until the upper flat portion of the curve is reached. The effect, as shown by his curves, of oxidizing the oil with no potassium hydroxide in the flask to absorb the volatile products is very instructive and indicates why results from

[1] Loesner also arrives at this conclusion, J. Soc. Chem. Ind., 17, 608 (1898).
[2] Z. angew. Chem., 19, 2087 (1906).

methods which neglect this factor can have little or no value. His results are expressed in manometer readings from each determination and are thus a function of the particular size of vessel used. He does state, however, that his final results correspond to about 26 per cent of oxygen absorbed, 34.7 per cent in the case of pure oxygen at 95° C.

Those of Fahrion's results[1] which are based on conclusions depending on the increase in weight of a film of oil as a measure of the oxidation are not very conclusive. The same applies to Fokin's results.[2]

Genthe's work apparently made little impression. Sabin,[3] who had tried to measure the volatile products of oxidation, used the change in weight of a film to show the rate of oxidation. He duplicated the observations of Cloez (loc. cit.) on the shape of the curves obtained by plotting this change against time. This phenomenon is also disclosed on analyzing Kissling's data.

In an attempt to show a relation between the iodine number of the oil and the total percentage of oxygen it will absorb, Ingle[4] also uses the increase in weight of an oil film to indicate the amount of oxygen taken up. He also observed that the weight decreases after the maximum is reached, a direct evidence of volatile products of oxidation, yet neglected them in his value for the final percentage of oxygen taken up. This renders his explanation of the mechanism of the reaction, which is based on this value, of doubtful significance. He later used the time required for the oil supported on cotton wool to reach 200° C in his tester as a characteristic property,[5] and compares the relative efficiency of different metallic soaps in this respect.

Comparison of the rate of oxidation of linseed, soya-bean, china-wood, and fish oils is given by Rodman, Weith, and Brock[6] using the change of weight in films of the oils as a measure of this rate.

Baly[7] shows the absence of lead in the vapours from paints and shows the presence of unsaturated aldehydes. Gardner[8] arrives at the same conclusion as Baly and also detects the presence of carbon monoxide in the vapours. He states that the character of a pigment affects the nature of the volatile products. However, Klein[9] has questioned the validity of this result and indicates that the amount of carbon monoxide found by Gardner can be accounted for by the action of the sulphuric acid used in the absorption system on the formic acid in the vapours. But King[10], taking the precautions suggested by Klein, found carbon monoxide present.

---

[1] Z. angew. Chem., 4, 540 (1891); 5, 171 (1892); 23 I, 722 (1910); Chem. Ztg., 28, 1196 (1904).
[2] Z. angew. Chem., 22 II, 1451 (1909).
[3] J. Soc. Chem. Ind., 25, 579 (1906); J. Ind. Eng. Chem., 3, 84 (1911).
[4] J. Soc. Chem. Ind., 32, 639 (1913).
[5] J. Soc. Chem. Ind., 35, 454 (1916); 36, 317 (1917).
[6] J. Ind. Eng. Chem., 5, 630 (1913).
[7] J. Soc. Chem. Ind., 31, 515 (1912).
[8] J. Ind. Eng. Chem., 6, 91 (1914).
[9] J. Ind. Eng. Chem., 7, 99 (1915).
[10] J. Ind. Eng. Chem., 7, 502 (1915).

Wise and Duncan[1] show the effect of various metallic soaps on the rate of change in weight of oil films, and by a close control of conditions obtain smooth curves. The significance of the maxima in these curves is explained by Friend.[2] They represent an equilibrium between amounts of oxygen taken up and the loss of volatile products. Any condition altering the loss will alter this maximum. This would make all the previous figures for the total percentage of oxygen absorbed much too low, the difference between them and the true value being roughly the percentage of volatile products formed. The values range from 15 to 20 per cent, the usual figure obtained is 18 per cent. Olsen and Ratner[3] supported linseed oil on glass wool and passed dry, carbon dioxide free, air over it for a period of 74 days. The volatile products were absorbed from the air coming from the flask containing the oil. The oil increased in weight by 18.05 per cent, 14.51 per cent of water was formed, and 5.21 per cent of carbon dioxide and organic matter was given off, thus giving a total of 37.80 per cent for the final amount of oxygen absorbed.

Coffey[4] credits Friend (Proc. Paint and Varnish Soc. May, 1914) with the first true oxygen absorption curves. It would seem that Genthe (loc.cit.) has the prior claim. In his calculations he assumes that the rate of oxidation is dependent on the oxygen pressure. However, Genthe has shown that this is not the case at 95° C and over the time used by Coffey. His curves are thus too steep and would have been more nearly correct had he neglected to correct for the variation in oxygen pressure during the reaction. Recently Rhodes and van Wirt[5] have raised the figure for final oxygen absorption, which Coffey placed at 28 per cent, to 36 per cent. The higher value is supported by Olsen and Ratner (loc. cit.) and by Genthe using pure oxygen at 95° C. Had Coffey extended his observations over a greater period of time he would have undoubtedly arrived at a higher figure. Our experiments have shown that even when 36 per cent of oxygen has been absorbed oxidation is still occurring though slowly. In light the oxidation is faster and may be continued until the whole film is oxidized.

In a later paper, Coffey[6] attempts to prove that driers are not catalysts. He observed that when he dusted the surface of the oil with drier his values for final oxygen absorption were lowered, thus showing that they change the course of the reaction. He is not sustained in this by Rhodes and van Wirt nor by Genthe. The result is probably due to his method of dusting the surface of the oil with the drier, thus covering the surface; and, as Weger has pointed out, a drier must be intimately mixed if not in solution with the oil to be effective. Consequently his deduction that driers are not catalysts is erroneous.

---

[1] J. Ind. Eng. Chem., 7, 202 (1915).
[2] J. Chem. Soc., 111, 164 (1917).
[3] J. Soc. Chem. Ind., 31, 937 (1912).
[4] J. Chem. Soc., 119, 1152, 1408 (1921).
[5] J. Ind. Eng. Chem., 15, 1125 (1923).
[6] J. Chem. Soc., 121, 17 (1922).

His method of dusting probably produced metallic soaps and hydrolysed products of different oxidation capacities.

The above résumé of the literature concerning the rate of oxidation of linseed oil is given to show the difficulties in approaching a problem of this sort. Most of the data are confusing and often contradictory. Statements to the effect that sunlight cuts the drying time in half are not very enlightening unless we have a definite criterion for dryness and know the intensity of the light falling on the oil. Comparison of the relative efficiency of driers as well as different concentrations of the same drier are not reliable unless we have a reproducible method for the study of the reaction. It is felt by us that the method originally proposed by Genthe, and used with practical modifications by Coffey and Rhodes and van Wirt, offers such a possibility.

The action of inhibitors on different autoxidizable organic compounds such as styrolene, aldehydes, and acrolein has been studied by Moureu and Dufraisse.[1] The inhibitors in general are compounds of the phenol type such as naphthol, hydroquinone, pyrogallol, and the like. Their conclusions are, that inhibitors are true negative catalysts, that they remain unchanged at the end of the reaction, and in no way alter the total amount of oxygen absorbed. They only reduce the rate of the reaction. They found that a film of linseed oil containing an inhibitor remained in the fluid state for three years.

This research was undertaken to give a convenient method for determining the rate of oxidation of non-volatile oils at different temperatures, to study the effect of varying the concentration of drier on the rate of oxidation of linseed oil, to note the action of inhibitors on the catalysed and normal reactions, to show the effect of temperature on these reactions, and to give a quantitative statement on the effect of light on the reaction.

## Experimental Part

The apparatus used was essentially that proposed by Genthe, with practical modifications suggested by experimental difficulties met in an earlier investigation. It consisted of a vessel of the gas-wash-bottle type, about 200 cc. in volume. It was fitted with a mercury sealed ground glass stopper, having inlet and outlet tubes of the usual form. A vacuum-tight stop-cock was sealed to the inlet tube, a manometer to the outlet tube. For use at 100° C. the vessel was made in test tube form.

The oil was made up in solutions of the same strength, so that one cubic centimeter of solution contained 0.200 g. of oil. The drier was added as an 8 per cent solution of cobalt linoleate in turpentine. The required amount of drier or inhibitor was weighed in a 50 cc. volumetric flask, 10 g. of oil were then weighed in the flask, and the contents diluted to the mark with absolute ether or ligroine (B.P. 50°-60°). A piece of filter paper, 15 cm. x 6 cm., folded to go in the vessel readily absorbs one cubic centimeter of such solutions. The bottom of the vessel was covered with a layer of grains of potassium hydroxide and covered with glass wool. The solvent was partially evaporated before placing the paper in the reaction vessel. The oiled paper

[1] Compt. rend., **174**, 258; **175**, (1922); **176**, 624, 797 (1923).

was put in place, the stopper fitted and sealed with mercury, and a current of dry carbon dioxide free air blown through the apparatus for five minutes. It was then placed in the thermostat, a rapid current of air passed through for one minute, and one minute allowed for filling the manometer. The stopcock was closed and readings made at regular intervals. When the dimunition in pressure reached 100 mm. the oxygen was replenished from a burette at known conditions of temperature and pressure. This volume of oxygen gave a calibration for the apparatus. From this calibration the manometer readings were transformed to percentage of oxygen taken up, expressed in terms of per cent by weight of oil.

Coffey (loc. cit.) has drawn atten'ion to the futility of making equations with any physical significance fit the oxidation curves of such a complex mixture as linseed oil. Consequently it has been deemed best to use the curves themselves as the medium for showing our results.

The following is a typical set of data for the curves.

TABLE I

Rate of oxidation of linseed oil with 0.003% Co at 40° C.

| Time in min. | Manometer readings in mm. | Atmospheric pressure. | Corrected manometer readings. | Percentage of oxygen absorbed. |
|---|---|---|---|---|
| 0 | 0.0 | 750 | 0.0 | 0.00 |
| 23 | 0.0 | 750 | 0.0 | 0.00 |
| 30 | −1.0 | 750 | −1.0 | 0.19 |
| 40 | −2.0 | 750 | −2.0 | 0.37 |
| 60 | −6.0 | 750 | −6.0 | 1.11 |
| 80 | −12.0 | 750 | −12.0 | 2.22 |
| 100 | −19.5 | 750 | −19.5 | 3.61 |
| 120 | −27.5 | 750 | −27.5 | 5.10 |
| 140 | −37.0 | 750 | −37.0 | 6.86 |
| 160 | −46.0 | 750 | −46.0 | 8.53 |
| 180 | −54.0 | 750 | −54.0 | 10.00 |
| 200 | −62.0 | 750 | −62.0 | 11.11 |
| 220 | −69.0 | 750 | −69.0 | 12.80 |
| 240 | −75.0 | 750 | −75.0 | 13.90 |
| 280 | −84.5 | 751 | −83.5 | 15.65 |
| 380 | −100.0 | 754 | −96.0 | 17.77 |
| | 0.0 | | | |
| 410 | −2.0 | 754 | −98.0 | 18.15 |
| 580 | −17.0 | 757 | −110.0 | 20.40 |
| 600 | −18.0 | 757 | −111.0 | 20.59 |
| 1120 | −44.0 | 760 | −134.0 | 24.80 |
| 1520 | −64.0 | 763 | −151.0 | 28.00 |
| 2660 | −74.5 | 767 | −157.5 | 29.40 |

When the manometer read 100 mm., after 380 min., the oxygen was replenished from a burette; 28.40 cc. of oxygen at 24°.0 C. and 754 mm. were required. This was equivalent to 25.91 cc. at standard conditions, and from

the following calculation, $25.91 \times 96/100 = 24.88$, the amount of oxygen actually absorbed is obtained. This corresponded to 17.77 per cent of oxygen. From this value, the value of each division on the manometer scale can be determined and the readings transformed to percentage of oxygen absorbed. The percentages so obtained are plotted against time, and the curves drawn through these points represent the rate of oxidation of the oil.

## Discussion of Results

The effect of the temperature on the rate of oxidation of raw linseed oil is shown in Fig. 1. The increase in temperature has shortened but not

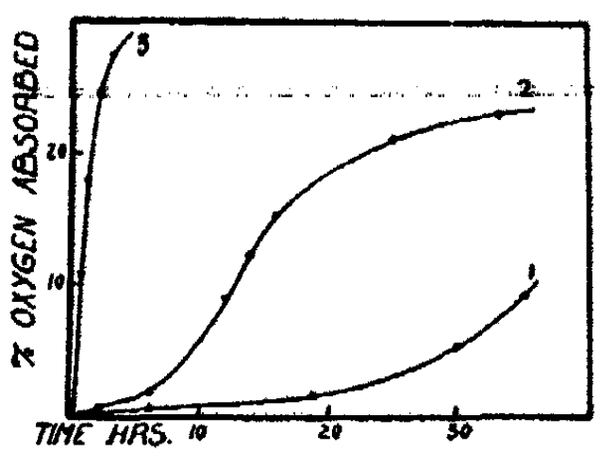



FIG. 1
Linseed Oil
Curve 1 at 40°, Curve 2 at 50°, Curve 3 at 100°.

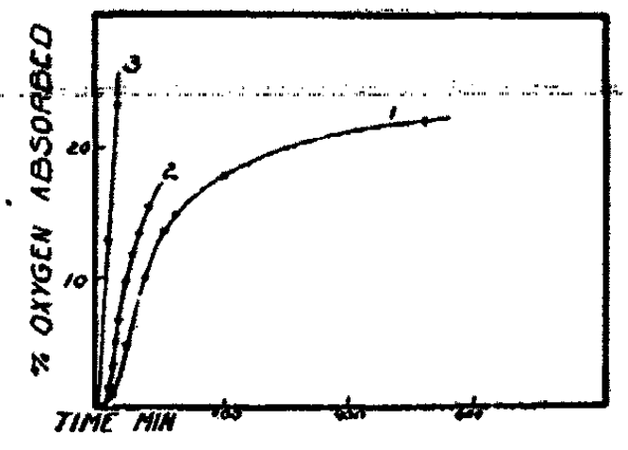



FIG. 2
Linseed Oil with 0.03% Co.
Curve 1 at 40°, Curve 2 at 50°, Curve 3 at 100°.

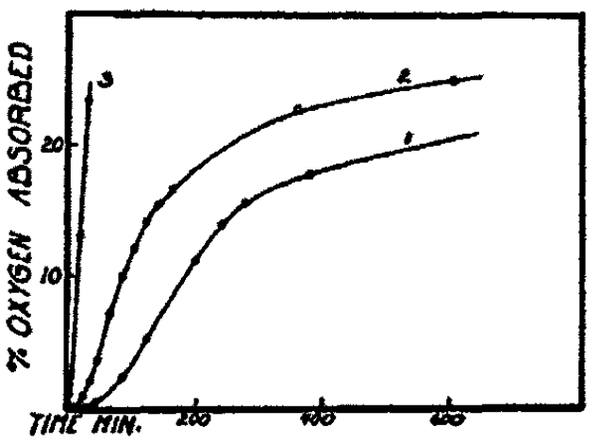



FIG. 3
Linseed Oil with 0.003% Co.
Curve 1 at 40°, Curve 2 at 50°, Curve 3 at 100°.

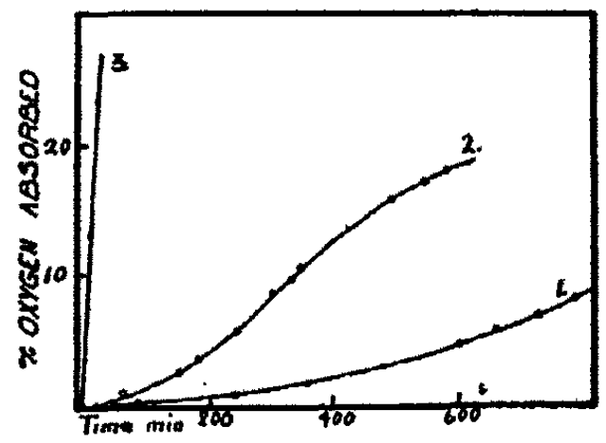



FIG. 4
Linseed Oil with 0.0003% Co.
Curve 1 at 40°, Curve 2 at 50°, Curve 3 at 100°.

eliminated the induction period. This is not apparent in the curve representing the reaction at 100° due to the large units employed as abscissae but will be shown later.

Cobalt linoleate used as a catalyst does not eliminate this induction period as shown in Figs. 2, 3, and 4. The catalyst was used in three different concentrations corresponding to 0.0003%, 0.003%, and 0.03% of cobalt. These Figs. show the effect of increasing the concentration of the catalyst and increasing the temperature. From Figs. 2 and 3 it is interesting to note that

at 40°, 0.03% of cobalt gives approximately the same rate of oxidation, up to 16% of oxygen absorbed, as 0.003% of cobalt at 50°. Over this part of the curve an increase of ten degrees in temperature is equal to a ten-fold increase in drier.

As the concentration of the drier is increased the effect of increasing temperature is less marked. For instance, the increase in the rate of oxidation indicated in curve 2, Fig. 2 over that of curve 1, Fig. 2 is not as great as the increase of curve 2, Fig. 3 over that of curve 1, Fig. 3. In other words, using 0.03% of cobalt there is not as great an increase in the rate of oxidation at

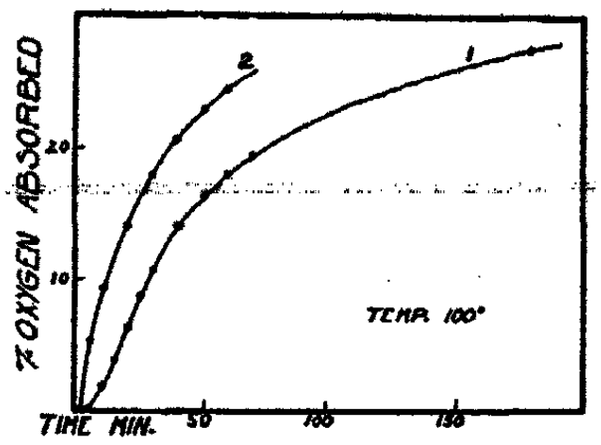



FIG. 5

Curve 1 Linseed Oil

Curve 2 { Linseed Oil with 0.003% Co.
Linseed Oil with 0.003% Co.
Linseed Oil with 0.03% Co.

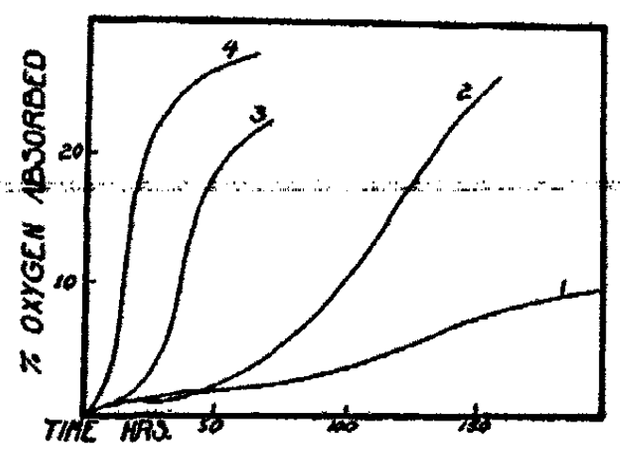



FIG. 6

Curve 1 Linseed Oil + 1% Hydroquinone at 40°
Curve 2 Linseed Oil + 1% Hydroquinone at 50°
Curve 3 Linseed Oil at 40°
Curve 4 Linseed Oil at 50°

50° over that at 40° as in the case of 0.003% of cobalt over the same temperature range. The same applies to curves 1 and 2, Fig. 4 compared with curves 1 and 2 in Fig. 3. A temperature rise from 40° to 50° gives a greater increase in reaction rate using 0.0003% of cobalt than using 0.003% of cobalt.

As the concentration of the catalyst is increased, the induction period is shortened but never eliminated. The general shape of the curve is also not affected. These facts support the theory that the driers act as catalysts for the formation of the auto-catalytic substances formed during the reaction.

Furthermore, at any definite temperature, as the catalyst concentration is increased, the rate of oxidation approaches a maximum value. This indicates that the effect of successive increments in the concentration of the drier is not directly proportional to this increase; and at any temperature a point will be reached beyond which the increase will not further accelerate the rate of oxidation. A startling demonstration of this is shown in curve 2, Fig. 5 which represents the rate of oxidation of the catalysed reaction, using the three different concentrations indicated, at 100°. It means that an hundred-fold increase in the concentration of the catalyst produces no further acceleration in the rate of reaction. Weger (loc. cit.) has already shown that an increase of 0.04% to 0.84% of manganese as manganese resinate, and an increase of 0.1 to 0.7 per cent of manganese as manganese linoleate did not appreciably affect the time required for a linseed oil film to harden at room temperature.

Much credence cannot be attached, however, to results determined from the touching method. But these curves show the truth of Weger's deduction that increasing the concentration of drier beyond a certain value will not further accelerate the rate of oxidation.

An attempt was made to study the effect of inhibitors on the normal and catalysed rates of reaction. Hydroquinone was first tried. The results with this inhibitor were very unsatisfactory. The curves could not be dulpicated within the range of accuracy desired. Fig. 6 shows the average result of the runs at 40° and 50°. Curve 1 Fig. 7 is the average result of ten runs. They do show the trend of the results with inhibitors. This variability may be attributed to the insolubility of hydroquinone in the oil. The heterogeneity of distribution resulting from the separation when the solvent was evaporated would cause the different results. To test this idea 5 mg. of hydroquinone were shaken with 5 cc. of linseed oil at 40° and did not dissolve.

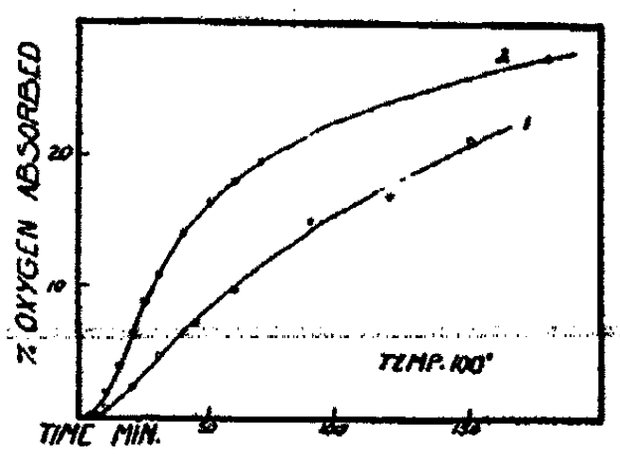



FIG. 7
Curve 1 Linseed Oil + 1% Hydroquinone
Curve 2 Linseed Oil

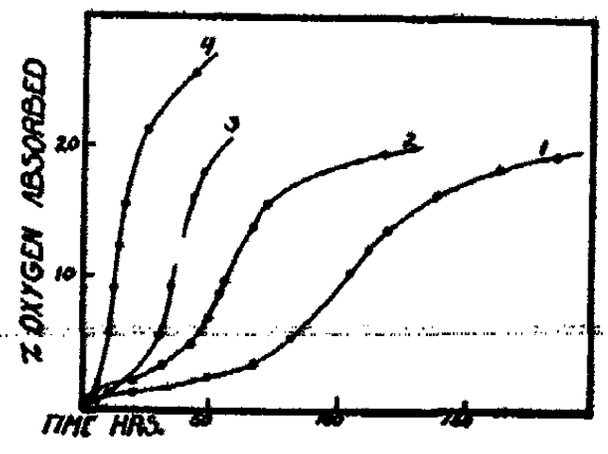



FIG. 8
Curve 1 Linseed Oil+1% β- Naphthol at 40°
Curve 2 Linseed Oil+1% β- Naphthol at 50°.
Curve 3 Linseed Oil at 40°
Curve 4 Linseed Oil at 50°

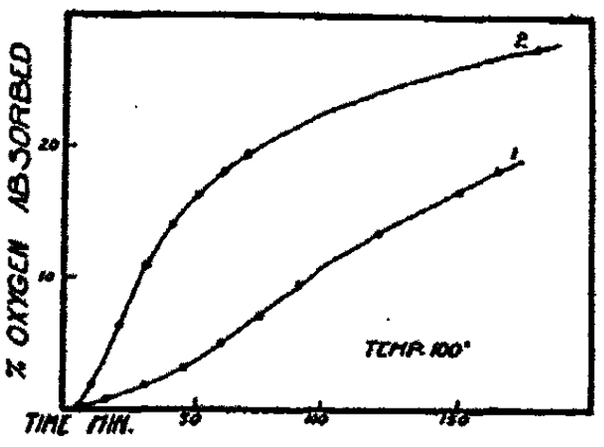



FIG. 9
Curve 1 Linseed Oil+1% β- Naphthol.
Curve 2 Linseed Oil.

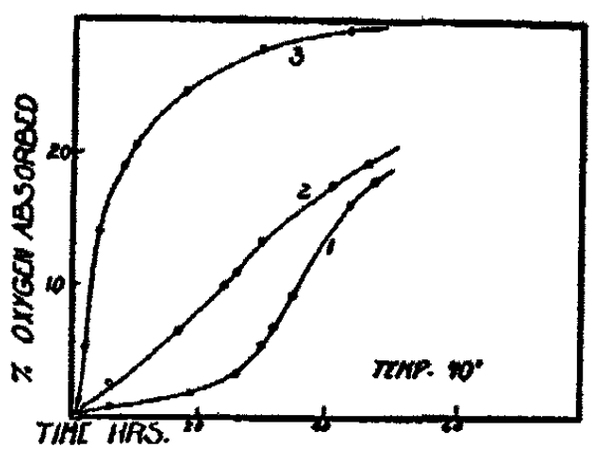



FIG. 10
Curve 1 Linseed Oil Diphenylamine.
Curve 2 Linseed Oil+0.003% Co.+1%.
Curve 3 Linseed Oil+0.003% Co.

Diphenylamine and beta-naphthol were found to be quite soluble in the oil and gave reproducible results. Figs. 8 and 9 represent the results with linseed oil containing one per cent of beta-naphthol at 40°, 50°, and 100°.

Figure 8 shows the effect of temperature on the rate of the inhibited reaction. The effect of one per cent of diphenylamine present at 40°, 50°, and 100° on the normal and catalysed reaction is shown in Figs. 10, 11, and 12. From a close study of the early stages of the absorption, there is evidence of a rapid reaction which ends quickly. The inhibitors seem to have little effect on this, consequently it is shown very clearly in their curves. Those showing the oxidation rate of raw linseed oil show this reaction also, but it is obscured at 100° and in the presence of catalysts. It points to the presence of a small amount of very readily oxidisable substances or to the absorption of oxygen

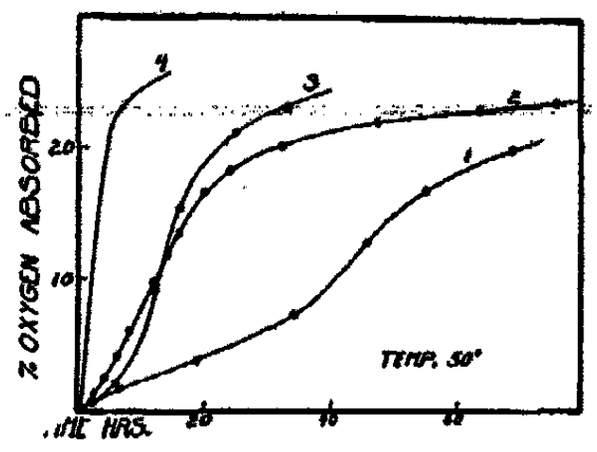



FIG. 11

Curve 1 Linseed Oil+1% Diphenylamine.
Curve 2 Linseed Oil+1% Diphenylamine+0.003% Co.
Curve 3 Linseed Oil.
Curve 4 Linseed Oil+0.003% Co.

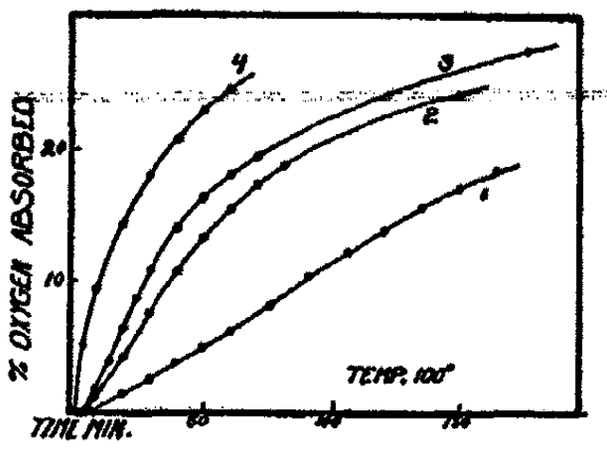



FIG. 12

Curve 1 Linseed Oil+1% Diphenylamine.
Curve 2 Linseed Oil+1% Diphenylamine+0.003% Co.
Curve 3 Linseed Oil.
Curve 4 Linseed Oil+0.003% Co.

more rapidly than the oxidation. The latter explanation is open to serious objection on the ground that the oil film has been in contact with the air for ten minutes before being placed in the thermostat, and in Fig. 8, curves 1 and 2 as well as Fig. 11, curve 1, the three cases in which it is most evident, there is a period of about thirty minutes before the reaction starts. Thus the film has been in contact with the air for forty minutes.

It seems unlikely that the film would remain quiescent for this period and then suddenly saturate itself, which would be the case were this mechanical absorption. Furthermore we would have to assume that oxygen is more soluble in the oil at higher temperatures, as a study of Fig. 8 shows that this rise is greater and occurs sooner at 50° than at 40°. Thus it would seem that this does indicate the presence of small amounts of readily oxidisable substances.

The proportion by which the inhibitors reduce the rate of oxidation is not affected much by temperature. Table II shows how much longer it takes the inhibited reaction, in the case of beta-napthol, to reach the indicated percentages as compared with the normal rate of oxidation of raw linseed oil.

TABLE II

The Proportional Increase in Time of the Inhibited Reaction over the Normal Reaction. Beta-naphthol is the Inhibitor.

| Percentage of oxygen absorbed. | Increase at 40° | Increase at 50° | Increase at 100° |
|---|---|---|---|
| 2.00 | 2.5 | 3.0 | 3.0 |
| 6.00 | 2.8 | 4.8 | 3.8 |
| 12.00 | 2.9 | 4.0 | 3.2 |
| 18.00 | 3.2 | 4.5 | 2.8 |

In Table III is indicated the ratio of oxygen absorbed in the inhibited reaction to the oxygen absorbed in the raw oil reaction at the times indicated in the left hand column.

TABLE III

Ratio of the Percentages of Oxygen absorbed in the Inhibited Reaction to that in the Normal Reaction, using Beta-naphthol.

| Time, hrs. for 40° and 50° columns, min. for 100°. | Ratio at 40° | Ratio at 50° | Ratio at 100° |
|---|---|---|---|
| 10 | 1.00 | 0.23 | 0.12 |
| 20 | 0.50 | 0.11 | 0.16 |
| 30 | 0.23 | 0.13 | 0.17 |
| 40 | 0.13 | 0.16 | 0.18 |
| 50 | 0.12 | 0.26 | 0.22 |

Thus it is seen that the inhibitor is slightly more effective at the lower temperature, and that it reduces the rate of oxidation more after six per cent of oxygen is absorbed than before.

Figs. 10, 11, and 12 show the result of using one per cent of diphenyl-amine as an inhibitor on the catalysed reaction, using 0.003 per cent of cobalt as the catalyst in the form of cobalt linoleate. This was done in the hope that some light might be cast on the "modus operandi" of inhibitors. The results show that an inhibitor does not act by suppression of catalyst alone. For if this were the case, from Fig. 10, curves 1 and 2 we must assume that one per cent of diphenyl-amine does not suppress all of the 0.003 per cent of cobalt. For the rate of reaction indicated by curve 2 is quite perceptibly greater than the linseed oil rate of oxidation. And so at 100° the same reaction, represented by Fig. 12, curve 2, would be expected to show a greater rate than that of Fig. 12, curve 3. It is, however, smaller than the rate of the raw oil reaction at this temperature. This points to the fact that the inhibitor and the catalyst exert their influence on the rate of reaction independently of each other even when present in the oil simultaneously.

Table IV shows the ratio of the time required for the inhibited reaction, using one per cent of diphenyl-amine as the inhibitor, to reach the percentages indicated in the left-hand column to the time required for the raw oil reaction to reach the same percentages. Both reactions are also catalysed with 0.003 per cent of cobalt.

TABLE IV

Ratio of the Time in the Reaction using Inhibitor and Catalyst to the Time in the Catalysed Reaction at the Indicated Corresponding Percentages.

| Percentage of oxygen absorbed. | Ratio at 100° | Ratio at 50° |
|---|---|---|
| 2.00 | 5.0 | 8.0 |
| 5.00 | 2.0 | 8.25 |
| 10.00 | 3.4 | 9.6 |
| 15.00 | 2.6 | 8.0 |
| 20.00 | 2.4 | 8.0 |
| 24.00 | 2.5 | 9.4 |

This accentuates the point made earlier in the discussion that inhibitors are slightly more efficient at lower temperatures. In this case the inhibitor is retarding the rate of reaction approximately three times as much at 50° as at 100°.

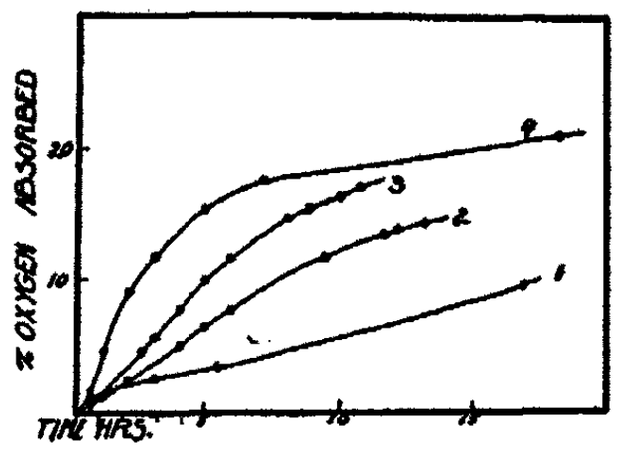



FIG. 13

Effect of Light on Oxidation of Linseed Oil.
Curve 1 Glass Vessel 30 cm. from lamp.
Curve 2 Quartz vessel 60 cm. from lamp.
Curve 3 Quartz vessel 30 cm. from lamp
Curve 4 Quartz vessel 15 cm. from lamp.

Fig. 13 represents the reaction in the presence of light. An Hanovia quartz mercury arc lamp was used as the source of light. Curve 1 shows the rate of oxidation of raw linseed oil in a soft glass vessel. Curves 2, 3, and 4 represent the results in a fused quartz apparatus. The following Table V shows the conditions of the experiments.

TABLE V

Light Intensity Data

| Curve no. | Voltage of lamp. | Amperage. | Distance from lamp. | Temperature |
|---|---|---|---|---|
| 1 | 40 | 2.4 | 30 cm. | 20°.5 |
| 2 | 47 | 2.4 | 60 cm. | 21°.0 |
| 3 | 40 | 2.4 | 30 cm. | 20°.5 |
| 4 | 46 | 2.3 | 15 cm. | 27°.0 |

All of the reaction can be ascribed to the action of light, for at these temperatures the dark reaction does not start during the time used for these observations. The curves show the rate of oxidation is not directly proportional to the intensity of the light falling on the system. The distance from the lamp in curve 4 is one half of that of curve 3, which in turn is one half of that of curve 2. The rate of curve 4 is roughly double that of curve 3, and the increase of curve 3 is only one half the rate of curve 2. The intensity varies inversely as the square of the distance from the lamp, consequently direct proportionality would call for a quadruple increase from curve 2 to 3, and the same from curve 3 to 4. In as much as curve 1 represents the reaction in a glass vessel, which cuts out most of the ultra-violet light, this curve represents the effect of visible light of this intensity on the reaction. The increase in rate of curve 3 over that of curve 1 shows the effect due to ultra-violet light alone.

Mr. H. L. J. Bäckström, of this laboratory, has obtained evidence that those reactions which are capable of being inhibited also give photo-chemical reactions in which more than one molecule of reacting substance undergoes combination per quantum of light energy. Thus, it was of interest to determine if this reaction did the same. The formula,

$$\frac{\text{Volts} \times \text{Amperes} \times 10^7 \times A/4r^2}{5 \times 5 \times 6 \times 10^{-12}}$$

gives the number of quanta which are available in promoting the reaction, falling on a given area, A, of reacting space per second. The following assumptions are made in this formula. (1) One fifth of the electrical energy is given out as light energy. (2) None of the light falling on the system is reflected. (3) One fifth of the light energy is in the chemically active region. Table VI shows the number of oxygen molecules reacting per quantum of light energy in the four reactions, up to ten per cent of oxygen absorbed.

TABLE VI

Minimum Ratio of Molecules reacting per Quantum of Light Energy absorbed

| Curve | Number of quanta per second | Number of molecules per second | Number of molecules per quantum | Distance from lamp |
|---|---|---|---|---|
| 1 | $1.7 \times 10^{16}$ | $0.19 \times 10^{16}$ | 0.10 | 30 cm. |
| 2 | $0.5 \times 10^{16}$ | $0.67 \times 10^{16}$ | 1.30 | 60 cm. |
| 3 | $1.7 \times 10^{16}$ | $1.05 \times 10^{16}$ | 0.06 | 30 cm. |
| 4 | $75.0 \times 10^{16}$ | $2.27 \times 10^{16}$ | 0.03 | 15 cm. |

It must be emphasized that from the assumptions made in calculating the number of quanta, the number so obtained is a maximum value, consequently the number of molecules reacting per quantum are minimum values. The number actually reacting is probably greater than this. It will be noted that the further away the light source, the greater the yield per quantum. Taken in conjunction with the recorded deviation from the inverse square law, which will hold more precisely the greater the distance, it may be concluded that a chain reaction will reveal itself definitely under improved experimental con-

ditions. That the length of the chains is small is indicated by the low efficiency of inhibitors as compared with their effect in other reactions, notably the benzaldehyde oxidation.

We have pointed out that Genthe showed how little the oxygen pressure affected the rate of oxidation. A study of our curves supports this view. When the manometer read 100 mm. the oxygen in the vessel was replenished. This point on the curves will vary with the particular size of apparatus used but is about 14.00 per cent in most cases. We have raised the oxygen pressure from 50 mm. to 150 mm. at this point, a three-fold increase in pressure, yet the points on either side of this show no discontinuity in the curve. This leads to an interesting conclusion. It shows that this method eliminates any difficulties from a film of oxidized linseed oil forming over the unoxidized oil. For, were this the case the rate of oxygen absorption would be governed by the rate of diffusion of oxygen through a film. That this is not the case is evidence that we are measuring the true rate of oxidation of the oil.

## Summary

(1). A simple and convenient apparatus has been described for studying the rate of oxidation of non-volatile oils. This apparatus gives true oxidation values.

(2). When the concentration of a drier in linseed oil is increased, there is a certain concentration of drier at any one temperature beyond which further increase produces no effect on the rate of oxidation. This value is reached with 0.0003 per cent of cobalt in the form of cobalt linoleate at 100°.

(3). As the temperature is raised the effect of driers is less pronounced.

(4). The effect of three inhibitors, hydroquinone, beta-naphthol, and diphenyl-amine, on the rate of oxidation of linseed oil has been studied. In general, the inhibitor is more effective at lower temperatures, and must be soluble in the oil to lend itself to quantitative study.

(5). Indication that the inhibitor does not act solely by suppression of a catalyst has been given, and that both inhibitor and catalyst may exert their influence independently.

(6). The effect of visible and ultra-violet light on the rate of oxidation of linseed oil at room temperature has been shown, using light of different and known intensities. The rate of reaction is not directly proportional to the intensity of the light as deduced from measurements made close to the light source. The reaction is very probably a chain reaction.

# THE SURFACE TENSION OF CHARGED SURFACES

BY OSCAR KNEFLER RICE

## Introduction

The surface tension at the boundary of two immiscible solvents is affected by the electrical and chemical forces concerned with the adsorption of the solute. If the solute is ionized the electrical forces become particularly important, and, also, they are easier to handle theoretically. We propose to investigate these forces and their effect on the surface tension from the standpoints of electrostatics and thermodynamics, with particular reference to the relation between the two points of view.

We can imagine a number of situations which might arise at a charged surface. For example, suppose we had two adjacent immiscible solutions, which we will call A and B, each containing ions of the same kind. Suppose ions could not of themselves cross the boundary but we had some device for taking them across. If we took more charge of one sign than the other across, and if the ions were free to move in their respective solutions, negative ions would be attracted to the surface from the negative side of the boundary and positive ions would be repelled, and *vice-versa* for the other side. These ions would form two diffuse atmospheres, one on either side of the boundary. Gradually we would build a potential difference, $\phi$, across the boundary, which we will consider as positive if the potential of A is greater than that of B. If the solutions were so extensive that our transfers did not appreciably alter the composition of either, the change in the surface tension, $\gamma$, at the boundary would be given by the differential equation

$$d\gamma = - Qd\phi \qquad (1)$$

where Q is the excess of positive over negative charge per unit surface on the A side of the boundary (or, what amounts to the same thing, the excess of negative over positive charge on the B side). It is thus seen that $\gamma$ has a maximum where Q is zero. $\phi$ will in general be zero when Q is zero unless there are forces acting which tend to separate charges which are on the same side of the boundary and so create a double layer which does not extend across it. This has been discussed by Gouy[1] and also by Frumkin[2].

The capillary electrometer, though the details are somewhat different, presents a situation which is essentially similar to the above. Equation (1) was long ago derived for the electrometer on the assumption that the mercury meniscus was completely polarized[3].

We can imagine another situation which may be of some importance in connection with colloid theory. Suppose the double layer to consist of a monomolecular layer of ions adsorbed from the solution A at the boundary of the solution and a dielectric B, and a diffuse layer of ions in the solution A.

[1] Gouy: Ann. Physique, (9) 7, 129 (1917).

[2] Frumkin: Phil. Mag. (6) 40, 363, 375 (1920).

[3] See Freundlich: "Kapillarchemie", 394.

1348

Let the chemical potential of the ions which are adsorbed be $\mu$, that of those in the interior of A far from the boundary $\mu'$. $\mu$ will be a function of Q and hence of $\phi$ (which are now defined as the charge per unit surface of the monomolecular layer and the excess of its potential over that of the solution, respectively), provided we assume equilibrium to be established instantaneously in the diffuse layer. $\mu'$ will be independent of Q provided the amount of solution is so great that the composition in its interior is not appreciably changed in the processes to be considered. (It is to be noted that we are still considering a polarized surface; that is, equilibrium is not necessarily established between the monomolecular layer of ions on the surface and those in the solution, but only in different parts of the solution.) Let $\epsilon$ be the charge per unit quantity for the adsorbed ions. We then have

$$d\gamma = -Qd\phi - \frac{Q}{\epsilon}\frac{d\mu}{d\phi}d\phi \qquad (2)$$

This we may easily prove. Increase the surface by unity, maintaining the charge per unit surface at Q. During the increase of surface $Q/\epsilon$ units with a charge of Q are brought up to the surface. The change in free energy, due to the surface tension and the transfer of ions to the surface is consequently $\gamma+Q\phi+ Q/\epsilon\,(\mu-\mu')$. Now, holding the extent of surface constant, increase the potential by $d\phi$. At the same time the chemical potential will increase by $d\mu = (d\mu/d\phi)\ d\phi$ and the charge per unit surface will increase by

$$dQ = (dQ/d\phi)\ d\phi.$$

The increase of free energy in this change will be $\phi dQ+(\mu-\mu')\ dQ/\epsilon$ Now decrease the surface by unity with a change in free energy of

$$-(\gamma+d\gamma) - (Q+dQ)\,(\phi+d\phi) - (Q/\epsilon+dQ/\epsilon)\,(\mu-\mu'+d\mu)$$

Now the change in free energy in the whole cycle should be zero, and neglecting second order quantities we find that this gives us (2). A practically identical derivation will hold for (1), the work due to chemical potential dropping out (if we assume that there is so much of both solutions that the chemical potential of neither is appreciably changed in the processes considered.)

If there are $n$ different kinds of ions in the monomolecular layer at the surface we get instead of (2)

$$d\gamma = -\sum_{i=1}^{n} Q_i d\phi_i - \sum_{i=1}^{n}\frac{Q_i}{\epsilon_i}\frac{d\mu_i}{d\phi}d\phi \qquad (3)$$

where the subscript $i$ is appended to quantities belonging to the $i$th ion. Since the electrical potential is the same for all ions we may write (3) in the form

$$d\gamma = -Qd\phi - \sum_{i=1}^{n}\frac{Q_i}{\epsilon_i}\frac{d\mu_i}{d\phi}d\phi \qquad (3a)$$

where Q is the total charge per unit area.

We can write equation (2) in the integrated form

$$\gamma_1 = \gamma_0 - \int_0^{\phi_1} Q d\phi - \int_0^{\phi_1} \frac{Q}{\epsilon} \frac{d\mu}{d\phi} d\phi \qquad (4)$$

where $\gamma_0$ is the surface tension when $\phi$ is zero and $\gamma_1$ when $\phi$ is $\phi_1$. We can write equation (1) in the integrated form

$$\gamma_1 = \gamma_0 - \int_0^{\phi_1} Q d\phi \qquad (4a)$$

If the only forces due which act on ions in the neighborhood of the boundary are due to ions which have crossed the boundary then Q and $\phi$ are zero together, as already stated. Also $\gamma_0$, the surface tension when Q is zero, will not vary at all in solutions in which the ions are present in different concentrations. For Gibbs's adsorption equation, which says that the change in surface tension with the concentration is proportional to the amount of solute adsorbed, will hold under the restriction that Q is zero. But if Q is zero there will be, by hypothesis, no forces on the ions near the boundary, hence no adsorption.

## Electrostatics of the Surface

Let us now proceed to investigate the meaning of the various terms in equations (4, 4a). We shall show that the term $-\int_0^{\phi_1} Q d\phi$ gives us just the change in surface tension that we would expect from the electrostatic forces involved.

Our general method of attack will be to consider the pressure in a sphere whose surface is charged and which is surrounded by an atmosphere of ions whose density is a function of the distance from the center. We can then relate surface tension to pressure and pass to the limiting flat surface.[1]

We first note that there is a negative or outward difference of pressure between the inside of the sphere and the solution immediately outside it, due to the action of the field on the surface charge. The magnitude of this pressure, P'', is $2\pi Q^2/K$, where Q is the surface density of charge, and K is the dielectric constant of the medium surrounding the sphere.

Besides this there will be a positive difference in pressure between a point at a distance $r$ from the center of the sphere and a point at an infinite distane from the shpere, whose magnitude we will call P'. The charge in the solution surrounding the sphere has a force pulling it toward the sphere, whose value per unit volume is $-\rho E$, where $\rho$ is the volume density of charge and E is the magnitude of the electric force vector. (E is to be considered as positive when a positive charge tends to move away from the sphere.) If $r$ is the distance from the center of the sphere, then we may write $dP'/dr = -\rho E$, the minus sign indicating that the pressure decreases when $r$ increases. If $a$ is the radius of the sphere

$$P'(\text{at a}) = \int_a^{\infty} \rho E dr$$

The volume of a shell of small thickness, $dr$, and at a distance $r$ from the center of the sphere is $4\pi r^2 dr$, and the amount of charge included in the shell

[1] For a consideration of the electrostatics of the surface from a different point of view, see Herzfeld: Physik. Z., 21, 31 (1920); v. Laue: Jahrb. Radio. Elektronik, 15, 238 (1918); Möller: Ann. Physik, 27, 670 (1908).

is $4\pi r^2\rho dr$. Now $Kr^2E$ is equal to the total amount of charge within the distance $r$; or

$$Kr^2E = 4\pi Qa^2 - \int_a^r 4\pi r^2\rho dr$$

Differentiating with respect to $r$

$$K\frac{d(r^2E)}{dr} = -4\pi r^2\rho$$

or

$$\rho = -\frac{K}{4\pi r^2}\frac{d(r^2E)}{dr}$$

So, putting into the equation for P′ (at $a$)

$$P'(\text{at } a) = -\frac{K}{4\pi}\int_a^\infty \frac{E}{r^2}\frac{d(r^2E)}{dr}dr$$

$$= -\frac{K}{4\pi}\left(\int_{r=a}^{r=\infty} EdE + \int_a^\infty \frac{2E^2}{r}dr\right)$$

$$= -\frac{K}{8\pi}E^2\Big/_{r=a}^{r=\infty} - \frac{K}{4\pi}\int_a^\infty \frac{2E^2}{r}dr$$

$$= -\frac{K}{8\pi}\left\{0 - \left(\frac{4\pi Q}{K}\right)^2\right\} - \frac{K}{4\pi}\int_a^\infty \frac{2E^2}{r}dr$$

$$= \frac{2\pi Q^2}{K} - \frac{K}{4\pi}\int_a^\infty \frac{2E^2}{r}dr$$

From this $P'' = 2\pi Q^2/K$ must be subtracted, to get the net pressure between the inside of the sphere and the solution at an infinite distance from it, whence

$$P = -\frac{K}{4\pi}\int_a^\infty \frac{2E^2}{r}dr$$

But as $P = 2(\gamma-\gamma_o)/a$, from capillary theory, we get

$$\gamma-\gamma_o = -\frac{Ka}{4\pi}\int_a^\infty \frac{E^2}{r}dr$$

Now, as a matter of fact, the only part of this integral which contributes an appreciable amount (if the surface tension is to have any meaning at all) is the part within some limit $a'$ which is very close to $a$, so that we may write

$$\gamma-\gamma_o = -\frac{Ka}{4\pi}\int_a^{a'} \frac{E^2}{r}dr$$

This, of course, is only true if the system as a whole, including both the charged sphere and the surrounding atmosphere of ions, is electrically neutral. If we now allow $a$ to increase indefinitely it will become very much greater than a′-a, so we may take the $r$ out of the integral sign, as it is nearly constant and equal to $a$, whence

$$\gamma - \gamma_o = -\frac{K}{4\pi}\int_a^{a'} E^2 dr$$

But the integral $\int_{a'}^{\infty} E^2 dr$ is very much smaller than the integral $\int_a^{a'} E^2 dr$, so adding them together and letting x be the distance from the now flat surface of the sphere, we get for our final expression

$$\gamma - \gamma_o = -\frac{K}{4\pi}\int_a^{\infty} E^2 dx \qquad (5)$$

We may express this in words by saying that the surface tension due to the electrical charge is minus twice the energy of the field. It is of particular interest that we can only get this for the limiting case of a flat surface. Most surfaces are flat, however, for all practical purposes. While the situation considered above corresponds to the case of the monomolecular layer and one diffuse layer (which we are now about to consider further), it will readily be seen that (5) also holds for the other cases mentioned in the introduction, a fact that will later be of use.

### Comparison with Thermodynamic Expression

In order to make this comparison we will transform (5) by writing $KE/4\pi = Q_x$ and $Edx = -d\phi_x$. (5) then becomes

$$\gamma - \gamma_o = -\int_{x=-\infty}^{x=o} Q_x d\phi_x \qquad (6)$$

which has much the same form as the first part of equation (4). What is the meaning of this coincidence? Let us fix our attention on a point whose distance from the charged surface, which we shall refer to as $S_o$, is $b$. Then we may consider that all charges whose distance from $S_o$ is greater than $b$ are being attracted to a surface $S_b$ drawn through $b$, but whose charge per unit surface is found by subtracting the surface density of charge between b and $S_o$ from that of $S_o$. $Q_b$ (i.e., $Q_x$ for $x = b$) is then seen from its definition together with Gauss's law connecting normal flux with enclosed charge, to be this charge per unit surface, which we may call the effective surface density of charge of $S_b$. It is seen that the distribution of charge on the far side of $S_b$ (i.e., $x > b$) is exactly the same as the distribution back of $S_o$ would be were its charge per unit surface $Q_b$, provided, and only provided, there are no forces acting which are not due to the charge on the surface but belong to the surface itself and are a function of the distance from the surface. If there are no such forces the potential $\phi_b$ at $b$ above the potential at $x = \infty$ is exactly the same as the potential at $S_o$ would be were its charge $Q_b$. It is thus seen that $\int_{x=-\infty}^{x=o} Q_x d\phi_x = \int_o^{\phi} Q d\phi$ where in the first integral we integrate by moving up to the surface and in the second we integrate by charging the surface. This equality will hold even if the ions do not form perfect solutions, for the forces the ions exert on each other at any point will depend only on their concentration and not on where they are. Thus we see that the integral $\int_o^{\phi} Q d\phi$, which contains only electrical terms gives the surface tension which we would calculate directly from the electrostatic forces, but only when there are no other surface forces involved.

A slight modification of this line of reasoning will enable us to deal with the case of a diffuse layer on either side of the boundary. In this case equation (4a) will hold, and we will show that the change in surface tension is entirely accounted for by the electrostatic effects. It is easy to see that $\int E^2 dx$ may be expressed in terms of effective charge and potential, much as before, but that it breaks up into the sum of two integrals

$$\int_{x'=\infty}^{x'=0} Q_{x'} \frac{d\phi_{x'}}{dx'} dx' + \int_{x''=\infty}^{x''=0} Q_{x''} \frac{d\phi_{x''}}{dx''} dx'',$$

where the primes refer to one side of the boundary, the double primes to the other, and where $x'$ and $x''$, respectively, have the value zero at the boundary and increase as we go from it. Now we may choose a series of positions on one side of the boundary which is in one to one correspondence with a set of positions on the other side of the boundary, such that the effective charge per unit surface $Q_{x'}$ for the position on one side is in equal in magnitude and opposite in sign to the effective charge per unit surface $Q_{x''}$ for the corresponding position on the other side. (We assume that the potential is continuous and always increases in the same direction in space.) It is then seen, assuming the system as a whole to be neutral, that the limits of the two integrals are respectively corresponding points in the sense indicated. With the understanding that we are to take the proper corresponding values for the double prime side of the boundary we may write $x''$ as a function of $x'$ and get $\int_{x'=\infty}^{x'=0} (Q_{x'} \frac{d\phi_{x'}}{dx'} dx' - Q_{x'} \frac{d\phi_{x''}}{dx'} dx')$ because for corresponding points $Q_{x''} = -Q_{x'}$. Here, for a given $dx'$, $d\phi_{x'}$ and $d\phi_{x''}$ are corresponding differentials. We may write $Q_{x'}$ simply as $Q_x$, $x'$ as $x$, and let $\frac{d\phi_{x'}}{dx'} - \frac{d\phi_{x''}}{dx'} = \frac{d\phi_x}{dx}$

Our integral then becomes $\int_{x=\infty}^{x=0} Q_x \phi_x$ and it is seen that $\int_{x=\infty}^{x=0} d\phi_x$ is equal to the total potential difference across the boundary while $\int_{x=x}^{x=0} d\phi_x$ is the potential difference across the boundary minus the potential difference which a surface of charge $Q_x$ would have.[1] The same correspondence as before is now seen to exist with the thermodynamic equation.

### Kinetics of the Adsorbed Ions

Let us now attempt to interpret the second integral of (4). This we easily do for an ideal case with the help of the Boltzmann probability principle, $dS = \frac{R}{N} d \log P$, where S is the entropy per unit mass of the ions adsorbed in the monomolecular layer, R the gas constant, N the number of ions in unit mass, and P the thermodynamic probability of the system consisting of unit mass of ions. This gives us, as is readily seen by dividing the surface

[1] In comparing with equation (4a), which is the integral of equation (1), notice the arbitrary manner in which the signs of the quantities in that equation were determined.

into surface cells in the same way that we divide the volume of a gas into volume cells, and computing the change in probability when the concentration is changed[1], $dS = -R d \log Q$, Q being analogous to the concentration of a perfect gas. Since $d\mu = dH - TdS$, where H is the heat content per unit amount of adsorbed substance (T being considered constant), and since for an ideal adsorbed substance as for a perfect gas we may assume dH to be zero, we get $d\mu = RTd \log Q = RTdQ/Q$

Hence
$$\frac{Q}{\epsilon}\frac{d\mu}{d\phi}d\phi = \frac{RT}{\epsilon}\frac{dQ}{d\phi}d\phi$$

and
$$\int_0^{\phi_1}\frac{Q}{\epsilon}\frac{d\mu}{d\phi}d\mu = \int_0^{Q_1}\frac{RT}{\epsilon}dQ = \frac{RTQ_1}{\epsilon}$$

where $Q = Q_1$ when $\phi = \phi_1$

So for the ideal case.

$$\gamma_1 = \gamma_0 - \int_0^{\phi_1} Qd\phi - \frac{RTQ_1}{\epsilon} \qquad (7)$$

This may be readily generalized if more than one kind of ion is adsorbed.

## Summary

An electrical charge may arise at the surface bounding two liquids in various ways. Three cases are considered. (1) Suppose we have two solvents, each of which contains various ions, all the kinds of ions being present in both solvents. If ions cannot cross the boundary, but if they can be transferred in some way from one solvent to the other, we may build up a potential difference between the solvents by transferring more positive ions than negative from one side of the boundary to the other, as the ions will form a double layer at the surface. (2) The capillary electrometer is essentially similar to the above. (3) We might conceive of ions adsorbed at the boundary of two liquids and forming there a monomolecular layer, while *one* of the liquids contains dissolved ions (the ions at the boundary not necessarily being in equilibrium with those in the solution).

In the first two cases the expression for the surface tension is

$$\gamma_1 = \gamma_0 - \int_0^{\phi_1} Qd\phi$$

where $\gamma_0$ is the surface tension of the surface when its potential $\phi$ is 0, $\gamma_1$ its surface tension when $\phi$ is equal to $\phi_1$, Q being the charge per unit surface.

In the third case (if we assume that only one kind of ion is adsorbed at the surface) the expression for the surface tension is

[1] Such a change could be effected, for example, by the transfer of all the ions from the given surface to an empty surface of slightly different area. There would then be a different number out of the sum total of all the cells in the two surfaces filled and each one would then contain a different number of ions, the actual calculation of the change in probability being readily carried out in the usual manner. See W. C. M. Lewis: "A System of Physical Chemistry," Vol. III, p. 11 (1924) and Lewis and Randall: "Thermodynamics" p. 120 (1923).

$$\gamma_1 = \gamma_0 - \int_0^{\phi_1} Q d\phi + \int_0^{\phi_1} \frac{Q}{\epsilon} \frac{d\mu}{d\phi} d\phi$$

where $\mu$ is the chemical potential of the adsorbed ion and $\epsilon$ its charge per unit mass. (This expression can be generalized if several kinds of ions are adsorbed at the surface.) A proof for this expression is given.

By considering the pressure inside a charged sphere which is surrounded by a diffuse atmosphere of ions symmetrically distributed about the sphere, the surface tension is found in the case in which the sphere is very large. It is then possible to show that, if no forces other than the electrical forces act on the ions in the neighborhood of the boundary, that the term $\int_0^{\phi_1} Q d\phi$ is equal to the surface tension thus found.

The term $\int_0^{\phi_1} \frac{Q}{\epsilon} \frac{d\mu}{d\phi} d\phi$ is discussed in terms of the kinetics of the ions forming the monomolecular layer at the boundary.

*Department of Chemistry,*
*University of California,*
*Berkeley, California.*

# THE IONISATION POTENTIALS OF NITROGEN AND HYDROGEN ON IRON AND OTHER METALS*

BY GEORGE B. KISTIAKOWSKY**

The work done in the last ten years, chiefly in the Princeton Chemical Laboratory, has thrown much light on the action of metal catalysts in several chemical reactions. A theory of H. S. Taylor[1] brought the various data together and gave them a general explanation, but the main question as to the nature of activation produced by catalysts, was still open. Recently, several attempts to solve this problem have been undertaken.

Gauger[2] and later Wolfenden[3] studied the activation of hydrogen using low-speed electrons for the determination of its critical potentials when adsorbed on metal surface. Although the results of Gauger were not very conclusive, the later work of Wolfenden gave more evidence for the assumption that adsorbed hydrogen is present partly in the atomic state. Wolfenden studied especially ionisation potentials, which has the advantage that only a few breaks are observed in the current-voltage curves and therefore their interpretation is far easier. He found ionisation in presence of nickel and copper at 11.3, 13.4 and 16.0 volts. The break at 16 volts was ascribed to molecular hydrogen, that at 13.4 volts to adsorbed atomic hydrogen, but no satisfactory explanation for the ionisation at 11.3 volts could be given. As, in the present work, an attempt has been made to explain this ionisation and other experiments of Wolfenden have been repeated, the general discussion of Wolfenden's results will be given in the last paragraph.

The researches of Bonhoeffer[4] and Marshall and Taylor[5] supplied evidence that atomic hydrogen does not combine with molecular nitrogen to form ammonia and that, therefore, active iron, used as catalyst in the Haber-Bosch ammonia synthesis, activates not only hydrogen but also nitrogen. The nature of this activation is the subject of the present investigation.

## Apparatus and Method

An apparatus similar to that used by Wolfenden was employed and is shown in Fig. 1. The tube was connected to a rapidly working pump through two liquid air traps, in order to avoid the entry of mercury vapour to the apparatus.

In the figure, 1 represents the collecting disc connected to a sensitive electrometer; 2, 3, and 4 are grids; 5, the filament, an oxide coated platinum

*Contribution from the Laboratory of Physical Chemistry, Princeton, N. J.

**International Research Fellow, Princeton University, N. J.

[1] J. Phys. Chem., **30**, 145 (1926).

[2] J. Am. Chem. Soc., **46**, 674 (1924).

[3] Proc. Roy. Soc., **110** A, 464 (1926).

[4] Z. Elektrochem, **31**, 521 (1925).

[5] J. Phys. Chem., **23**, 1140 (1925).

foil having a notch, so that the filament is, practically, an equipotential source of electrons; 6, a grid; 7, a target with powdered catalyst on it.

As nitrogen has many strong radiation potentials the distinction between them and ionisation potentials, when the usual voltage scheme (that of

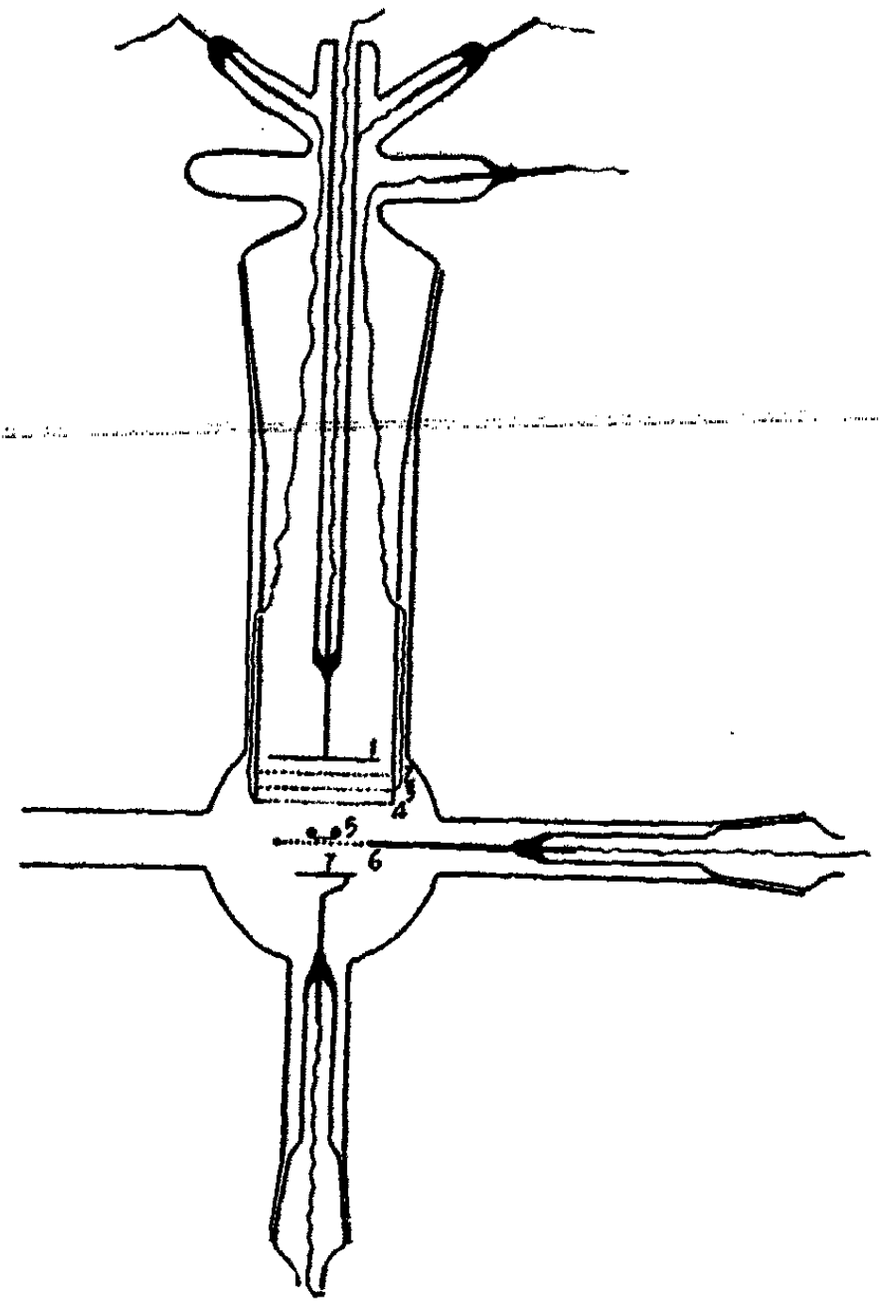



FIG. 1

Wolfenden) was used, is rather difficult and so a special method was required. Such a method was found in the following arrangement[1] of potentials.

| | | |
|---|---|---|
| 1. | 0 | volts |
| 2. | −16 | " |
| 3. | 0 | " |
| 4. | 0 | " |
| 5. | +16 | " |
| 6. 7. | +16 + $U_{acc}$ | volts. |

Such an arrangement has the advantage that, in the case of photo-effect, the electrons do not go from the collecting disc to the grid 2 (usually at a positive potential) but in the reverse direction, so that the observed current changes

not only its magnitude but also its direction when positive ions reach the disc.

Compared with the apparatus of Wolfenden, another improvement was made: Grid 6, very near to the filament, was introduced, so that practically all collisions of electrons with non-adsorbed gas molecules occurred in a field-free space and therefore the determination of the aggregate correction was more accurate.

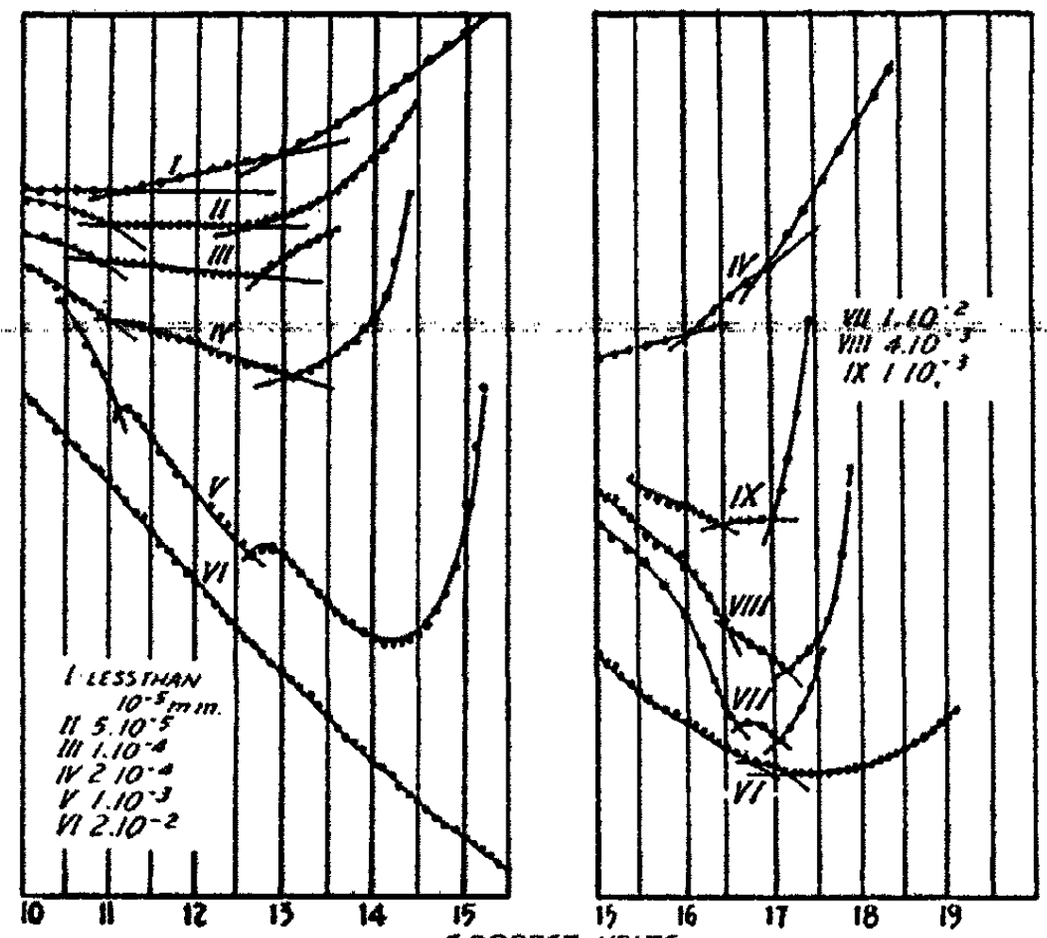



FIG. 2.

As the standard for such a determination, argon was used. It showed ionisation (measured in good agreement by both Wolfenden's and the present methods) at 15.63 ±0.04 Volts. The value of Herz[2] is 15.2 volts for argon, and so the correction was found to be −0.43 volts. In all the following diagrams the observed potentials are correspondingly corrected.

Nitrogen was prepared from a solution of ammonium nitrite and all possible care was taken in its purification.

Hydrogen was prepared electrolytically and also thoroughly purified and dried.

A promoted iron catalyst of the Fixed Nitrogen Research Laboratory type, an iron oxide containing 1 percent $K_2O$ and 3 percent $Al_2O_3$ and obtained from L'Azote Inc., was used. It was reduced by hydrogen. During the process the temperature was raised to 550°; then, hydrogen was replaced by nitrogen and, after a while, the furnace was slowly cooled.

[1] A similar method was first employed by B. Davis and Goucher: Phys. Rev. (2) 13, 1 (1919). Later, Brandt (Z. Physik, 8, 32 (1921)) criticized it; but his objections are not applicable to the above-described apparatus as the pressures used in these experiments are sufficiently low and the potential differences between different parts of the apparatus are large.

[2] Z. Physik, 18, 351 (1923).

## Results

The tube with catalyst on the target was baked in vacuo at 400° for several hours but, nevertheless, the catalyst still contained much residual gas, so that the curves obtained immediately after baking or after some nitrogen was admitted and then pumped off were only slightly different.

Fig. 2 shows typical curves (I to VI) obtained at different pressures of nitrogen. The observed effects are of different character: the effect of radiation (due essentially to the non-adsorbed gas) is rapidly increased at higher pressures and therefore the slope of the curves below the zero line is increasing, but the breaks in the opposite direction indicating ionisation are rather independent of the pressure and therefore they disappear at high pressures (for Curve VI a shunt 20 times smaller in sensitivity was used). Two of such breaks were observed in the low part of the curves. The corresponding potentials were determined as: 11.1 volts (16 observations, average deviation ±0.09 volts) and 12.9 ± 0.17 volts (10 observations). At higher potentials two other breaks (curve IV) were observed: at 16.00 ±0.08 volts and at 17.05±0.05 volts. The first one is noticeable only when the pressure is low, so that in the runs made at higher pressures (Curve VI) only one distinct ionisation was found at 17 volts belonging undoubtedly to the molecular (gaseous) nitrogen.

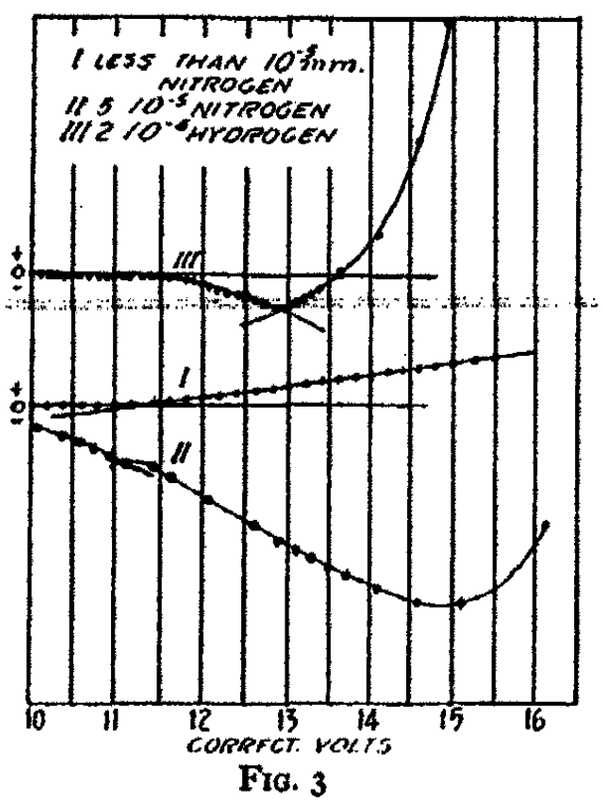


FIG. 3

A special study (in absence of catalyst) showed (Curves VII to IX) that nitrogen has probably a double ionisation potential, as the strong ionisation at 17 volts is preceded by a faint one at nearly 0.4 volts lower potential.

In order to obtain more conclusive data on the nature of different ionisations the following experiments were undertaken. A small amount of oxygen which is known to be a catalytic poison, was admitted and the tube was heated. Fig. 3 shows, I, the run made immediately after the tube was cooled and oxygen removed, II, after $5.10^{-5}$ mm. of nitrogen was admitted, III represents the experiment after the tube was heated again, this time with some hydrogen in it. The first two runs show no break at 12.9 volts and a very faint one at 11.1 volts. In the third experiment, practically no break is distinguishable at 11.1 volts but the break at 12.9 volts is very strong.

Finally, some experiments with a plate of pure plain iron as target were made. The gauze 6. was replaced by a special grid made of 15 fine parallel tungsten wires, which could be used as an auxiliary powerful filament. Applying a high potential (+1500 v.) to the target it was heated by electron bom-

bardment to incandescent temperatures and, in this way, completely degassed. In Fig. 4 some of the results are represented. The aggregate correction was determined again and found to be slightly different and also the position of the ionisation breaks was a little changed, but the general character of the curves remained the same. Curve I shows the run made after 10 hours baking in vacuo at 400° with the usual breaks, now at 10.8; 13.0; 16.0 and 17.0 (corrected) volts, as the average of several observations. Then the iron plate was heated to the melting point and the succeeding run is represented by Curve II.

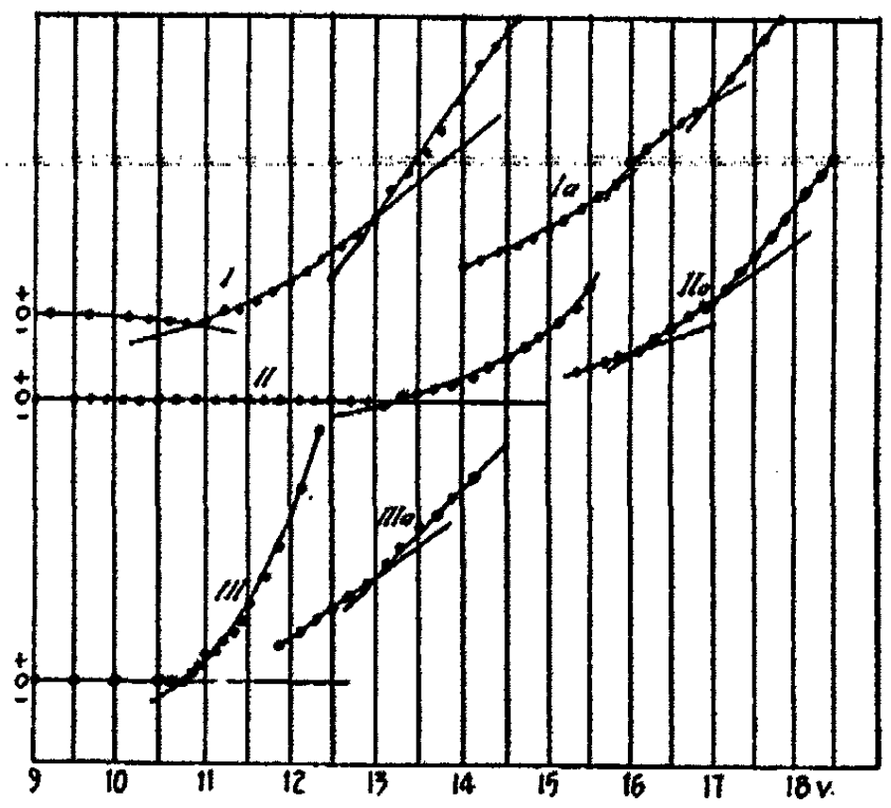



FIG. 4

No break at 11 volts is observable and the break at 13 volts is rather faint. After this run was made, 1 mm. of nitrogen was admitted for 5 min. and then the system was evacuated. In the following run (Curve III) strong ionisation at 10.8 volts was found. The gas pressure in the runs I and II was nearly the same, which can be concluded from the practical identity of the slopes of the curves Ia and IIa above 17 volts. In run III the pressure was higher. These experiments were completely reproducible although they were difficult and extremely time-consuming since the vacuum required was very high. Later observations with a calibrated ionisation gauge connected to the apparatus showed that, at $10^{-6}$ mm. pressure, adsorption of gas on a cooled metal was too quick for observations similar to those just described.

It seemed to be of interest to extend the experiments to other metals and, in the following table, the results are given of experiments with plain nickel, copper and platinum as targets. For each metal the aggregate correction was separately determined but no degassing experiments were undertaken on account of the difficulty already discussed.

TABLE I

| Metal | 1st break | 2nd break |
|---|---|---|
| Catal. Iron | 11.1 V. ±0.1 | 12.9 V. ±0.2 |
| Plain Iron | 10.8 V. ±0.2 | 13.0 V. ±0.2 |
| Plain Nickel | 10.8 V. ±0.2 | 13.1 V. ±0.2 |
| Plain Copper | 10.8 V. ±0.2 | 13.3 V. ±0.2 |
| Plain Platinum | 11.0 V. ±0.2 | 13.3 V. ±0.2 |

## Discussion

The experiments described above leave no doubt as to the origin of the observed ionisation at 11 volts. It is a surface effect due to adsorbed nitrogen. To decide in what form nitrogen is present on the metal surface we must consider that the ionisation energy of an adsorbed atom or molecule is probably different from that of a free atom or molecule. It is composed of the energy required to ionise a gaseous system plus the heat of adsorption of this system on the metal minus the absorption energy (work function) of an electron. The last two terms are not necessarily of the same magnitude. The unknown values of the heat of adsorption of nitrogen on metals and of the work function for metallic surfaces covered by adsorbed gas or for metal catalysts make any comparison between the calculated and observed values impossible. However, the ionisation at 11 volts cannot belong to the non-excited nitrogen molecule, as its heat of adsorption is undoubtedly positive and the work function of the metals in question is not higher than 5 volts. It must belong to the nitrogen atom or a kind of "excited" nitrogen molecule. The experiments give no conclusive decision as to what this modified nitrogen is. On the other hand, the work of Fryling[1] supplied the evidence that hydrogen on nickel is partly dissociated into atoms. Our experiments, in concordance with those of Wolfenden, showed that the ionisation at 13 volts belongs to the adsorbed hydrogen. This value is different only by a few tenths of a volt from the value for a free hydrogen atom (13.5 v.). We suggest that the ionisation energy of the free nitrogen system showing in the adsorbed state an ionisation at 11 volts, may not be far from this value. As the observations of the periodicity of the atomic ionisation potentials lead to a value near to 11 volts for nitrogen, the observed ionisation may be ascribed with some degree of certainty to the nitrogen atom.

The ionisation at 17 volts, as stated above, belongs to molecular nitrogen, that at 16 volts to molecular hydrogen. The source of hydrogen in the apparatus was not only the iron catalyst and other metals which undoubtedly contained some occluded gas, but also the water vapour coming from the deKhotinsky cement and dissociated by the hot filament.

The ionisation in the neighborhood of 11 volts has already been observed by several investigators. Olmstead[2] studying the critical potentials of hydrogen found it and ascribed it to the process $H_2 \longrightarrow H_2^+ + e$. Wolfenden (loc. cit.) showed that it is a surface effect and affirmed that the corresponding break in Olmstead's curves was observable only when dissociated hydrogen was pres-

[1] J. Phys. Chem., 30, 818 (1926).
[2] Phys. Rev., (2) 20, 613 (1922).

ent. Our opinion is that Olmstead's work shows no evidence for such an assumption but that the origin of this ionisation is the same as in our experiments. This is rather evident, as the apparatus of both investigators contained several metal parts which could not be sufficiently degassed.

Wolfenden determined the ionisation potentials on nickel as 11.3 and 13.4 volts applying a correction of $-1.6$ volts to the observed values. He estimated this correction on the assumption that only the ionisation of the hydrogen molecule was observed at higher gas pressures. A thorough study of the printed curves shows, however, that the lower break was also faintly present. Therefore, the straight lines should be drawn in a different fashion and the ionisation of the molecule located at 18.0 observed volts, that is, at the same potential as the breaks observed at low pressures, but left by Wolfenden out of consideration. This changes the applied correction to $-2.0$ volts, and the observed ionisations are now at 10.9 and 13.0 corrected volts, in very good agreement with the values given here. In the case of copper the correction was applied by Wolfenden probably in a right way, but as the ionisation due to nitrogen is very faint on copper he missed its beginning and determined a slightly higher value. The intensity of the nitrogen ionisation on different plain metals diminishes very noticeably in the direction Fe:Ni:Cu:Pt but it is difficult to draw any quantitative conclusions, as the effect is undoubtedly very dependent on the nature of the metallic surface. In the case of a metal with a very uneven surface (catalysts) only the ions from the outstanding points go partly through the field-free space and reach the collecting disc, the others being again adsorbed by the metal. This consideration explains the fact that the ionisation from the iron catalyst was fainter than from the piece of polished iron.

The apparatus used was not suited to quantitative study of the effects described and it is hoped that later work will give more data on the conditions of gas adsorption by metals and the amount of ions produced by electron bombardment.

I take this opportunity to express my sincere thanks to Professor Hugh S. Taylor for suggesting the present work and to Professor Karl T. Compton for his valuable advice.

I wish also to thank the International Education Board for the fellowship which enabled me to carry out this investigation in the Palmer Physical and Chemical Laboratories of Princeton University during the period January-May, 1926.

## Summary

1. An apparatus and method are described for the measurement of the positive ion current produced by slow electron impacts on metal surfaces.

2. It is shown that on iron, nickel, copper and platinum the positive ionisation starts at 11 and 13 v. For different metals the values are slightly different but the differences are not much larger than the possible experimental error.

3. Special experiments lead to the conclusion that the ionisation at 11 v. belongs to nitrogen adsorbed in the metal surface, that at 13 v. to adsorbed hydrogen.

4. It is shown theoretically that the ionisation at 11 v. cannot possibly belong to molecular nitrogen and is due to an excited molecule or a nitrogen atom. Analogies in favor of the latter suggestion are discussed.

5. The work of Wolfenden is critically examined and it is shown that his results are in concordance with the experiments here described.

*Princeton, N. J.*

# ADSORPTION BY HUMIC ACID

BY K. KAWAMURA

## Introduction

Before defining humic acid, we must first state what humus is. The term "humus" seems to be generally employed to designate the whole of the black substance which is regarded as an intermediate decompoeition product of organic matter in soil. Van Bemmelen[1] and later Baumann and Gully[2] showed humus to be a colloid complex. It may, however, be simply regarded as a mixture of numerous organic compounds as was thought by old chemists. Many attempts were made to fractionate humus into constituents of definite composition. Among such attempts, we should cite Schreiner and Shorey's investigation[3] as a splendid piece of work.[4] They succeeded in isolating over thirty organic compounds from humus. However, the yields of these compounds were respectively small as compared with the total amount of humus submitted for the separation. And furthermore, no black colloidal substance was isolated. Accordingly such compounds as found by Schreiner and Shorey are sometimes regarded as impurities of humus.[5]

The characteristic properties of humus are due essentially to the groups of humic acid and humin. The term "humic acid" was at first given to the substance which comes down as a brown precipitate from alkaline extract of humus on acidifying it.[6] Later it was found by Hoppe-Seyler[7] that the precipitate contained an impurity named "hymatomelanic acid" which differs from humic acid in its solubility in alcohol. This was confirmed by Odén.[7] Hence, humic acid is at present defined as one of the humus constituents which is soluble in alkali, and insoluble in water, acid and alcohol.

Existence of very much hymatomelanic acid in natural humus can not be expected, for it is a product derived from humic acid in the course of the fractionation[8]. "Humin" is designated as another portion of humus which differs from humic acid in that it is insoluble or difficultly soluble in alkali, being regarded as derived from humic acid.[9]

Thus the distinction of humic acid from humin is made merely by solubility in alkali. However, humic acid not only dissolves really in alkali, but also is apt to be peptized as in the case with humin. And hence, we are much

---

[1] J. M. van Bemmelen: "Die Absorption" (1910).
[2] A. Baumann: Mitt. bayr. Moorkulturanstalt, 3, 53 (1909); 4, 31 (1910).
[3] Schreiner and Shorey: U. S. Dept. Agr. Bur. of Soils, Bull. 53 (1909); 74 (1910).
[4] See also Lyon, Fippin and Buckman: "Soils, Their Properties and Management," 131-138 (1920).
[5] Ehrenberg und Bahr: J. Landwirtschaft 61, 428 (1913).
[6] See J. Russell: "Soil Conditions and Plant Growth," 139 (1921).
[7] Odén: Ber. 35, 651 (1912); also "Die Huminsäuren," (1919),
[8] Odén: "Die Huminsäuren" 108 (1919).
[9] See Bottomley: Biochem. J., 9, 260 (1915).

confused in deciding whether the colloidal particles come from humin or from humic acid. Accordingly, the so-called humin may be regarded as an irreversible or difficultly reversible gel of humic acid.

Analogous relation seems to hold in the case of the discrimination between humic acid and hymatomelanic acid by treatment with alcohol, because humic acid is also apt to be peptized by alcohol in the presence of a suitable amount of an electrolyte.

For the purpose of preparation of "pure humic acid," it is absolutely necessary to treat the precipitate obtained from alkaline extract with hot alcohol in order to make it free from hymatomelanic acid and from the impurities found by Schreiner and Shorey. This trea'ment, however, seems to cause certain changes in the physical or chemical nature of the humic acid, for it is converted into the substance which is difficultly soluble in alkali resembling humin or Odén's "difficultly soluble modification".[1] Beckley[2] assumed that the alcohol-insoluble humic acid was still a mixture of pyridine-soluble and -insoluble parts. But he did not give any information as to whether the whole alcohol-soluble substance submitted to treatment with the weak alkaline pyridine, was entirely soluble in other alkalies. Thus the preparation of "pure humic acid" is an extremely difficult task.

*Is humic acid a real acid?*—There have been two opposite opinions respecting the acidity of humus in connection with the humic acid problem. Old chemists, e. g. Sprengel, Berzelius, Mulder, settled this problem very simply by stating that humus contained an acid or acids. Since van Bemmelen demonstrated that humus is a colloid, a theory of non-existence of such acid or acids, seemed to prevail for a while. Cameron[3] writes in his book that "the existence of humic acid is purely hypothetical and without experimental or scientific verification." Baumann and Gully put forth a colloidal theory of the sourness of humus, indicating by their extensive works a colloidal nature for humus. This was, however, opposed by Tacke and Schüchting[4] who advocated the existence of real acid in humus. Soon after their disputes, there appeared Odén's work. He succeeded in preparing practically pure humic acid and found that the conductivity of an ammoniacal solution of the humic acid was greater than that of ammonia water. On this basis, he assumed that the humic acid combined with the ammonia, forming a salt whose degree of dissociation was higher than that of the ammonia water.

Ehrenberg and Bahr[5] studied the dissociation-isotherm of the substance resulting from combination of humic acid and ammonia, at different pressures, comparing the results with those obtained with stearate and arachinate of ammonia; and concluded that humic acid is a real acid. However they, failed to give exact information as to whether the specimen used was free from hymatomelanic acid.

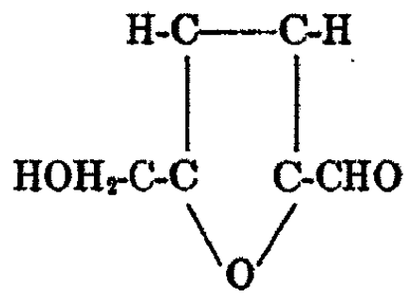
---

[1] Odén: "Die Huminsäuren," 90 (1919).
[2] Beckley: J. Agr. Sci., 2, 66 (1921).
[3] Cameron: "The Soil Solution," 55 (1911).
[4] Tacke and Schüchting: Landw. Jahrbücher, 41, 717 (1911).
[5] Ehrenberg and Bahr: J. Landwirtschaft, 61, 427 (1913).

*Artificial humic acid.* As previously stated, the separation and the purification of humic acid from natural humus is not an easy task. It is especially difficult in case a comparatively large amount is required, and, it is therefore preferable to make it synthetically in such case. Studies of artificial humic acid have been made from early times by many investigators. Braconnot and Malaguti prepared a substance resembling humus from cane sugar by decomposing it with hydrochloric acid, and detailed studies were followed by Berzelius, Mulder, and others. Nevertheless, their exhaustive works were not conclusive in identifying the artificial substance with that occurring in nature, although there was no criticism as to their resemblance in appearance, solubility and behavior toward alkali. However, positive verifications have been made by recent investigators in this respect.

Bottomley found that, when purified with alcohol, both humic acids—prepared from cane sugar and HCl, and separated from peat—yielded almost the same percentages of carbon, hydrogen and oxygen on analysis. He came to the conclusion that the reason the results of former investigators(Robertson, Irving and Dobson, 1907) indicated considerable difference between the compositions of the artificial and the natural humic acids, was due to the fact that the samples were not purified by alcohol before the analysis.

Maillard[1] found that when a mixture of sugar (e.g. glucose), amino acid (e.g. glycin), and water was warmed, it was converted into humus which was soluble in alkali. He accordingly put forth the theory that natural humus was derived from carbohydrates by the action of amino acids during the decomposition of decayed plants. Beckley[2] studied along this line and showed, going a step foward, that the formation of humus from carbohydrate and amino acid, proceeds in the following two stages:-

1 Carbohydrate $\xrightarrow{\text{amino acid}}$ 

(hydroxymethylfurfural)

2 Hyroxymethylfurfural $\longrightarrow$ Humus + Furfural + $CO_2$

Expressed in words, the most part of natural humus is derived from the polymerization of hydroxymethylfurfural which is formed from carbohydrate by the action (probably catalytic) of amino acid. And he explains that keto-hexose and keto-hexosans yield a greater quantity of humus than do other carbohydrates[3] because their structures resemble that of hydroxymethylfurfural. Futhermore, Beckley detected the intermediate substance, hydroxymethylfurfural, when cane sugar was converted into humus-like sub-

[1] Maillard: Compt. rend., **154**, 66; **155**, 1554 (1912); **156**, 1159 (1913).
[2] Beckley: J. Agr. Sci., **11**, 69 (1921).
[3] This fact was also noted by Bottomley.

stance by the action of HCl, and concluded that the black substance thus obtained, was the same in nature as that prepared from sugar and amino acid.

As far as Maillard's theory holds, Beckley's results are enough to afford great support for the assumption that the artificial humic acid from cane sugar and HCl is the same substance as the natural humic acid.

Thus all the results obtained by recent investigators confirm that the artificial humic acid is identical with the natural one, and as a consequence, they show us that it is best to investigate the artificial humic acid prepared from cane sugar for the purpose of obtaining some imformation about the nature of soil humic acid.

There are other methods for preparation of artificial humus substance. Bottomley found that "lactic, acetic, propionic, butyric, citric, tartaric, and oxalic acids when boiled with either cane sugar, dextrose or fructose yield humic acid and humin." But the yields thus obtained seem to be comparatively small. Eller and Koch[1] prepared humic acid from hydroquinone, quinone, pyrocatechol, and phenol by respective oxidation with potassium persulphate or air; and verified the fact that its composition, solubility, etc., are almost the same as those of natural humic acid. Furthermore, he assumes that quinone may be produced as an intermediate substance when hexose converts to humus substance by oxidation and dehydration.

*Purpose of the present investigation.*—As briefly noted before, the humic acid problem still leaves many questions to be further investigated in the fields of both organic and colloidal chemistry. However, so far as the writer knows, nobody has ever attempted to determine how pure humic acid behaves toward bases and acids—whether the reaction is really chemical or entirely physical. It is needless to say here much about the great significance of such study for soil chemistry. Hence the writer has undertaken to investigate the adsorption-isotherm of pure humic acid prepared from cane sugar. The detailed work and results will be given in the following.

## Experimental

I. *Preparation of Humic Acid.*

The details of preparation of humic acid were as follows: 200 grams of pure cane sugar were placed in a large evaporating dish, and 20 cc of 10% HCl were poured into it. The mixture was then warmed on a water bath for over three hours, stirring it occasionally by means of a glass rod. The mixture changed gradually to yellow, then to brown, and finally a black substance was formed, emitting a strong oder of furfural. Thus a mass of crude humus was obtained. A considerable quantity of hot water was then added to the black mass and the lumps were broken up by means of a porcelain pestle. was then filtered off. The black substance held behind on the filter paper, was washed with hot water until the wash water showed almost no coloration and almost no trace of the chlorine ion. Thus it was made free from Mulder's so-called "apocrenic acid."

[1] Eller and Koch: Ber. 53, 1469 (1920).

The separation and the purification of humic acid from the substance thus obtained, was carried out according to the methods employed by Odén[1] and by Beckley.[2] However, some modifications were introduced so as to make the methods applicable for preparation of the specimens on a comparatively large scale. That is, the crude humus was then treated with warm (60°C) solution of NaOH (5%) overnight, and then filtered through clean white cotton cloth.

The black filtrate obtained in this way, was then transferred to a 10-liter bottle and NaCl was dissolved in it until the total concentration reached about two normal. This was allowed to stand for four days in order to precipitate most of the solid particles in the solution.

A half portion of the supernatant liquid was then transferred to another bottle by means of a siphon, and was diluted with water until its color was brown but transparent when observed in a 4 mm glass tube. Afterwards, a considerable quantity of NaCl was again added so as to make the concentration of NaCl nearly the same as before. The solution was again allowed to stand for four days. Then a half portion of the alkaline solution of humus was siphoned, and the liquid obtained was filtered through hard fiber paper on a Buchner funnel. In this way, a practically true solution of humic acid was obtained. However when, examined under the ultramicroscope, it still showed more or less colloidal particles. The solution was then acidified with HCl, and a voluminous dark brown precipitate—crude humic acid—was obtained.

After the precipitate had settled to some extent, the supernatant liquid was siphoned off, and the suspended voluminous precipitate was transferred to a flask and heated to boiling; because, otherwise the precipitate was apt to be peptized again after the most of electrolytes contained were washed away in the process given below. The hot suspended matter was then filtered through hard filter paper by means of a large Buchner funnel connected to a suction pump.

The residue held behind on the funnel was then washed, at first with acidulated hot water and later, with a considerable amount of pure hot water without stopping the pump. The washing was continued for 2-3 days after the wash water showed no reaction for chlorine ion and no coloration. The residue was then placed in a round-bottomed flask and boiled with 95% alcohol under a reflux condenser 4-5 hours. Then the alcohol was filtered off by means of a Buchner funnel. Such treatment was repeated 7-8 times with more alcohol until the wash alcohol showed very faint coloration. The humic acid was then placed in a flask and was shaken up with ether, the latter being removed several times. After it was dried in an oven at 60-70°C to free it from most of the solvent used. The humic acid was then washed thoroughly with hot water. It was dried in the oven again for 1-2 days and was then pulver-

[1] Odén: Ber. 35, 651 (1912); "Die Huminsäuren" (1919).
[2] Beckley: J. Agr. Sci., 2, 66 (1921).

ized by means of porcelain mortar and pestle. The powder which passed through 160 mesh sieve was allowed to dry in the air for 24 hours, and thus the sample used for the present investigation was obtained.

## II. *Action of Bases on Stearic Acid.*

Humic acid is still a substance of uncertain composition, purity, and properties. It is assumed, however, to be an insoluble acid which forms practically insoluble salts with certain bases. Before studying the property of humic acid, therefore, it seemed desirable to find out what a substance will do which is really an insoluble acid, in order to have some basis for determining whether humic acid behaves normally or not. Stearic acid seems to satisfy this request. The action of $Ba(OH)_2$ and NaOH on stearic acid was therefore studied.

To prepare the specimen to be investigated, commercial stearic acid was taken up and recrystallized from alcoholic solution four times in succession. The scale-like crystals (m.p.69°C) thus obtained were pulverized by means of a porcelain mortar and pestle; and the part which passsed through an 80-mesh sieve was used for the following experiment:

Procedure:—One gram of stearic acid was placed in a 200 cc bottle, and a 100 cc portion of $Ba(OH)_2$ solution of varying normalities was added to it. Since the reaction velocity between stearic acid and $Ba(OH)_2$ was very slow at room temperature, the treatment was at first carried out at high temperature but just below the melting point of stearic acid. That is, the bottle was immersed in a water bath of 65-67°C without a stopper for the first few minutes and then a rubber stopper was inserted. The treatment was continued for eight hours shaking vigorously by hand 3-4 times an hour.

The white film of stearic acid which had covered the inside wall of the empty part as well as the air-liquid surface of the bottle, disappeared when the $Ba(OH)_2$ in the bottle was totally taken up by the stearic acid. Such a phenomenon, however, never occurred when free $Ba(OH)_2$ remained in the bottle. From this we could find approximately the amount of $Ba(OH)_2$ equivalent to the stearic acid added.

The bottle was then taken out of the bath, and was cooled to room temperature (22°C). It was opened once and quickly stoppered again, and was then allowed to stand at room temperature for 48 hours, occasionally shaking by hand.

After the reaction reached equilibrium, the contents were filtered through three sheets of piled, dry filter papers about 2-3 times in succession. Thus a perfectly transparent filtrate was obtained. However, when the filtrate was neutral, it was rather difficult to make the liquid entirely free from white particles. Then a 10 cc portion of the filtrate was pipetted into an Erlenmeyer flask and was titrated with 0.1 or 0.01 normal HCl, using phenolphthalein as an indicator. From the number secured in the titration, the concentration as well as the amount of the base taken up by the humic acid was calcurated. The results are summarized in Table I.

Next, the examination of the NaOH adsorption was carried out. The procedure of the treatment was almost the same as used in the previous case but that the preliminary treatment was made at 62-63°C for 5.5 hours. However, at the final titration, some modification was found necessary in the this case, because, first, the sodium stearate formed, swelled up so that only a small quantity of the filtrate was obtainable; (such swelling was especially remarkable when the initial concentration of NaOH solution was equivalent to the amount of stearic acid brought into contact, or a little less than the equivalent); and the second, the sodium stearate formed dissolved partly in the solution, giving an alkaline reaction, so that we could not simply determine the NaOH concentration by such titration.

TABLE I
Adsorption of $Ba(OH)_2$ by Stearic Acid
(One gram stearic acid and 100 cc $Ba(OH)_2$ solution)

| No. | Concentration of $Ba(OH)_2$ in equivalent millimols per 1000c. | | Equivalent millimols of $Ba(OH)_2$ taken up by one gram of stearic acid |
|---|---|---|---|
| | Initial concentration | Final concentration at equilibrium | |
| 1. | 0.095 | 0.00 | 0.095 |
| 2. | 0.503 | 0.00 | 0.503 |
| 3. | 0.96 | 0.00 | 0.96 |
| 4. | 2.96 | 0.00 | 2.96 |
| 5. | 3.62 | 0.15 | 3.47 |
| 6. | 5.05 | 1.46 | 3.59 |
| 7. | 6.70 | 3.10 | 3.60 |
| 8. | 8.30 | 4.70 | 3.60 |
| 9. | 10.20 | 6.45 | 3.75 |
| 10. | 15.20 | 11.30 | 3.95 |

To overcome such difficulties 20 grams of NaCl were added to the bottle before the filtration of its contents, thus making the swelled stearate coagulate thoroughly and the dissolved stearate salt out entirely. Then the mixture was filtered out through dry filter paper as before.

10 cc of the filtrate were then pipetted out and titrated with standard HCl using phenolphthalein as indicator. Since the addition of NaCl causes volume change of the solution, 10 cc of the filtrate do not correspond to 10 cc of the initial solution. In order to determine this relation, 10 cc of all stock NaOH solutions used were titrated before and after addition of 20 grams of NaCl per 100 cc.; and the concentration change caused by the salt addition was found in this way. Then the number secured in the titration of the filtrate was checked up with that found when the filtrate did not have NaCl. Table II gives the simplified result thus obtained showing the relation between the concentration and the amount of NaOH taken by up one gram of stearic acid.

Result and discussion.—The results given in Tables I and II are shown graphically in Fig. 1. As shown by the tables and the chart, it is obvious in every case that the whole of the $Ba(OH)_2$ or NaOH is taken up when the initial concentration of the base is below 3.5 equivalent millimols per 100 cc. Beyond this point the amount taken may be regarded as approximately constant.

Now applying the phase rule to the following three component system:

$$2\,C_{17}H_{35}COOH + Ba(OH)_2 = (C_{17}H_{35}COO)_2Ba + 2\,H_2O$$

we will find two solid phases and one liquid phase so long as there is any free

TABLE II

Adsorption of NaOH by Stearic Acid

| No. | Concentration of NaOH in millimols per 100 cc. | | Millimols of NaOH taken up by one gram of stearic acid |
|---|---|---|---|
| | Initial concentration | Final Concentration at equilibrium | |
| 1 | 0.0915 | 0.00 | 0.0915 |
| 2 | 0.443 | 0.00 | 0.443 |
| 3 | 0.965 | 0.00 | 0.965 |
| 4 | 2.865 | 0.00 | 2.865 |
| 5 | 3.50 | 0.00 | 3.50 |
| 6 | 5.00 | 1.41 | 3.59 |
| 7 | 6.55 | 2.81 | 3.74 |
| 8 | 8.00 | 4.30 | 3.71 |
| 9 | 10.00 | 6.50 | 3.50 |
| 10 | 50.00 | 45.83 | 4.17 |
| 11 | 100.00 | 95.70 | 4.30 |

stearic acid left. In such case the system has two degrees of freedom—temperature and pressure. Therefore the concentration of $Ba(OH)_2$ should be constant as long as the salt formation is not completed. On the other hand, when the stearic acid is converted completely into stearate, there will be one solid phase and one liquid phase at equilibrium, and in turn, the system will have three degrees of freedom. If so, the concentration of $Ba(OH)_2$ can be altered without altering the composition of the solid phase. In other words, the amount of $Ba(OH)_2$ taken up by the stearic acid is to be constant at any concentration. Therefore, the adsorption-concentration diagram should yield a right-angled curve. In a similar way, the rule is applicable to the system of stearic acid and NaOH solution.

The results secured above indicate that the rule holds fairly well in every case; the vertical portion of the curve, the portion of zero concentration in the liquid, represents the formation of a chemical compound, the salt, while the horizontal portion denotes zero adsorption. But strictly speaking,

we cannot neglect the fact that the amount taken up increases at a slight rate with increase of concentration, indicating slight adsorption by the stearate formed.

The point where the stearic acid is changed completely into stearate, is found in the place where 3.5 equivalent millimols of base is taken up. This

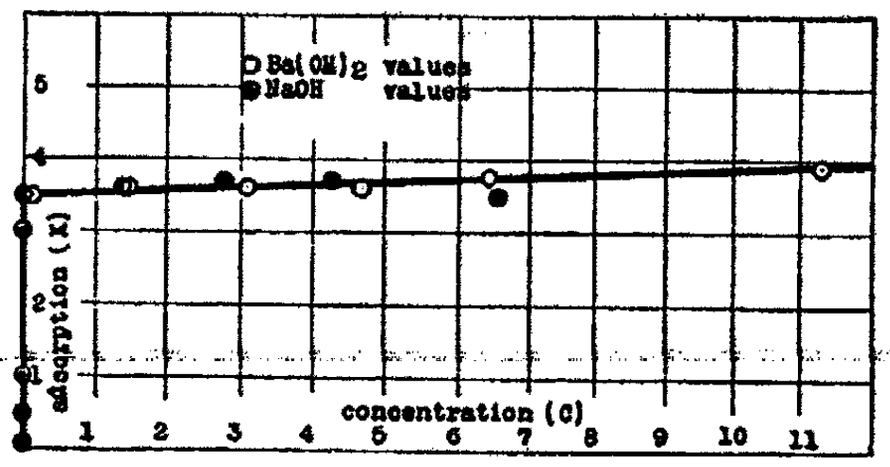



FIG. 1
Adsorption—Concentration Diagram of Bases by Stearic Acid.

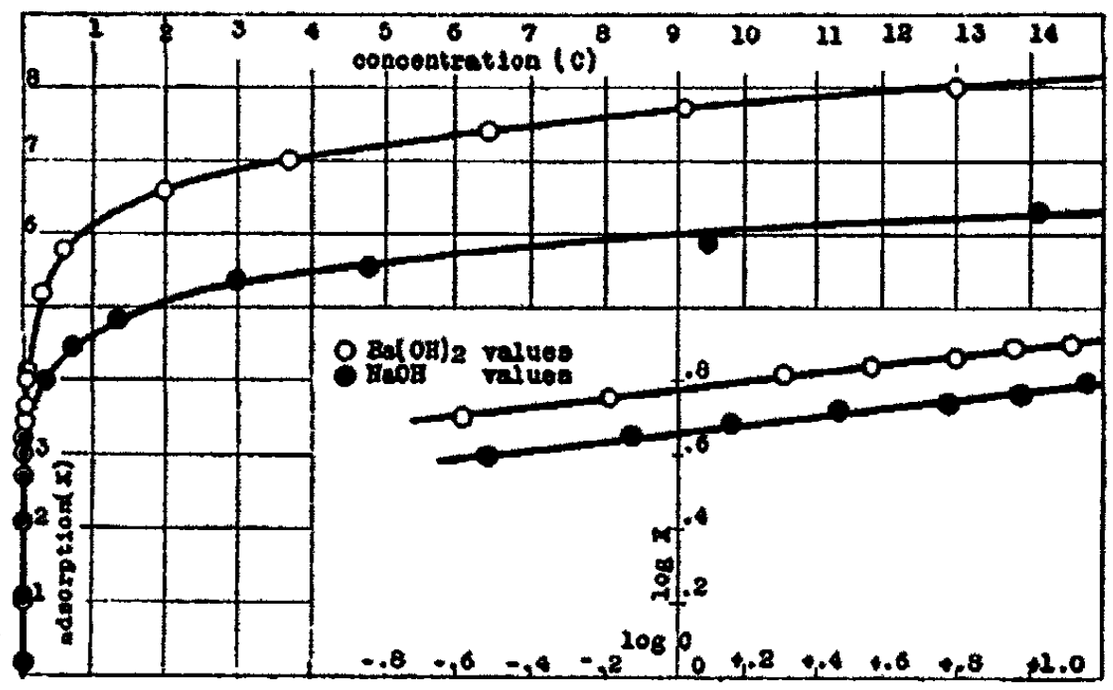



FIG. 2
Adsorption—Concentration Diagram of Bases by Humic Acid.

agrees very well with the point theoretically found; for, the molecular weight of stearic acid is 284.34, and as a consequence, the equivalent amount of base should be 3.516 equivalent millimols per one-gram of the acid.

III. *Action of Bases on Humic Acid.*

The preceding experiments show how a real insoluble acid behaves toward bases. We can now determine whether humic acid behaves in the same way that stearic acid does.

Procedure. The experiment was carried out similarly to that employed in the case of stearic acid. The details were as follows:—

One gram of air-dry humic acid (moisture content[1] 7.0%) obtained by the method described before, was treated with 100 cc of $Ba(OH)_2$ solution of various concentrations in a 200 cc rubber stoppered bottle. The treatment was carried out at 60-62°C for the first three hours, then the bottle was allowed to stand at room temperature for 48 hours, shaking occasionally by hand. After equilibrium was thus established, the mixture was filtered

TABLE III

Adsorption of $Ba(OH)_2$ by Humic Acid

| No. | Concentration of $Ba(OH)_2$ in equivalent millimols per 100 cc. | | | Equivalent millimols of $Ba(OH)_2$ taken up | | |
|---|---|---|---|---|---|---|
| | Initial Conc. | Concentration at equilibrium | | by 1 gram of air-dry humic acid | by 1 gram of dry humic acid | |
| | | C | log C | | x | log x |
| 1 | 0.095 | 0.00 | | 0.095 | 0.10 | |
| 2 | 0.186 | 0.00 | | 0.186 | 0.20 | |
| 3 | 0.98 | 0.00 | | 0.98 | 1.05 | |
| 4 | 1.96 | 0.00 | | 1.96 | 2.11 | |
| 5 | 2.51 | 0.00 | | 2.51 | 2.70 | |
| 6 | 2.78 | 0.00 | | 2.78 | 2.99 | |
| 7 | 3.015 | trace | | 3.015 | 3.24 | |
| 8 | 3.25 | 0.015 | —1.8239 | 3.24 | 3.48 | 0.5416 |
| 9 | 3.50 | 0.034 | —1.4685 | 3.47 | 3.73 | 0.5717 |
| 10 | 3.76 | 0.056 | —1.2518 | 3.70 | 3.98 | 0.6999 |
| 11 | 3.96 | 0.070 | —1.1549 | 3.89 | 4.18 | 0.6212 |
| 12 | 5.04 | 0.265 | —0.5768 | 4.78 | 5.14 | 0.7110 |
| 13 | 6.07 | 0.623 | —0.2055 | 5.35 | 5.75 | 0.7597 |
| 14 | 8.11 | 2.02 | 0.3054 | 6.09 | 6.55 | 0.8162 |
| 15 | 10.20 | 3.70 | 0.5682 | 6.50 | 6.99 | 0.8445 |
| 16 | 13.25 | 6.40 | 0.8062 | 6.85 | 7.36 | 0.8669 |
| 17 | 16.30 | 9.10 | 0.9590 | 7.20 | 7.74 | 0.8887 |
| 18 | 20.40 | 13.00 | 1.1139 | 7.40 | 7.96 | 0.9009 |

through dry filter paper repeatedly. The filtrate thus obtained was transparent but slightly yellow colored, indicating that humic acid is slightly soluble in $Ba(OH)_2$ solution. A 10 or 25 cc portion of the filtrate was placed in an Erlenmeyer flask and was titrated with 0.1 or 0.01 normal HCl, using phenolphthalein as an indicator. From the secured number, the concentration and the amount of the base taken up by the humic acid were calcurated. The results are given in Table III and Fig. 2.

Next, the adsorption of NaOH was examined in a similar way as before. When the warm mixture of humic acid and NaOH was shaken up, there was found some difference among the stabilities of foams which appeared on air-

[1] The determination was made by drying the humic acid at 110°C.

liquid surface in the bottle. The maximum stability seemed to appear when 0.0276 normal NaOH was applied. But further detailed studies in this respect were not made.

After the equilibrium of the reaction was established at room temperature, 20 grams of NaCl were dissolved in the mixture. The purpose of this was merely to make the experiment run parallel to that carried out with stearic acid. For, the effect of the salt addition was not appreciable in the coagulation

TABLE IV

Adsorption of NaOH by Humic Acid

| No. | Concentration of NaOH in millimols per 100 cc. | | | Millimols of NaOH taken up | | |
|---|---|---|---|---|---|---|
| | Initial conc. | Concentration at equilibrium | | by 1 gram of air-dry humic acid | by 1 gram of dry humic acid | |
| | | C | log C | | x | log x |
| 1 | 0.10 | 0.00 | | 0.10 | 0.11 | |
| 2 | 0.21 | 0.00 | | 0.21 | 0.23 | |
| 3 | 1.04 | 0.00 | | 1.04 | 1.12 | |
| 4 | 1.98 | 0.00 | | 1.98 | 2.13 | |
| 5 | 2.49 | 0.00 | | 2.49 | 2.68 | |
| 6 | 2.76 | 0.00 | | 2.76 | 2.97 | |
| 7 | 2.99 | 0.03 | —1.5229 | 2.96 | 3.18 | 0.5024 |
| 8 | 3.98 | 0.30 | —0.5229 | 3.68 | 3.96 | 0.5977 |
| 9 | 4.96 | 0.745 | —0.1278 | 4.215 | 4.53 | 0.6561 |
| 10 | 6.00 | 1.43 | 0.1553 | 4.57 | 4.91 | 0.6911 |
| 11 | 8.00 | 2.96 | 0.4713 | 5.04 | 5.42 | 0.7340 |
| 12 | 10.05 | 4.80 | 0.6812 | 5.25 | 5.64 | 0.7513 |
| 13 | 15.00 | 9.49 | 0.9773 | 5.51 | 5.92 | 0.7723 |
| 14 | 19.95 | 14.10 | 1.1492 | 5.85 | 6.29 | 0.7987 |

of the dissolved or peptized humate as was the case with sodium stearate. Then the mixture was filtered repeatedly and rapidly through dry filter paper, and in this way, a yellow to deep brown colored filtrate was obtained. The color of the filtrate was more intense the more concentrated the NaOH added, thus obstructing the color change of phenolphthalein during the titration. Hence, 10 cc or 25 cc of the filtrate were pipetted into an Erlenmeyer flask and diluted, before titration, with distilled water until it showed a light yellow color of definite intensity to the naked eye. Then it was titrated with a standard HCl solution as usual.

Table IV gives the final results secured. The alkalinity change caused by the addition of NaCl was taken into account in the calculation as previously described.

Discussion. As shown in the above results, one gram of dry humic acid takes up the whole of the $Ba(OH)_2$ and NaOH from their solutions as long as their initial concentrations do not reach about 3.0 equivalent millimols per 100 cc. That is, in such cases, the concentration is found to be always zero

at equilibrium. This seems as if we were dealing with two solid phases just the same as in the case of stearic acid and stearate. Thus the results indicate the formation of the definite chemical compounds, barium humate and sodium humate.

However, when strong solutions of the bases (above 3.0 equivalent mills per 100 cc) are brought in contact, the humic acid behaves differently from stearic acid. That is, as shown in Table II, the amount of base taken, is found to be a logarithmic function of the concentration. This is represented by the ordinary adsorption equation:

$$\log x = K + n \log C$$

where $x$ and C are respectively the amount taken and the concentration, given in Tables III and IV; and K and $n$ are constants which can be found from the logarithmic curves shown in Fig. 2.

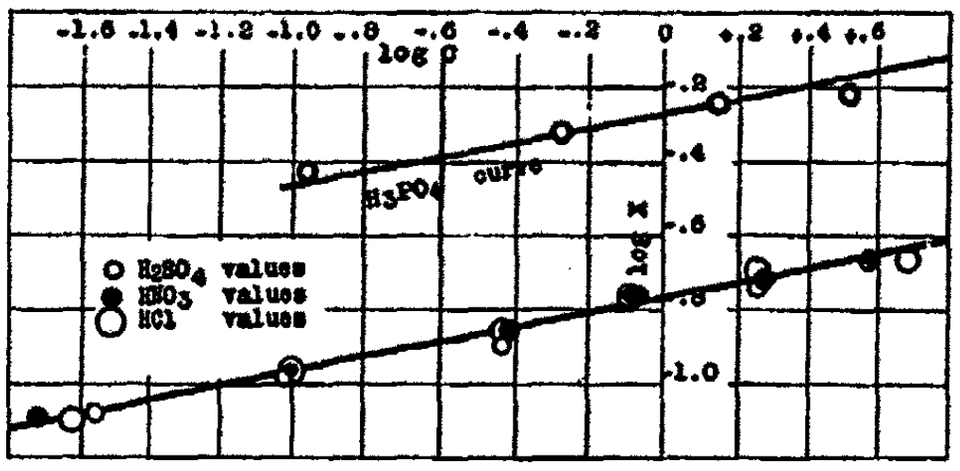



FIG. 3
Adsorption—Concentration Diagram of Acids by Humic Acid.

From these facts we come to the conclusion that the barium and sodium humates that are formed, adsorb $Ba(OH)_2$ and NaOH respectively from the solution.

The adsorptive powers of the humates are markedly high while those of the stearates are not appreciable. This is the only difference between the adsorption isotherms of humic acid and stearic acid which are shown in Fig. 1 and 2 respectively.

Comparing the adsorptive powers of sodium humate and barium humate, the former is somewhat less than the latter. This seems to be due to the fact that sodium humate is markedly soluble while barium humate is only slightly soluble. Accordingly, the titration number of the filtrate resulting from the reaction of humic acid with NaOH, would not be regarded as indicating the strength of NaOH only, because the sodium humate dissolved would give an alkaline reaction to phenolphthalein, owing to its hydrolysis.

IV. *Adsorption of Mineral Acids by Humic Acid.*

We have shown in the previous experiments how humic acid behaves toward bases. Now we will demonstrate how it behaves toward mineral acids in order to determine further its properties. The following are studies of adsorptions of $H_3PO_4$, $H_2SO_4$, $HNO_3$ and HCl by humic acid.

Procedure. One gram of air-dry humic acid (moisture content 9.7%) was placed in a 200 cc bottle, and treated with 100 cc of mineral acid solution of varying concentrations at room temperatures for four days, shaking vigorously by hand. The contents was filtered as usual. Then 10 or 25 cc of the filtrate were pipetted into an Erlenmeyer flask, and titrated with 0.01 normal NaOH solution using phenolphthalein as an indicator except in the case of $H_3PO_4$ where methyl orange was employed.

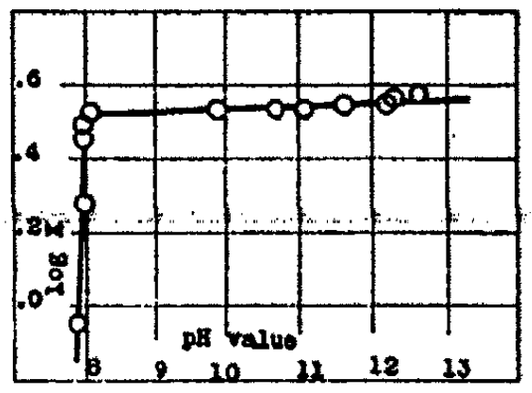



FIG. 4
Adsorption—pH Diagram of $Ba(OH)_2$ by Stearic Acid.

Results and Discussion. The results are given in Tables V-VIII. These results indicate that a portion of the mineral acid added always remains without being taken up by the humic acid—that is, we find no zero concentration in every case of the experiments. And the amount of the mineral acid taken up by the humic acid is found to be always a logarithmic function of the concentration. Thus there is no evidence of the formation of a definite chemical compound between humic acid and the mineral acids, Fig. 3.

The amounts of $H_2SO_4$, $HNO_3$ and HCl adsorbed are quite the same, while more $H_3PO_4$ seems to be adsorbed relatively. The strict comparison, however, may not be allowed, because a different indicator was employed in the titration of $H_3PO_4$ as mentioned above. However, the adsorptions of all mineral acids by humic acid are markedly low as compared with those of bases.

TABLE V

Adsorption of $H_3PO_4$ by Humic Acid

| No. | Concentration of $H_3PO_4$ in equivalent millimols per 100 cc. | | | Equivalent millimols of $H_3PO_4$ adsorbed | | |
|---|---|---|---|---|---|---|
| | Initial concentration | Concentration at equilibrium | | by 1 gram of air-dry humic acid | by 1 gram of dry humic acid | |
| | | C | log C | | x | log x |
| 1 | 0.10 | acid to bromcresol purple | | | | |
| 2 | 0.20 | acid to methyl red | | | | |
| 3 | 0.45 | 0.11 | —0.9586 | 0.34 | 0.38 | —0.4202 |
| 4 | 0.95 | 0.52 | —0.2840 | 0.43 | 0.48 | —0.3188 |
| 5 | 1.92 | 1.40 | 0.1461 | 0.52 | 0.58 | —0.2366 |
| 6 | 3.88 | 3.34 | 0.5237 | 0.54 | 0.60 | —0.2218 |

TABLE VI

Adsorption of $H_2SO_4$ by Humic Acid

| No. | Concentration of $H_2SO_4$ in equivalent millimols per 100 cc. | | | Equivalent millimols of $H_2SO_4$ adsorbed | | |
|---|---|---|---|---|---|---|
| | Initial concentration | Concentration at equilibrium | | by 1 gram of air-dry humic acid | by 1 gram of dry humic acids | |
| | | C | log C | | x | log x |
| 1 | 0.102 | 0.028 | —1.5528 | 0.074 | 0.082 | —1.0862 |
| 2 | 0.194 | 0.098 | —1.0088 | 0.096 | 0.106 | —0.9747 |
| 3 | 0.49 | 0.37 | —0.4318 | 0.12 | 0.13 | —0.8861 |
| 4 | 0.98 | 0.83 | —0.0809 | 0.15 | 0.17 | —0.7696 |
| 5 | 1.98 | 1.82 | 0.2601 | 0.16 | 0.18 | —0.7447 |
| 6 | 3.99 | 3.79 | 0.5786 | 0.20 | 0.22 | —0.6576 |

TABLE VII

Adsorption of $HNO_3$ by Humic Acid

| No. | Concentration of $HNO_3$ in millimols per 100 cc. | | | Millimols of $HNO_3$ adsorbed | | |
|---|---|---|---|---|---|---|
| | Initial concentration | Concentration at equilibrium | | by 1 gram of air-dry humic acid | by 1 gram of dry humic acid | |
| | | C | log C | | x | log x |
| 1 | 0.094 | 0.019 | —1.7212 | 0.075 | 0.083 | —1.0809 |
| 2 | 0.198 | 0.100 | —1.0000 | 0.098 | 0.109 | —0.9626 |
| 3 | 0.51 | 0.38 | —0.4202 | 0.13 | 0.14 | —0.8539 |
| 4 | 1.025 | 0.87 | —0.0605 | 0.155 | 0.17 | —0.7696 |
| 5 | 2.02 | 1.85 | 0.2672 | 0.17 | 0.19 | —0.7212 |
| 6 | 4.00 | 3.8 | 0.5798 | 0.20 | 0.22 | —0.6576 |

TABLE VIII

Adsorption of HCl by Humic Acid

| No. | Concentration of HCl in millimols per 100 cc. | | | Millimols of HCl adsorbed | | |
|---|---|---|---|---|---|---|
| | Initial concentration | Concentration at equilibrium | | by 1 gram of air-dry humic acid | by 1 gram of dry humic acid | |
| | | C | log C | | x | log x |
| 1 | 0.096 | 0.024 | —1.6198 | 0.072 | 0.08 | —1.0969 |
| 2 | 0.20 | 0.10 | —1.0000 | 0.10 | 0.11 | —0.9586 |
| 3 | 0.50 | 0.37 | —0.4318 | 0.13 | 0.14 | —0.8539 |
| 4 | 0.99 | 0.84 | —0.0757 | 0.15 | 0.17 | —0.7696 |
| 5 | 2.00 | 1.82 | 0.2601 | 0.18 | 0.20 | —0.6990 |
| 6 | 5.00 | 4.80 | 0.6812 | 0.20 | 0.22 | —0.6576 |

V. *Hydrogen Ion Function of the Adsorption.*

Since humic acid behaves peculiarly toward bases, it needs to be carefully investigated with a more refined method to determine whether the reaction is partly, at least, salt formation or entirely adsorption. In the present work, therefore, the hydrogen ion function of adsorption was studied with stearic and humic acids.

Stearic acid and humic acid used in the present investigation were prepared according to the same method employed before. They were both pulverized very finely and screened through a 160-mesh sieve.

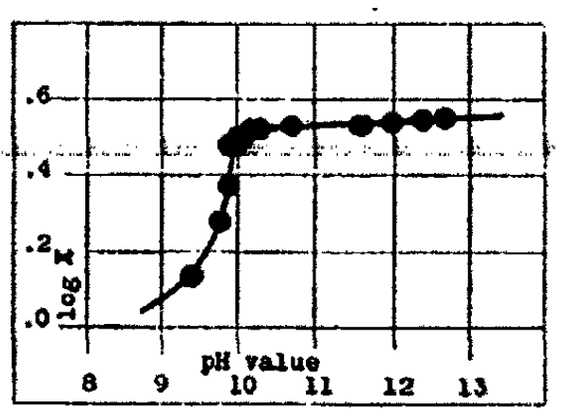



FIG. 5
Adsorption—pH Diagram of NaOH by Stearic Acid.

The color of the humic acid powder turned to black brown, then brown, and finally light brown as its particles became finer on further pulverization. The humic acid thus obtained had a lighter color than that used in the previous work; in other words, it was finer than that previously prepared.

General procedure. The procedure was similar to that employed in the previous experiments. That is, one gram of stearic acid or humic acid (moisture content 7.19%) was placed in a 200 cc rubber stoppered bottle, and 100 cc of $Ba(OH)_2$ or NaOH of varying concentrations were added to it. The mixture was treated at 60°-65°C for the first 3-8 hours using a water bath, and later at room temperature for 72 hours, frequently shaking by hand. Then the contents in the bottle were filtered through dry paper filter as usual.

A 10 or 25 cc portion of the filtrate thus obtained was pipetted into an Erlenmeyer flask and titrated with standard HCl solution, phenolphthalein being used as an indicator. Taking up another portion of the filtrate, its hydrogen ion concentration was determined electrometrically or colorimetrically. However, the methods employed after establishment of the equilibrium were varied somewhat in reference to the nature of the products of the acids and the bases. These will be described in their individual cases.

Stearic Acid and $Ba(OH)_2$. The treatment of stearic acid and $Ba(OH)_2$ was carried out in the usual way. Hydrogen ion concentration of the filtrate obtained, was determined electrometrically. The results secured are summarized in Table IX and the adsorption-pH diagram is charted in Fig. 4.

The most outstanding feature of the results is that there is a great gap of pH value at the point where 3.5 equivalent millimols of $Ba(OH)_2$—the amount equivalent to one gram of stearic acid—was added to the reaction. As long as the added amount of the base did not reach 3.5 equivalent millimols, the pH value of the liquid remained constant while the base added was totally taken up by the acid. Beyond 3.5 equivalent millimols, the amount taken re-remained constant while the pH value increased. Consequently, the adsorp-

tion-pH diagram yielded a practically right angled curve. But strictly speaking, we may point out the fact that the amount taken increased slightly but unmistakably as pH increased, thus indicating slight adsorption.

Stearic Acid and NaOH. The reaction product of stearic acid and NaOH was filtered through hard filter paper by means of a Buchner funnel. Since the filtrate thus obtained was then titrated in the usual way, the secured alkalinity was regarded as indicating the total sum of free NaOH and sodium

TABLE IX

Relation between Hydrogen Ion Concentration and Adsorption of $Ba(OH)_2$ by Stearic Acid

| No. | Concentration of $Ba(OH)_2$ in equivalent millimols per 100 cc. | | pH | $Ba(OH)_2$ taken up by 1 gram of stearic acid in equivalent millimols | |
|---|---|---|---|---|---|
| | Initial Conc. | Conc. at equilibrium (C) | | x | log x |
| 1 | 0.92 | | 7.9 | 0.92 | −0.3620 |
| 2 | 1.91 | | 8.0 | 1.91 | 0.2810 |
| 3 | 2.88 | | 8.0 | 2.88 | 0.4594 |
| 4 | 3.19 | | 8.0 | 3.19 | 0.5038 |
| 5 | 3.35 | | 8.1 | 3.35 | 0.5250 |
| 6 | 3.53 | 0.04 | 9.9 | 3.49 | 0.5428 |
| 7 | 3.58 | 0.09 | 10.7 | 3.49 | 0.5428 |
| 8 | 3.66 | 0.16 | 11.1 | 3.50 | 0.5441 |
| 9 | 3.96 | 0.38 | 11.6 | 3.58 | 0.5539 |
| 10 | 4.95 | 1.37 | 12.2 | 3.58 | 0.5539 |
| 11 | 6.06 | 2.28 | 12.3 | 3.72 | 0.5705 |
| 12 | 8.00 | 4.15 | 12.6 | 3.85 | 0.5855 |

stearate dissolved. In cases where the original amount of NaOH added was less than 3.5 millimols, the titration alkalinities represented only the amount of dissolved stearate. However, the amount of dissolved stearate was found to be pratically constant for the range between 3.0–3.5 millimols of the initial concentration per 100 cc.

The hydrogen ion concentration was determined colorimetrically and was checked up by the electrical method; for, the writer found some difficulty in applying the latter method to the solution which contained only sodium stearate.

The results are given in Table X and Fig. 5. Reference to these results indicates that as long as the salt formation is not completed, the pH remains practically constant; but after the total stearic acid is converted into stearate, the NaOH amount taken up by the solid phase is practically constant while the pH value increases. Consequently, as far as it concerns the neighbourhood of the point where the stearic acid phase disappears, the adsorption-pH diagram shows a similar curve to that obtained with $Ba(OH)_2$. However, in the case of NaOH, we meet no sudden change of pH at the 3.5 millimol point

as obtained with $Ba(OH)_2$. This reason is obviously due to the formation of soluble sodium stearate which gives an alkaline reaction and produces a buffer action to such a sudden change.

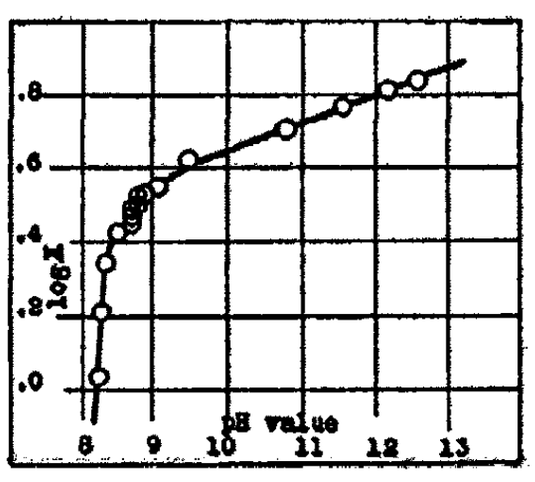



FIG. 6
Adsorption—pH Diagram of $Ba(OH)_2$ by Humic Acid.

Humic Acid and $Ba(OH)_2$. The treatment of humic acid and $Ba(OH)_2$ was carried out in a manner similar to that employed before. The filtrate obtained possessed a slightly yellow color, showing that humic acid is slightly soluble in $Ba(OH)_2$ solution. A portion of the filtrate was titrated as usual. And another portion was submitted for electrometrical measurement of its hydrogen ion concentration. The final results are given in Table XI and the adsorption-pH diagram is charted in Fig. 6.

As shown in the table, the results are nearly the same as obtained in Experiment 3. That is, as long as the initial concentration of the base does nor reach a value of about 3.0 equivalent-millimols per 100 cc, it is almost totally taken up by humic acid, while the pH value changes "very slightly" as the initial concentration varies. Beyond the 3.0 equivalent millimol point, however, the adsorption increases gradually while the pH value increases appre-

TABLE X

Relation between Hydrogen Ion Concentration and Adsorption of NaOH by Stearic Acid

| No. | Concentration of NaOH in milligram-atoms per 100 cc | | pH | NaOH taken up by 1 gram of stearic acid in mg.-atoms | |
|---|---|---|---|---|---|
| | Initial Conc. | Conc. at equilibrium (C) | | x | log x |
| 1 | 0.98 | 0.00 | 7.5 | 0.98 | −0.0088 |
| 2 | 1.48 | 0.04 | 9.4 | 1.44 | 0.1584 |
| 3 | 2.00 | 0.08 | 9.8 | 1.92 | 0.2833 |
| 4 | 2.49 | 0.10 | 9.9 | 2.39 | 0.3784 |
| 5 | 3.00 | 0.11 | 9.9 | 2.89 | 0.4609 |
| 6 | 3.12 | 0.13 | 10.0 | 2.99 | 0.4757 |
| 7 | 3.20 | 0.13 | 10.0 | 3.07 | 0.4871 |
| 8 | 3.30 | 0.14 | 10.0 | 3.16 | 0.4997 |
| 9 | 3.38 | 0.14 | 10.1 | 3.18 | 0.5024 |
| 10 | 3.49 | 0.14 | 10.2 | 3.35 | 0.5250 |
| 11 | 3.56 | 0.14 | 10.3 | 3.42 | 0.5340 |
| 12 | 3.66 | 0.20 | 10.7 | 3.46 | 0.5391 |
| 13 | 4.02 | 0.515 | 11.6 | 3.505 | 0.5447 |
| 14 | 5.05 | 1.57 | 12.0 | 3.48 | 0.5416 |
| 15 | 6.00 | 2.47 | 12.4 | 3.53 | 0.5478 |
| 16 | 8.15 | 4.62 | 12.7 | 3.53 | 0.5478 |

ciably. Accordingly, the logarithmic curve of the adsorption-pH diagram (Fig 6) bends comparatively sharply at the 3.0 equivalent millimol point. Hence the curve seems to consist of two straight lines as an approximation. But, strictly speaking, the adjacent portions of the two lines are connected with a curve whose direction changes gradually from one direction of the line to the other so that we are unable to find out any sharp point of intersection of the two lines.

TABLE XI

Relation between Hydrogen Ion Concentration and Adsorption of $Ba(OH)_2$ by Humic Acid

| No. | Concentration of $Ba(OH)_2$ in equivalent millimols per 100 cc. | | pH | Equivalent millimols of $Ba(OH)_2$ taken up | | |
|---|---|---|---|---|---|---|
| | Initial conc. | Concentration at equilibrium (C) | | by 1 gram of air-dry humic acid | by 1 gram of dry humic acid | |
| | | | | | x | log x |
| 1 | 1.02 | | 8.0 | 1.02 | 1.10 | 0.0414 |
| 2 | 1.50 | | 8.2 | 1.50 | 1.62 | 0.2095 |
| 3 | 2.02 | | 8.3 | 2.02 | 2.18 | 0.3385 |
| 4 | 2.46 | | 8.5 | 2.46 | 2.65 | 0.4232 |
| 5 | 2.64 | | 8.7 | 2.64 | 2.84 | 0.4533 |
| 6 | 2.73 | | 8.7 | 2.73 | 2.94 | 0.4683 |
| 7 | 2.885 | | 8.7 | 2.885 | 3.11 | 0.4928 |
| 8 | 2.98 | trace | 8.8 | 2.98 | 3.21 | 0.5065 |
| 9 | 3.06 | trace | 8.8 | 3.06 | 3.30 | 0.5185 |
| 10 | 3.16 | trace | 8.9 | 3.16 | 3.40 | 0.5315 |
| 11 | 3.52 | 0.04 | 9.1 | 3.48 | 3.75 | 0.5740 |
| 12 | 3.99 | 0.06 | 9.5 | 3.93 | 4.23 | 0.6263 |
| 13 | 5.00 | 0.19 | 10.8 | 4.81 | 5.18 | 0.7143 |
| 14 | 6.10 | 0.64 | 11.7 | 5.46 | 5.88 | 0.7694 |
| 15 | 8.10 | 2.10 | 12.3 | 6.00 | 6.46 | 0.8102 |
| 16 | 10.10 | 3.70 | 12.6 | 6.40 | 6.90 | 0.8388 |

The lower line leans slightly to the right side from the vertical position respecting the abscissa, pH. However, it may be regarded as "practically vertical." The upper line may be represented as the following equation:

$$\log x = K + n\,pH$$

where x is the amount taken and K and $n$ are constants, both of which can be found from the figure. Therefore, we may say that the upper line represents adsorption while the lower line shows chemical combination. Detailed discussion will be given later.

Humic Acid and NaOH. In this case, the treatment of the two substances was carried out as usual. The filtrate had a light brown color. The intensity of the color was measured by means of a colorimeter using an alkaline solution of about 0.075% humic acid as a standard color. The results are given in

Table XII. In this table, the term "relative intensity of color" represents that figure which is compared with the most intense color of the filtrates, assuming the latter as 100.

As shown in the results, the color intensity increases as the initial concentration of NaOH, or pH at equilibrium, increases.

The colored filtrates were diluted, before the titration, with distilled water until a yellow color of definite intensity was produced so as to overcome

TABLE XII
Relative Solubility of Humic Acid in NaOH Solution

| No. | Initial concentration of NaOH in millimols per 100 cc | pH at equilibrium | Length of column of unknown compared with 20 mm. standard in millimeters | Relative intensity of color |
|---|---|---|---|---|
| 1 | 1.0 | 8.6 | 27.0 | 15 |
| 2 | 1.5 | 8.6 | 16.8 | 24 |
| 3 | 2.0 | 8.7 | 15.8 | 25 |
| 4 | 2.51 | 8.94 | 13.6 | 30 |
| 5 | 2.6 | 9.0 | 13.0 | 31 |
| 6 | 2.63 | 9.24 | 10.6 | 38 |
| 7 | 2.79 | 9.3 | 10.6 | 38 |
| 8 | 2.9 | 9.4 | 10.6 | 38 |
| 9 | 3.01 | 9.7 | 10.6 | 38 |
| 10 | —— | —— | —— | — |
| 11 | 3.8 | 10.06 | 8.6 | 46 |
| 12 | 4.06 | 10.8 | 7.0 | 57 |
| 13 | 4.95 | 11.5 | 5.6 | 71 |
| 14 | 6.04 | 11.9 | 4.0 | 80 |
| 15 | 7.97 | 12.3 | 4.0 | 100 |
| 16 | 9.95 | 12.54 | 4.0 | 100 |

obscurity of color change of the phenolphthalein used as an indicator. The writer knew, by preliminary experiment with the filtrate of the most intense color, that it was necessary for such purpose to dilute 1 cc to 40 cc. Hence the dilutions of the other filtrates were carried out according to the following equation:

$$\text{Final volume after dilution} = \frac{40 \times \text{I.V.}}{100}$$

where I is relative intensity of color, and V is volume in cc to be diluted. Then it was titrated as usual.

The hydrogen ion concentration was determined electrometrically with the original filtrate, that is, with one which was not diluted.

The results are summarized in Table XIII and are charted in Fig. 7.

In the case where comparatively strong NaOH was added, the amount of NaOH taken up by humic acid was found to be a little lower than that obtained with $Ba(OH)_2$. This seems to be due to the fact that in the present work no

NaCl was added before filtration, and futhermore that the sample was finer than the previous specimens so that a greater quantity of humic acid might have been dissolved or peptized than was in the previous case.

In the case where comparatively dilute NaOH was added to the reaction, the pH value was a little higher than that obtained with $Ba(OH)_2$.

Generally speaking, however, the results obtained herein with NaOH, are similar to those secured with $Ba(OH)_2$. The logarithmic curve of adsorption-pH diagram bends at the point where 3.0 millimols of the base were taken

TABLE XIII
Relation between Hydrogen Ion Concentration and Adsorption of NaOH by Humic Acid

| No. | Concentration of NaOH in millimols per 100 cc. | | pH | Millimols of NaOH taken up | | |
|---|---|---|---|---|---|---|
| | Initial conc. | Conc. at equilibrium (C) | | by 1 gm. of air-dry humic acid | by 1 gm. of dry humic acid | |
| | | | | | x | log x |
| 1 | 1.00 | | 8.6 | 1.00 | 1.08 | 0.0334 |
| 2 | 1.50 | | 8.6 | 1.50 | 1.62 | 0.2095 |
| 3 | 2.00 | | 8.7 | 2.00 | 2.15 | 0.3324 |
| 4 | 2.51 | trace | 8.94 | 2.51 | 2.70 | 0.4314 |
| 5 | 2.60 | do | 9.0 | 2.60 | 2.80 | 0.4472 |
| 6 | 2.68 | do | 9.24 | 2.68 | 2.89 | 0.4609 |
| 7 | 2.79 | do | 9.3 | 2.79 | 3.01 | 0.4786 |
| 8 | 2.90 | do | 9.4 | 2.9 | 3.12 | 0.4942 |
| 9 | 3.01 | 0.04 | 9.7 | 2.79 | 3.20 | 0.5051 |
| 10 | 3.10 | 0.065 | 9.7 | 3.03 | 3.26 | 0.5132 |
| 11 | 3.38 | 0.11 | 10.06 | 3.27 | 3.52 | 0.5465 |
| 12 | 4.06 | 0.40 | 10.8 | 3.64 | 3.92 | 0.5933 |
| 13 | 4.95 | 0.90 | 11.5 | 4.05 | 4.36 | 0.6395 |
| 14 | 6.04 | 1.67 | 11.9 | 4.37 | 4.71 | 0.6730 |
| 15 | 7.97 | 3.18 | 12.3 | 4.79 | 5.16 | 0.7126 |
| 16 | 9.95 | 4.90 | 12.54 | 5.05 | 5.44 | 0.7356 |

up by the humic acid. Hence the curves seem to consist of two straight lines of which the adjacent parts are connected with a gradually bended curve. The lower line runs at a very small angle to the ordinate; and the upper line is undoubtedly represented by the equation:

$$\log x = K + n\,pH$$

Thus it is obvious that the reaction represented by the upper line is of different nature from that represented by the lower line which is almost vertical to the abscissa, pH.

Discussion 1: Existence of humates. We have the information from the present studies that the pH values observed are all in the alkaline range even

in those cases where titration cannot be run. However, in such cases, we have some reason to assume that such alkalinities are due to the presence of dissolved "humates" which causes an alkaline reaction due to their hydrolysis.

Now from Table XI we will consider such filtrates that have low titration alkalinities and will again cite their alkalinities and pH value in Table XIV.

TABLE XIV

Humic Acid and Barium Hydroxide

| No. | Titration alkalinity in normality | pH | | |
|---|---|---|---|---|
| | | Observed | Calculated | Difference |
| 11 | 0.0004 | 9.1 | 10.6 | 1.5 |
| 12 | 0.0006 | 9.5 | 10.8 | 1.3 |
| 13 | 0.0010 | 10.8 | 11.3 | 0.5 |
| 14 | 0.0064 | 11.7 | 11.8 | 0.1 |
| 15 | 0.0210 | 12.3 | 12.3 | 0.0 |

As shown in these figures, each titration alkalinity is so weak that if the reaction is derived from free $Ba(OH)_2$, we should expect complete ionic dissociation of the base. If that is the case, the pH can be easily sought by calculation from the titration number, and the calculated value should agree with the observed pH. But the results do not verify this except in the case where titration alkalinity is appreciably high. That is, the observed value is lower than that calculated as shown in the Table. Consequently, the solutions 11 to 14 given in the Table should contain, together with $Ba(OH)_2$, an alkaline substance whose degree of ionic dissociation is far smaller than that of $Ba(OH)_2$. Such a substance should be barium humate; for, we cannot consider the existence of any other alkali in the mixture of pure humic acid and $Ba(OH)_2$ solution. This fact affords certain proof that humic is a real acid.

The difference between the two pH values, observed and calculated, seems to become greater as the titration alkalinity becomes lower. Hence, the humate produced, should play a greater role as the alkalinity becomes lower. In other words, the ratio $Ba(OH)_2$/Ba-humate decreases with decrease in the titration alkalinity until $Ba(OH)_2$ disappears from the solution leaving only the humate.

Accordingly, the alkalinities of the solutions 1 to 10 given in Table XI should be regarded as indicating the existence of the humate only.

Therefore, the diminution in titration alkalinity of the alkaline solution placed in the reaction, would not give an exact amount of $x$ especially with the solutions 11 to 13 in Table XI, although it would make no appreciable difference in the results.

The same explanation holds in the case of NaOH solution of humic acid. As demonstrated in Table XV, taking important figures from Table XIII, the observed pH values in the solutions 10 to 13 are respectively lower than those calculated from the titration alkalinities. Hence the colored NaOH solutions of humic acid should contain sodium humate. And the smaller the titration

TABLE XV

Humic Acid and Sodium Hydroxide

| No. | Titration alkalinity in normality | pH | | |
|---|---|---|---|---|
| | | Observed | Calculated | Difference |
| 10 | 0.00065 | 9.7 | 10.8 | 1.1 |
| 11 | 0.0011 | 10.1 | 11.0 | 1.0 |
| 12 | 0.0040 | 10.8 | 11.6 | 0.8 |
| 13 | 0.0090 | 11.5 | 11.95 | 0.45 |
| 14 | 0.0167 | 11.9 | 12.2 | 0.3 |
| 15 | 0.0318 | 12.3 | 12.5 | 0.2 |

alkalinity, the more the alkalinity seems to be controlled by the dissolved humate.

The alkalinities of the solutions 1 to 10 shown in Table XIII would be mostly derived from the alkaline humate. The pH values of these solutions are in the range between 8.6 and 9.7 This is higher than the corresponding range obtained with $Ba(OH)_2$, 8.2-8.8. This is because sodium humate is more soluble than barium humate.

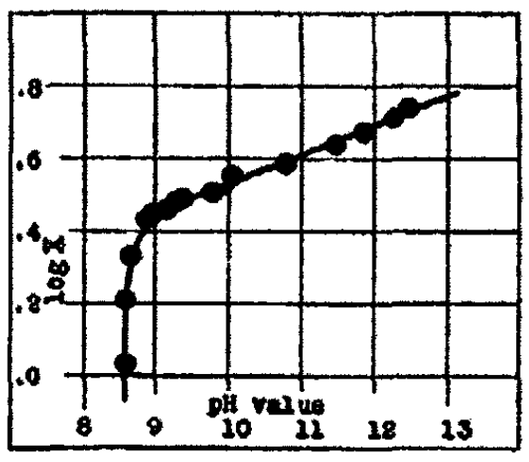



FIG. 7
Adsorption—pH Diagram of NaOH by Humic Acid.

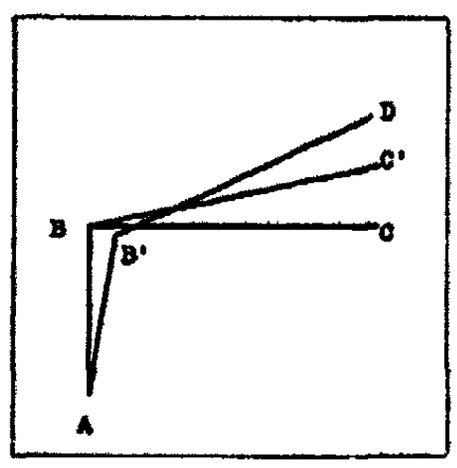



FIG. 8
Ideal Adsorption—pH Diagram.

Discussion 2: Adsorption-pH diagram. From the results secured above, we find some difference between humic acid and stearic acid in that the former adsorbs base markedly while the latter does not appreciably. However, as previously described, the adsorption of humic acid seems to take place after it took up a certain amount of base (about 3.0 equivalent millimols per one gram of dry humic acid) completely. Hence we find the similarity between humic acid and stearic acid that they both take up the total amount of base as long as the amount added does not reach a definite quantity.

As we learned with stearic acid, the pH is constant during the salt formation. After it is completed, the amount of the base taken remains practically constant throughout the change in the pH. Therefore, the logarithmic diagram of adsorption-pH function is to be represented by two straight lines, AB and BC as shown in Fig. 8.

In this chart, AB which is perpendicular to the abscissa pH, represents salt formation; and BC which is parallel to the abscissa denotes the portion of zero adsorption. However, if the salt formed is more or less soluble in the liquid and gives an alkaline reaction (e.g. sodium stearate), the line AB will take the position AB′, leaning to the alkaline side. We saw, however, that pH was a function of adsorption. Accordingly, if an adsorption takes place after the salt formation, line BC will take the position BC′ instead of BC. And the greater the adsorptive power, the larger will be the angle ABC′.

The adsorption-pH diagram of humic acid seems to correspond to the curve AB′D in the chart. That is, the curve of humic acid seems to be nothing but a modification of a curve of a real acid, being caused by the high adsorptive power and the appreciable solubility of the humate formed.

However, we meet some difficulty in the detection of point B in the curve which is the point where the humic acid phase disappears. This can be explained by the following: First, as already described, the dissolved humate has a buffer action to pH change so that we cannot find any sudden change in the pH value at that point. Second, the point of intersection of the two straight lines AB and BC is found to be more difficult to detect experimentally the greater becomes the angle ABC. And third, the transition between the salt formation and the adsorption by humic acid should be regarded a as gradual one.

## Summary

1. In the present work, adsorption isotherms of bases and acids by pure humic acid were investigated.

2. In order to determine whether or not humic acid behaves toward bases ($BaO_2H_2$ and NaOH) as does a real insoluble acid, the behavior of humic acid was compared with that of stearic acid.

3. Throughout this investigation, one gram of dry or air-dry adsorbent (humic acid or stearic acid) was treated with a 100 cc portion of adsorbate solution (base or acid) of varying concentrations, and the relation between the adsorption and the concentration (concentration of the adsorbate or hydrogen ion concentration) was examined at the equilibrium state of the reaction.

4. The humic acid used for this investigation, was isolated from the artificial humus prepared from cane sugar by decomposition with HCl.

5. When stearic acid was treated with a solution of base whose initial concentration was below 3.5 equilvalent millimols per 100 cc, the concentration at equilibrium was found to be always zero; that is, the total amount of the base added was taken up by the stearic acid. But when treated with the stronger solution, the amount of the base taken, remained approximately constant throughout the concentration change. Therefore, the adsorption-concentration diagram yielded a right-angled curve.

6. Humic acid behaved in the same manner as stearic acid as long as the initial concentration of base added was below 3.0 equivalent millimols per 100 cc. That is, the concentration at equilibrium was found to be zero in

such a case. But when stronger solution was added, the amount of base taken up by the humic acid, was found to be a logarithmic function of the final concentration. Therefore the results indicate the formation of the definite chemical compound, humate, which then adsorbs the free base.

7. The adsorption of NaOH is lower than that of $Ba(OH)_2$. This is due to the fact that sodium humate is markedly soluble while barium humate is only slightly soluble.

8. When adsorption of mineral acids ($H_3PO_4$, $H_2SO_4$, $HNO_3$ and HCl) by humic acid was studied, the amount adsorbed was found to be a logarithmic function in all cases, and hence, we had no evidence of the formation of any definite chemical compound.

9. The adsorption of mineral acid by humic acid is markedly low as compared with that of base by its humate.

10. When stearic acid was treated with $Ba(OH)_2$ of varying concentrations, we met a sudden change of pH at the point where 3.5 equivalent millimols of the base (amount equivalent to one gram of stearic acid) was taken up by the stearic acid. As long as the amount did not reach 3.5 equivalent millimols, the pH value remained constant while the base was totally taken up by the acid. However, beyond the 3.5 point, the amount taken remained constant through the pH change of the liquid. Consequently, the adsorption-pH diagram yielded a practically right-angled curve.

11. The adsorption-pH curve of NaOH by stearic acid is approximately the same as that of $Ba(OH)_2$. But no such a sudden change of pH takes place at the 3.5 point as occurring with $Ba(OH)_2$. The reason is that the sodium stearate dissolved, produces a buffer action to such a change.

12. When humic acid was treated with base, the pH value at equilibrium remained approximately constant, as long as the amount of the base taken up by the acid, did not reach 3.0 equivalent millimols. But beyond that point the pH increased as the amount of the base taken increased. And the amount of the base taken was found to be a logarithmic function of the pH. Accordingly, in the case of both $Ba(OH)_2$ and NaOH, the log. adsorption-pH yielded a curve consisting of two straight lines whose adjacent parts were connected with a gradually bended curve in the neighbourhood of the 3.0 point, indicating gradual change between the two directions. Therefore, we should regard the one line of the curve—the lower line in the diagram—as representing the formation of the definite chemical compound, humate; and the other line —the upper line—as denoting the adsorption by the humate. And the transition between the salt formation and the adsorption should be regarded as a gradual one. If the reaction between humic acid and the base was entirely adsorption and not compound formation, the log. adsorption-pH curve should have become one straight line instead of the two lines.

13. In the above work, the titration alkalinity of the filtrate resulting from the reaction between humic acid and NaOH or $Ba(OH)_2$, was so low that complete dissociation should have been expected to take place in the solution. Hence, if the alkalinity was entirely derived from the free base, the

pH value of the filtrate could be found by simple calculation from the titration number; and the calculated value should have agreed with the observed one. But the result was that the observed value was lower than the calculated one. This seems to afford some basis for the assumption that the alkaline solution should contain, together with free base, a humate dissolved, which causes an alkaline reaction due to its hydrolysis.

14. As above described, we have shown that one gram of dry humic acid takes up the total amount of base from its 100 cc solution whose content is below 3.0 equivalent millimols, and in turn, the concentration and the pH are found to be zero and constant respectively at equilibrium. This is quite analogous with the case where one gram of stearic acid is treated with a solution of base whose content is below 3.5 equivalent millimols. Humic acid therefore, should be regarded as a real acid. The only difference between humic acid and stearic acid is that the humate formed continues to further adsorb the base while the stearate does not so appreciably. The evidence that the intensely colored NaOH solution as well as the slightly colored $Ba(OH)_2$ solution of humic acid contains a chemical compound of the base, seems to afford a further proof of the theory that humic acid is a real acid.

This work was done under the direction of Professor W. D. Bancroft to whom the writer wishes to express his sincere thanks for his able guidance and helpful suggestions.

*Cornell University*

# THE EFFECT OF HYDROGEN ION CONCENTRATION ON THE VISCOSITY OF HYDROSOLS OF ALUMINUM, CHROMIC, AND FERRIC OXIDES*

BY JOHN H. YOE AND EGBERT B. FREYER

## Introduction

One of the most significant properties of colloidal solutions is the viscosity. The importance of this property was recognized by Graham almost three-quarters of a century ago when he referred to the viscometer as a "colloidoscope." In 1913 a general discussion[1] on colloids and their viscosity took place at a meeting of the Faraday Society and papers were presented by Wo. Ostwald, Henri, Pauli, Freundlich and Ishizaka, and Hatschek. Here, Ostwald again pointed out "the importance of viscosity for the study of the colloidal state" and Freundlich presented results "on the rate of coagulation of $Al(OH)_3$ sols as measured by the viscosity change." Freundlich had been interested in comparing the precipitation of $Al(OH)_3$ sol by various anions with the adsorption of these ions by $Al_2O_3$ [hydrous aluminum oxide] and found that the precipitation of the sol by electrolytes could best be studied by the change in viscosity and that likewise the rate of coagulation could thus be determined. Several years previous, Kawamura[2] had made use of the change in viscosity in his study of the precipitation of sols by electrolytes. Freundlich prepared his $Al(OH)_3$ sols by Crum's method, by gradual hydrolysis of aluminum acetate and expulsion of the acetic acid by continued heating. The colloidal solutions thus obtained were perfectly colorless, almost like pure water, and were only slightly turbid. Their viscosity was only slightly greater than that of pure water. The effiux time of the sol in an Ostwald viscometer was 52 seconds as compared with 49 seconds for water. The hydrosol was very stable and Freundlich says "we did not notice any change in the properties after several months, except that the precipitation value had decreased by a few per cent." After adding to the hydrosol a sufficient amount of an electrolyte to effect complete precipitation it was put in an Ostwald viscometer and the rate of effiux determined from time to time. It was observed that these rates increased in a regular manner and finally attained a maximum value which corresponded to complete precipitation.

In the above viscosity measurements various electrolytes ($KNO_3$, KCNS, $NH_4Cl$, $K_2SO_4$, $K_3Fe(CN)_6$, K-salicylate) were employed as precipitating reagents. Freundlich observed that "the maximum viscosity of an $Al(OH)_3$ sol which is completely precipitated by the addition of an electrolyte, increases proportionately to the amount of colloid particles in the sol," a result

* Contribution No. 29 from the Cobb Chemical Laboratory of the University of Virginia.

[1] Trans. Faraday Soc., 9, 34-107 (1913).

[2] J. Coll. Sci. Imp. Univ. Tokyo, 25, No. 8 (1908).

[3] Ann., 89, 156 (1854).

in agreement with previous experiments on suspension and emulsions; and, furthermore, that "the maximum viscosity is to a certain degree dependent upon the nature of the precipitating electrolyte," the results pointing to a lyotropic series "in so far as the viscosity is smaller with the anions $NO_3$, CNS than with sulphate, succinate, etc." In these measurements no attention was paid to the hydrogen ion concentration of the sols. Recently much work has been done on the effect of the hydrogen ion concentration on various properties of colloids. Loeb[1] studied the effect of the hydrogen ion concentration on colloidal protein substances. Tartar and Gaily[2] have made a study of the effect of hydrogen ion concentration on the precipitation of mastic and gamboge sols by acids and by salt solutions and found that "while different amounts of acids are required, each sol is precipitated at a quite definite hydrogen ion concentration regardless of the concentration of the colloid." "The negative ion of the acid is without effect." "Various potassium and ammonium salts precipitate the sols at the same concentration provided the hydrogen ion concentration is kept approximately constant. The precipitating values of the salts vary directly as the concentration of the colloid at the same hydrogen ion concentration. The stabilizing or peptizing effect of the ion bearing a charge similar to that of the colloidal particle has been shown to be very limited if it exists at all."

On the other hand, Michaelis and Hirabayashi[3] studying the precipitating power of salts when added to mastic sols at various hydrogen ion concentration find that the *anion has some effect*, the activity depending upon the hydrogen ion concentration of the sol. It had previously been observed by Linder and Picton,[4] and Whitney and Ober[5] that in the precipitation of a negative suspensoid, such as arsenious sulfide, by neutral salts, some of the positive ions are carried down by the precipitate, and that there is a simultaneous increase in the acidity of the supernatant liquid. Blum[6] found from observations made with a hydrogen electrode and with suitable indicators that "the precipitation of aluminum hydroxide by ammonium hydroxide is complete when $[H^+] = 10^{-6.5}$ to $10^{-7.5}$, points approximately defined by the color change of methyl red and of rosolic acid," and that "considerable aluminum hydroxide remains unprecipitated when the solution is just alkaline to p-nitrophenol [color change at $[H^+] = 10^{-6}$ approx.], while a smaller amount, but still appreciable, is redissolved when the solution is just alkaline to phenolphthalein" [color change at $[H^+] = 10^{-9}$ approx.].

Quite recently Bradfield[7] has studied the relation of hydrogen ion concentration to the flocculation of a colloidal clay. He found that hydrochloric,

[1] J. Gen. Physiol., 1, 2, 3 (1918-21); "Proteins and the Theory of Colloidal Behavior," 2nd ed. (1925).

[2] J. Am. Chem. Soc., 44, 2212 (1922).

[3] Kolloid.-Z., 30, 209 (1922).

[4] J. Chem. Soc., 67, 63 (1895).

[5] J. Am. Chem. Soc. 23, 842 (1901).

[6] J. Am. Chem. Soc., 38, 1282 (1916); also in a little more detailed form as Sci. Paper No. 286, Bureau of Standards (1916).

[7] J. Am. Chem. Soc., 45, 1243 (1923).

sulfuric, phosphoric, and acetic acids produced flocculation at the same hydrogen ion concentration but that greater acidity was required with citric acid.[1] In the case of potassium chloride and potassium hydroxide mixtures the amount of electrolyte required to produce flocculation was ten times greater at a pH of 8 than at a pH of 6.2. Further increases in alkalinity had no effect. "Dipotassium phosphate mixtures showed a similar variation in flocculating power with changes in hydrogen ion concentration." The phosphate curves differ, however, from the chloride curves in three respects: (1) the break occurs at a much higher hydrogen ion concentration, (2) the electrolyte requirement is about one-third higher, and (3) the curve is not linear after it reaches the maximum but shows a secondary minimum at pH 9.5. Bradfield concludes these "results indicate that the flocculating power of potassium salts is influenced by the nature of the anion even when compared at the same Sörensen value. Secondary reactions seem to be responsible."

Although much work has been done on the effect of hydrogen ion concentration on the viscosity of proteins sols and sols of other organic substances, little or no work seems to have been done with inorganic sols. It is true much work has been done on the effect of electrolytes on inorganic sols, but with few exceptions the effect of the hydrogen ion was not taken into consideration. The work recorded in this paper was designed to study the effect of the hydrogen ion concentration on the viscosity of hydrosols of inorganic substances. Hydrosols of aluminum, chromic, and ferric oxides were employed.

## Experimental

*Apparatus.* All glass ware used in this work was Pyrex, except the hydrogen electrode vessel and the viscometer. Calibrated volumetric apparatus was employed whenever the accuracy of the measurement justified it. The viscometer was an Ostwald capillary type. This was kept in a water-bath maintained at 25° ±0.05°. Effiux times were measured with a stop-clock which gave readings easily estimated to 0.1 second. The viscometer was thoroughly cleaned and dried before each new portion of sol was added. The hydrogen ion concentrations were determined potentiometrically with a Leeds and Northrup Type K potentiometer.

*Preparation of the Hydrosols.* The aluminum, chromic, and ferric oxide hydrosols were prepared by adding approximately normal ammonium hydroxide solution, slowly and with vigorous stirring, to dilute solutions of the corresponding chlorides. The amount of ammonium hydroxide added in each case corresponded to about half the stoichiometric equivalent, the excess of metal chloride acting as a peptizing agent and insuring a water-clear sol. The sols were then purified by hot dialysis according to the method of Neidle.[2] Each sol was poured into a large beaker and diluted to about 400 cc. A large parchment bag, through which distilled water circulated (one liter per hour),

[1] A. B. Weir has just published a paper (J. Chem. Soc., 127, 2245 (1925)) on the coagulation of a Prussian blue sol by hydrogen ions. Hydrochloric, sulfuric, acetic, and citric acids were used. Contrary to Bradfield, he finds that citric acid appears to behave normally.

[2] J. Am. Chem. Soc., 38, 1270 (1916); Neidle and Barab: 39, 71 (1917).

was then suspended in the beaker until the water level inside was 1 or 2 cm. higher than the level of the outside liquid, the inside level being kept constant by means of an automatic siphon. The top of the dialyzer was covered to prevent contamination by dust. The temperature of the sol was maintained at 60°-80°. The sols of aluminum and chromic oxides were dialyzed hot from the start, but that of the ferric oxide was first dialyzed at room temperature about 24 hours, after which the temperature was raised and kept at 60°-80°. This insured a perfectly clear brownish red sol. In each case dialysis was continued until only a minute amount of *chloride ion* remained, as indicated by the silver nitrate test. About one week of continous dialyzing was required. Although dialysis was continued in each case until only a minute amount of *chloride ion* remained, it should be remembered that each of the particles in the hydrosols consists of a complex of the oxide and a soluble metal chloride. Disregarding the hydrate water, the formulae for them may be roughly written as follows: $xAl_2O_3.yAlCl_3$; $xCr_2O_3.yCrCl_3$; $xFe_2O_3.yFeCl_3$. The chromic oxide hydrosol was perfectly clear and a deep green. The aluminum oxide hydrosol was faintly opalescent.

The oxide content of each sol was determined gravimetrically according to Blum's method[1] for the estimation of aluminum as oxide. The sols were then accurately diluted with distilled water to the desired percentage concentration and were kept in stoppered Pyrex flasks as "stock solutions." By suitable further dilution additional concentrations were obtained. The following concentrations of the three hydrosols were employed: 0.06, 0.03, and 0.015 percent oxide content. Two ferric oxide hydrosols of 0.85 and 0.12 percent, respectively, were also used.

*Method of Procedure.* Two portions of the dialyzed sol of the desired concentration were withdrawn from the standard solution. One portion was put in the viscometer, allowed to come to the temperature of the bath, and the viscosity measured by observing the rate of effiux through the capillary. Timings were made with a stop-clock accurate to 0.1 second (graduated to 0.2 sec.). The recorded reading was the mean of several timings which checked to within ±0.2 sec., except in those cases where precipitation had occurred. In the latter cases the precision was not quite so good, and varied with the extent of precipitation. In each case the hydrogen ion concentration and the viscosity were measured concurrently in order to avoid any possible effect due to "aging" of the sol.

Having obtained the pH and viscosity of the dialyzed sol, 50 cc. of the latter were withdrawn from the standard solution and to it added, drop by drop and with stirring, a few drops of ammonium hydroxide solution. The sol was then divided into two portions and its viscosity and hydrogen ion concentration measured at once as above described. Similarly, other portions of the standard solution were withdrawn, the pH increased by adding a little ammonium hydroxide, and the viscosity and hydrogen ion determined con-

[1] J. Am. Chem. Soc., **38**, 1282 (1916) and also as Sci. Paper 286, Bureau of Standards (1916).

currently, until a pH range of about 2.5(?) to 9 had been covered. The pH value of about 2.5 found for the freshly dialyzed sols indicates a surprisingly high acidity. The ferric oxide hydrosols termed "pure" by Thomas and Frieden,[1] i. e., calculated on the basis of moles of $Fe_2O_3$ to moles of $FeCl_3$ giving a ratio of about twenty one to one, all gave a pH value of 4.9.

The velocity of efflux of water was measured at frequent intervals during the investigation to insure against an accidental error in the readings.

The very slight dilutions of the sols by the addition of small amounts (usually less than 1 per cent by vol.) of ammonium hydroxide solution produced no measurable change in their viscosities as indicated by viscosity determinations on water to which had been added similar amounts of ammonium hydroxide solution.

## Results and Discussion

The results of the experiments in this investigation are shown graphically in Figs. 1-5. In the case of sols containing 0.06, 0.03, and 0.015 per cent oxide, respectively, the relative viscosities, $\eta$, at 25° are plotted against pH values (Figs. 1, 2 and 3). On account of the difficulty in obtaining reliable pH measurements on sols more concentrated than 0.06 per cent, in the case of ferric oxide sols containing 0.85 and 0.12 per cent $Fe_2O_3$, respectively, the change in viscosity is plotted against cc. of 0.006 N ammonium hydroxide added (Figs. 4 and 5).

Although both the hydrogen ion concentration and the viscosity were always measured concurrently in order to avoid any possible effect due to "aging" of the sol, experiments showed that the viscosity remained constant for at least several weeks in the case of sols having a pH about 6.5 or less. Above a pH of 6.5, however, the sols were unstable and gave an increasing viscosity upon "aging," even when allowed to stand only a few minutes. In such cases the viscosity was determined as rapidly as possible after changing the sol to the desired hydrogen ion concentration.

At a pH of 7.0 and above, precipitation occurred, but a marked difference in the rate of settling was observed among the three sols. Upon adding ammonium hydroxide to the aluminum oxide sol no visible change could be detected with each addition, until suddenly the whole sol became very turbid. The precipitate settled in about an hour. In the case of ferric oxide sol, the precipitation was very gradual. Each small addition of ammonium hydroxide solution produced a temporary nebulous precipitate which soon disappeared, leaving the sol slightly more turbid, until finally two phases could easily be distinguished. The precipitate settled rapidly, only a few minutes being required. The chromic oxide sol behaved like the ferric oxide sol in so far as it showed a very gradual increase in turbidity upon increasing pH, but it was unlike the latter in that the precipitate settled very slowly, requiring several hours in some cases.

An inspection of the curves shows that the change in viscosity with increase in pH is very small until a pH of about 7 is reached. At this point a

[1] J. Am. Chem. Soc., **45**, 2528 (1923).

very rapid increase in viscosity occurs, reaching a maximum at a pH of 7.3, 7.0, and 7.9 in the case of the 0.06 per cent sols of aluminum, chromic, and ferric oxides, respectively. The corresponding 0.03 per cent sols have a maximum viscosity at pH 7.9, 7.0, and 8.4, respectively. The 0.015 per cent sols of aluminum and chromic oxide had a maximum viscosity at pH 8.0 and

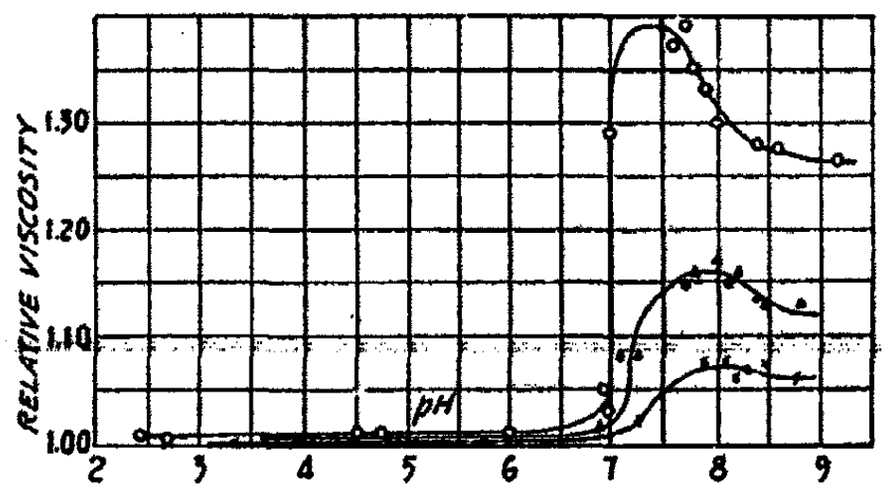



FIG. 1
Aluminum Oxide Hydrosol
Circles are 0.06% $Al_2O_3$ Triangles are 0.03% $Al_2O_3$ Crosses are 0.015% $Al_2O_3$

7.1, respectively. The corresponding concentration of ferric oxide was not determined. During the pH measurements of the dilute sols (0.03 and 0.015 per cent oxide) the potassium chloride of the calomel half cell diffused into the sols and caused partial precipitation. To avoid this, the saturated potassium chloride bridge was eliminated, liquid contact being maintained just long enough to take an E. M. F. reading after the cell had reached equilibrium. This procedure did not give the highest degree of accuracy. Moreover, since all the sols were precipitated at a pH of about 7, the viscosity measurements at pH and above show some irregularity as seen in the viscosity-pH curves.

In the following table the maximum viscosity of each of the sols is given, together with the corresponding pH:

| Hydrosol | Maximum Viscosity Per cent $R_2O_3$ | | | pH at Max. Viscosity Per cent $R_2O_3$ | | |
|---|---|---|---|---|---|---|
| | 0.06 | 0.03 | 0.015 | 0.06 | 0.03 | 0.015 |
| $xAl_2O_3 . yAlCl_3$ | 1.39 | 1.16 | 1.07 | 7.3 | 7.9 | 8.0 |
| $xCr_2O_3 . yCrCl_3$ | 1.325 | 1.125 | 1.06 | 7.0 | 7.0 | 7.1 |
| $xFe_2O_3 . yFeCl_3$ | 1.13 | 1.065 | —— | 7.9 | 8.4 | — |

In 1906 Einstein[1] developed the following formula for the viscosity of any liquid having suspended in it small, rigid, spherical particles:

$$\eta = \eta' (1 + Kf)$$

where $\eta$ = viscosity coefficient of system,

$\eta'$ = viscosity coefficient of liquid (continuous phase),

$f$ = ratio $\dfrac{\text{Total volume of particles (disperse phase),}}{\text{Total volume of system}}$

[1] Ann. Physik, 19, 289 (1906).

and K = a constant, which Einstein at first made equal to 1 but later[1] changed to 2.5, after Bancelin had checked the equation experimentally, using spheres of gamboge, and obtained a constant of 2.9. Hatschek[2] deduced a similar formula for the viscosity of liquids in which are suspended small, rigid spheres whose volume is less than 40 per cent of the total volume of the system. His formula differs from that of Einstein only in the numerical constant, which is 4.5 instead of 2.5. Harrison[3] tested Hatschek's formula

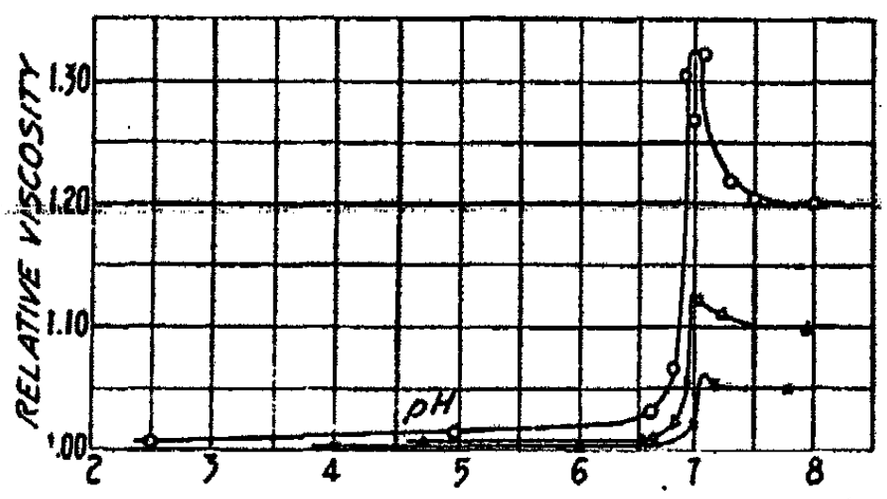



FIG. 2
Chromic Oxide Hydrosol
Circles are 0.06% $Cr_2O_3$ Triangles are 0.03% $Cr_2O_3$ Crosses are 0.015% $Cr_2O_3$

with starch suspensions in water and found it to hold good up to 30 per cent of disperse phase. On the other hand Odén,[4] working with sulfur sols, found the viscosity with particles about 10 $\mu\mu$ approximately 50 per cent greater than that of sols with particles 100 $\mu\mu$. Hatschek[5] says that the increase in viscosity with increase in dispersion is probably due to the adsorption of a film of liquid around the particles so that the "effective volume" is the sum of two factors: "volume of actual disperse phase (probably, but not necessarily proportional to the weight) plus volume of adsorption envelope." This explanation, in the case of Odén's sulfur sols at least, seems to be a very probable one and was not considered when Einstein's and Hatschek's formulas were deduced. Since the radius of the particles and the distance between them do not appear in the above formula, it is obvious that the viscosity is independent of the size of the particles and is a linear function of the volume of the disperse phase only. From this it would seem that an increase in viscosity of aluminum, chromic, and ferric oxide-hydrosols would represent, in part at least, an increase in degree of hydration, using the term "hydration" in its most general sense. The exact mechanism of this increase in hydration is yet to be satisfactorily explained. It seems probable that part of the water may be in (1) true chemical combination, (2) part adsorbed on the surface

[1] Kolloid-Z., 9, 154 (1911).
[2] Kolloid-Z., 7, 301 (1910); see also Trans. Faraday Soc., 9, 80 (1913).
[3] J. Soc. Dyers and Colourists, 27, April (1911).
[4] Z. physik. Chem., 80, 709 (1912).
[5] Kolloid-Z., 11, 280 (1912); see also Trans. Faraday Soc., 9, 80 (1913).

and in the capillaries (perhaps even causing a swelling), and (3) part occluded in the voids when the particles agglomerate into loose aggregates. In this connection we quote Bancroft:[1] "If the suspended particles aggregate into chains, the viscosity will be increased very much. If the particles form larger spherical particles which are homogeneous, there will be a decrease in the

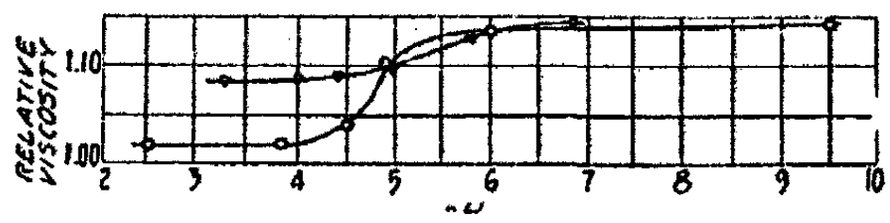



FIG. 3
Ferric Oxide Hydrosol.
Circles are 0.06% $Fe_2O_3$ Triangles are 0.03% $Fe_2O_3$

viscosity, because of the decrease in the surface and consequently in the amount of bound water. If, however, the particles simply agglomerate loosely into spherical masses, the viscosity will increase because the water in the voids inside the spherical agglomerates no longer counts as free water. We shall therefore expect to get an increase of viscosity as a result of agglomeration when the effect of agglomeration is not to increase the size of homogeneous drops." Referring to viscosity changes in some gelatine sols Bancroft[2]

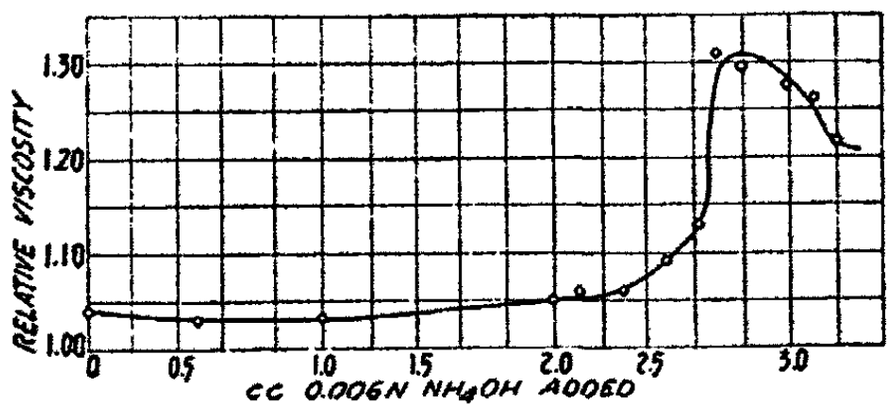



FIG. 4
Ferric Oxide Hydrosol. 0.12% $Fe_2O_3$.

further remarks: "The important point is that the increase in viscosity does go hand in hand with an increase in agglomeration which must mean that increasing agglomeration involves decrease in the amount of available free water."

The general character of the viscosity —pH curves for the hydrosols of aluminum, chromic, and ferric oxides indicate that very little increase in hydration occurs with increase in pH until finally a critical point (about $pH_7$) is reached; then rapid agglomeration takes place (with consequent rapid increase in viscosity) with further increase in pH, finally reaching a maximum (pH about 8), and beyond this point partial coalescence takes place thereby forcing out part of the "imprisoned" water, the latter once more becoming a part of the external phase and the viscosity accordingly lowered. Not all of

[1] "Applied Colloid Chemistry," 192, (1921).
[2] Ibid. p. 195.

the water taken up at the critical pH range would be released by a partial coalescence and, hence, the viscosity curve would not drop to its original value. If most of the occluded water is expelled fairly rapidly just beyond the critical pH range, the viscosity curve would drop steeply and then flatten out to an approximately constant value. As noted in Figs. 1-5, all of the curves, with the exception of the dilute (0.06 and 0.03 per cent) sols of ferric oxide, show a rapid drop after passing the maximum viscosity and then flatten out to an approximately constant value.

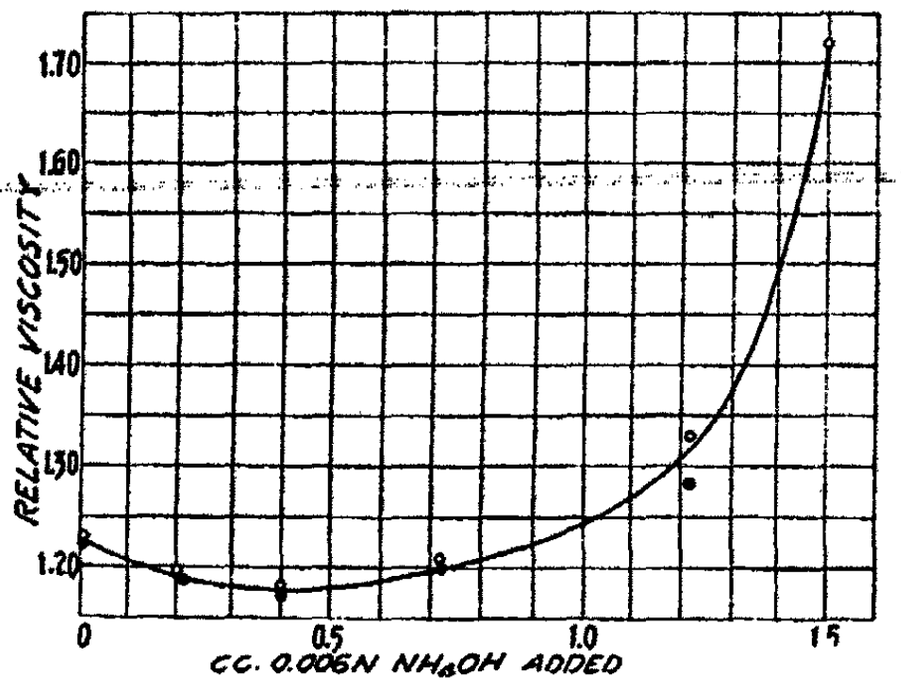



Fig. 5
Ferric Oxide Hydrosol (0.85% $Fe_2O_3$)
White and black dots represent duplicate experiments

Quite recently Dhar[1] has advanced the idea that the charge on the colloid particles determines the degree of hydration; that "charged particles because of their charge are not as much hydrated as the freshly coagulated sol"; that the viscosity is greater, the greater the hydration of the substance; and finally, that the change in viscosity of a sol on the addition of an electrolyte depends upon the ratio of the adsorbed positive ion to the adsorbed negative ion. This view is consistent with our experimental results on the effect of the hydrogen ion on the viscosity of hydrosols of aluminum, chromic, and ferric oxides, as well as the results of other workers on the viscosity of colloids in the presence of electrolytes. However, we do not agree with Dhar that the mechanism of the process of hydration and dehydration of the particles is as simple as he postulates, namely, that "the absorbed water may be squeezed out just as water can be squeezed out of a sponge." Our view is that each particle is surrounded by a semipermeable membrane and that upon the addition of an electrolyte, say $NH_4OH$, water diffuses into the external or continuous phase by ordinary osmosis, thereby causing a decrease in volume of the disperse

[1] Sen, Ganguly and Dhar: J. Phys. Chem., **28**, 313 (1924); Dhar: Z. Elektrochem., **31**, 261 (1925); J. Phys. Chem., **29**, 1556 (1925). The last two articles appeared after our experimental work had been completed but before this paper was finished. The experimental work recorded in this paper was completed in May, 1925.

phase and, hence, a decrease in viscosity. This would account for the slight decrease[1] in the viscosity of various sols referred to in the next paragraph. In addition to osmosis, there is a second process going on, namely, aggregation of the particles as more and more $NH_4OH$ is added which reacts chemically with the metal chloride (or its HCl of hydrolysis) of the complex. If we assume that a decrease in dispersity is characterized by an increase in viscosity and vice-versa,[2] then the decrease in volume of the disperse phase due to osmosis would be counterbalanced and finally exceeded by the aggregation of the particles. This would account for the minimum in the viscosity curves (see next paragraph) and also for the rapid rise to the right of the minimum.

The slight minimum in the viscosity curves just referred to was noted with the more concentrated hydrosols of ferric oxide (0.85 and 0.12 per cent). See Figs. 4 and 5. The curve, Fig. 4, for the 0.12 per cent sol was obtained first and it was thought the very slight minimum might be due to experimental error. As a check on this, a much more concentrated (0.85 per cent) sol was prepared. The viscosity curve again showed a minimum, much more pronounced than that of the diluter sol and undoubtedly not due to experimental error. Figure 5 shows how closely the curve could be duplicated. For the sake of economy of space the curve is extended only to a viscosity of 1.72, obtained upon adding 1.50 cc. of ammonium hydroxide to the sol. The addition of 1.55 cc. of ammonium hydroxide caused the viscosity to increase to 6.7. Higher viscosities were not obtained since further additions of ammonia gave practically a gel. That the sols containing 0.06, 0.03, 0.015 per cent of aluminium, chromic, and ferric oxide, respectively, show no "negative viscosity" seems unquestionably due to their low concentration. The above results with the more concentrated ferric oxide sols are in complete accord with the observation of Woudstra[3] who showed that the viscosity of ferric and chromic oxide sols slightly decreases on the addition of small amounts of electrolytes. Further additions of electrolytes causes the viscosity to rise rapidly. He[4] obtained a similar result with silver sols, the effect being even greater than in the case of the ferric and chromic oxide sols. Albanese[5] found the addition of small amounts of electrolytes to a gum arabic solution lowered its viscosity 30 per cent. Farrow[6] observed a minimum in the viscosity curve of sodium palmitate produced by the successive additions of small amounts of NaOH, NaCl and KCl. In explanation of this he says "water may be lost by the disperse phase, with a consequent diminution of the bulk of the latter. It is this shrinkage of the colloid particles due to dehydration which is expressed by the left-hand falling branch of the curves." Gokum[7] observed a similar effect on freshly prepared gelatin solutions, but the minimum disappeared

[1] Cf. Smoluchowski: Kolloid-Z., 18, 190 (1916).
[2] Cf. Farrow: J. Chem. Soc., 101, 347 (1912).
[3] Kolloid-Z. 3, 199 (1908); Z. physik. Chem., 63, 619 (1908); Kolloid-Z., 8, 73 (1911).
[4] Z. physik. Chem., 61, 607 (1908); Chem. Weekblad, 5, 303 (1908).
[5] Arch. Exp. Path. Pharm. Suppl., p. 16 (1908).
[6] J. Chem. Soc., 101, 347 (1912).
[7] Kolloid-Z., 3, 84 (1908).

when the viscosity was determined on solutions several hours old. Mayer, Schaefer and Terroine[1] state that the viscosity of soap solutions passes through a minimum in going from acid to alkaline solutions, but no data are given. Fernau and Pauli[2] found an immediate drop in the viscosity of a ceric hydroxide sol upon the addition of electrolytes in small amounts, insufficient to cause coagulation. Quite recently Thomas and Frieden[3] in their paper on "ferric salt as the "solution link" in the stability of ferric oxide hydrosol" report results which show the addition of ferric chloride to ferric oxide hydrosol "first decreases the viscosity and then increases it. The decrease in viscosity indicates a diminution in size of the particles which could only have been caused by a loss of water of hydration by the dispersed phase. The increase in viscosity observed upon the addition of larger amounts of ferric chloride is due to the coalescence of the particles preliminary to precipitation.

"As to the mechanism of the dehydration of the sol by ferric chloride, we can only venture to say that it is possibly due to the high hydration of the electrolyte added, thus causing a partial dehydration of the dispersed $Fe_2O_3-FeCl_3-H_2O$ phase, or in view of the fact that this sol migrates in an electrical field showing that the adsorbed and peptizing electrolyte is ionized, even though the degree be extremely small, then the Donnan effect of the added ferric chloride would result in a decrease in swelling (hydration) of the dispersed phase as in the case of the addition of hydrochloric acid or a neutral salt to gelatin jelly swollen in a solution of hydrochloric acid. Both suggested mechanisms may operate at the same time."

A paper has just appeared in which N. R. Dhar[4] makes the following assumptions and has cited, in corroboration of them, the experimental results of various workers on the viscosity of colloids in the presence of electrolytes: "(1) other things being identical, the uncharged substance is more hydrated than the sol; (2) the greater the hydration of a substance, the greater is its viscosity; (3) when a sol adsorbs an ion carrying the same charge as the sol because of chemical affinity, the charge on the sol is increased and consequently according to our view the viscosity of the sol should decrease."

In conclusion, it seems probable that the initial "negative viscosity" observed by different workers on various sols (ferric and chromic oxides, silver—probably much of it as hydroxide—ceric hydroxide, sodium palmitate, soap solutions, gelatin, gum arabic, etc.) is of the same nature in each case, and that it expresses a general property of colloidal solutions. This property may not manifest itself if the sol is very dilute.

## Summary

1. A study has been made of the effect of hydrogen ion concentration on the viscosity of hydrosols of aluminum, chromic, and ferric oxides. The viscosities were measured at 25° with an Ostwald viscometer over a range in

[1] Compt. rend., **146**, 484 (1908).
[2] Kolloid-Z., **20**, 20 (1917).
[3] J. Am. Chem. Soc. **45**, 2531 (1923).
[4] J. Phys. Chem., **29**, 1556 (1925).

pH of about 2.5(?) to 9 and with sols containing 0.06, 0.03, and 0.015 per cent of the respective oxide. The hydrogen ion concentration was determined potentiometrically.

2. The sols showed little or no change in viscosity with decreasing hydrogen ion concentration (increasing pH) until a "critical" concentration was reached. At this point the viscosity increased rapidly to a maximum, and then dropped fairly rapidly to an approximately constant value (except in the case of the more dilute ferric oxide sols). The "critical" pH was about 7 in each case. The pH at maximum viscosity varied a little with the different sols and with different concentrations, the range being 7 to 8.4.

3. In the case of two more concentrated ferric oxide sols (0.85 and 0.12% $Fe_2O_3$) the addition of small amounts of a dilute ammonium hydroxide solution caused a slight *decrease* in the viscosity. Further additions of ammonium hydroxide caused an *increase* in viscosity, at first very slight and then rapidly to a maximum, finally dropping fairly rapidly to an approximately constant value. The occurrence of this "negative viscosity" is in agreement with the experimental results of Woudstra ($Fe_2O_3$, $Cr_2O_3$, and Ag), Albanese (gum arabic), Mayer et al. (soap), Farrow (Na palmitate), Gokum (gelatin), Fernau and Pauli ($Ce(OH)_4$), and Thomas and Frieden ($Fe_2O_3$). It seems probable that the cause of these minima in the viscosity curves is of the same nature and that it is a general property of colloidal solutions, being more pronounced in concentrated sols and may even disappear in weaker ones. A possible explanation of this phenomenon has been made.

4. It has been suggested that a change in the viscosity of the oxide hydrosols is due, in part at least, to a change in the degree of hydration, using the term "hydration" in its most general sense. The water may be (a) partly in true chemical combination, (b) partly adsorbed on the surface and in the capillaries (perhaps even causing a swelling), and (c) partly occluded in the voids when the particles agglomerate into loose aggregates. A possible mechanism of the changes in degree of hydration (and hence changes in the viscosity) has been suggested.

We desire to express our thanks to Drs. Arthur W. Thomas and J. J. Beaver who read the manuscript of this paper and made helpful criticisms.

*University, Virginia.*

# THE EFFECT OF TEMPERATURE ON THE RATE OF COAGULATION OF GOLD SOL

BY MAUD GARNER AND W. C. M. LEWIS

## Introduction

The main object of the present investigation has been the determination of the effect of temperature on the coagulation, by electrolyte, of a typical metallic sol. From the magnitude of the effect a conclusion may be drawn as to whether the process of coagulation involves a critical increment or can be accounted for simply on the basis of a lowering of the viscosity of the medium.

From theoretical considerations, Smoluchowski,[1] has deduced an equation for the velocity of coagulation of a metallic sol. He makes the fundamental assumption that the rate of disappearance of the primary particles of a sol is greater than that anticipated from a simple bi-molecular process; because secondaries and other complexes may further react with primaries and with one another. Hence from probability considerations he arrives at the equation

$$\nu_1 = \frac{\nu_0}{(1 + \beta_0 t)^2}$$

where

$\nu_1$ = the initial number of primary particles;

$\nu_1$ = the number of primary particles remaining after time $t$;

and $\beta_0 = 4\pi D \rho \nu_0$

where

$\rho$ = the radius of the sphere of attraction of a primary particle;

$D$ = the diffusion constant as given by Einstein's equation, namely,

$$D = \frac{R.T}{N} \cdot \frac{1}{6\pi r \eta}$$

where $r$ = the radius of the particle

and $\eta$ = the viscosity of the medium.

Various investigations of Smoluchowski's equation have been carried out, notably by Zsigmondy[2], Westgren and Reitstötter,[3] Kruyt and Arkell,[4] Hatschek,[5] Mukherjee and Papaconstantinou[6] and Anderson[7]. These investigators find that the Smoluchowski equation holds fairly well in the region approximating to rapid coagulation, but during slow coagulation there is a marked decrease in the value of the coefficient.

---

[1] Z. physik. Chem., 92, 129 (1917).
[2] Z. physik. Chem., 92, 600 (1917).
[3] Z. physik. Chem., 92, 750 (1917).
[4] Rec. Trav. chim., 39, 656 (1920); Kolloid-Z., 32, 29 (1923).
[5] Trans. Faraday Soc., 17, 499 (1921).
[6] Phil. Mag., (6) 44, 305 (1922).
[7] Trans. Faraday Soc., 19, 623 (1924).

Smoluchowski has attempted to extend his equation to slow coagulation by the introduction of a probability factor to allow for the fact that, owing to incomplete discharge of the electrical double layers, the attractive forces of the particles are not at their maximum and hence only a fraction of the collisions result in union. The resulting equation is identical in form with that obtained for rapid coagulation except that the term $\beta_o$ is replaced by $\xi\beta_o$,

$$\text{i.e. } \nu_1 = \frac{\nu_o}{(1 + \xi\beta t)^2}$$

The probability factor $\xi$ is assumed by Smoluchowski to be a constant.

Anderson suggests that before Smoluchowski's equation can be applied to slow coagulation it requires modification to allow for two factors, (a) the decrease of the probability factor as coagulation proceeds, and (b) the existence of imcomplete coagulation as a consequence of unequal, and in some cases, therefore, of excessive, charge on the primary particles.

Anderson, working in this laboratory, coagulated gold sol by various electrolytes, but he obtained the most satisfactory values of $\beta_o$ (variation of about 12%) by the use of barium chloride. It was decided, therefore, in the present instance, to adhere to the use of gold sol, to employ barium chloride as coagulant, and to work in the sensibly rapid region in which $\beta_o$ is found to be fairly constant. It was then hoped to obtain values of $\beta_o$ by measurements of the velocity of coagulation at 25° C and at 80° C, comparison of which would determine the effect of temperature on the reaction. 80° C was chosen as the higher temperature in order to obtain as large a temperature range as was compatible with feasibility of experimentation.

If the expression

$$\beta_o = \frac{2RT}{3N} \cdot \frac{\rho\nu_o}{\eta r}$$

for the Smoluchowski constant be examined, it will be seen that for any one sol

$$\beta_o = \frac{T}{\eta} \cdot A.$$

where $A$ includes all the constants of the above expression, these being assumed independent of temperature. Consequently we may write

$$\beta_{T_1} = A \cdot \frac{T_1}{\eta_1} \qquad \text{and } \beta_{T_2} = \frac{A \cdot T_2}{\eta_2}$$

where $T_1$ and $T_2$ denote the temperatures in degrees absolute at which the experiments are carried out. Therefore

$$\beta_{T_2} = \frac{\eta_1 T_2}{\eta_2 T_1} \cdot \beta_{T_1}$$

Westgren[1] as the result of some experiments on the influence of temperature on the rate of coagulation, came to the conclusion that not only is the velocity of coagulation dependent upon increased Brownian movement of the

[1] Arkiv. Kemi Min. Geog. 7, 6.

particles, but also on the variation with temperature of the specific precipitating action of the electrolyte. Freundlich and Basu[1] on the other hand, find that the influence of temperature on the velocity of electrolyte coagulation is in strict accordance with the Smoluchowski conception.

## Materials Employed

The barium chloride employed as coagulant was recrystallised before use, and the conductivity water prepared from distilled water re-distilled from a

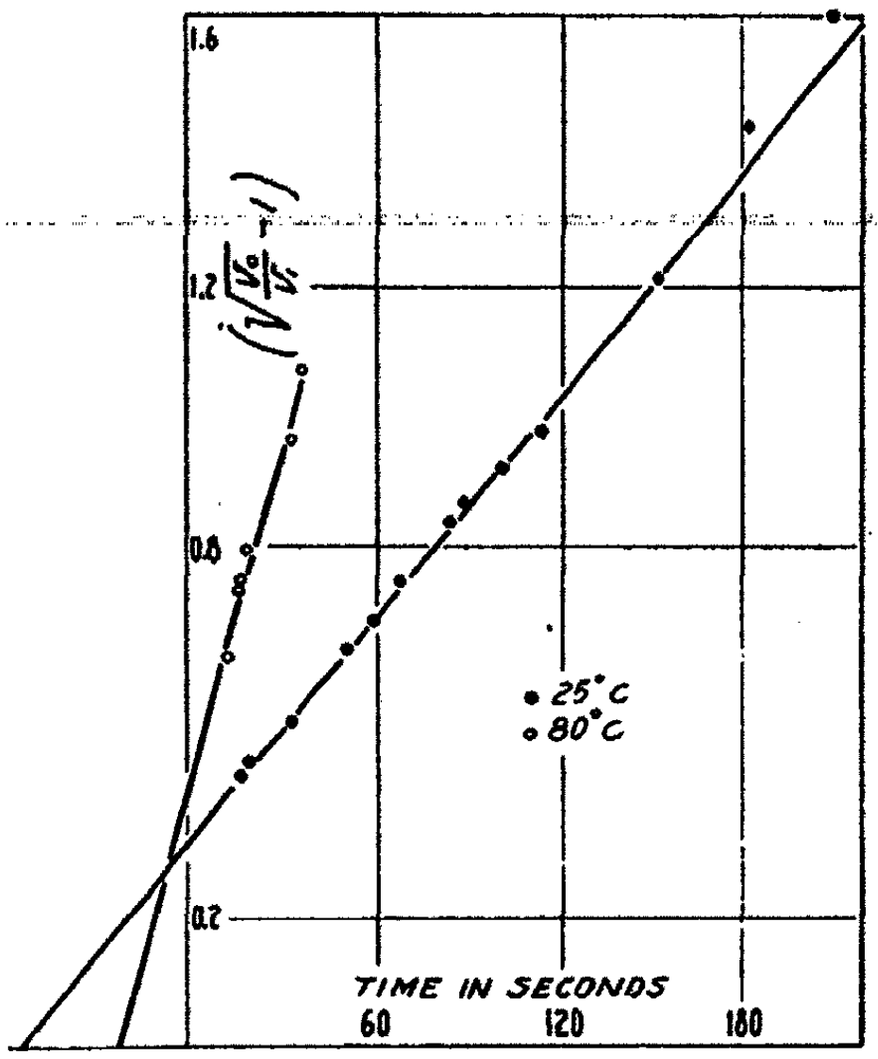



FIG. 1

silver-lined copper vessel. All glass vessels were either Duro or Jena glass. All vessels used for gold sol or electrolyte were carefully cleaned after each experiment with *aqua regia* followed by a mixture of alcohol and nitric acid, and were kept in chromic acid mixture when not in use. Immediately before use they were well washed with distilled water and finally sterilised by steam from the re-distilled water; the minimum time of steaming was three minutes.

Vessels used for gelatin cannot be cleaned in the above manner, since acids give an insoluble deposit with the protein; hence, these vessels were first treated with strong caustic soda to remove the gelatin, and subsequently well washed with soap and water. This was followed by a further thorough washing with distilled water, the vessels finally being steamed.

[1] Z. physik. Chem., 115, 203 (1925).

For the preparation of gold sols the formaldehyde method, as modified by Anderson[1] was employed. The clear ruby red sols were dialysed in collodion sacs against distilled water for three days, the water being changed twice a day. Experience showed that this length of dialysis gave the most nearly reproducible sols.

Hatschek's colorimetric method was used to determine the degree of coagulation. This method is based on the assumption that the red colour of the gold sol is due to primaries, while the blue colour which appears on coagulation is due to secondaries and other complexes. Hence at any time the percentage red remaining is proportional to the amount of uncoagulated sol in the mixture. This percentage red is measured by means of the Hatschek wedge. An 800 C. P. lamp provided a suitable source of light. In order to render the light sufficiently diffuse, it was first reflected from a sheet of thick white matt paper, and then passed through a sheet of matt glass.

The mode of experimentation was as follows: 250 ccs. of gold sol were introduced into one beaker and 5 ccs. of electrolyte into a similar one. When the contents of the beakers had come to equilibrium at the temperature of the thermostat, the gold sol was poured into the electrolyte and the time noted. From time to time approximately 50 cc. samples of the reacting mixture were withdrawn by means of pipettes and the reaction arrested as recommended by Zsigmondy by running the mixture into gelatin. The percentage red remaining was then determined.

The experiments described in the following section were conducted without shaking in order to eliminate all but the natural thermal diffusion in the quiescent system. The figures contained in the following tables represent the mean value of at least three readings, the mean variation between which was not greater than 0.5%.

## Experimental Results

### Measurements of the velocity of coagulation at 25° C

TABLE I

Coagulation of gold sol (Sol 22) by 0.001068 N $BaCl_2$ at 25° C.

| Time in Seconds | Per cent Red | $\beta_0$ | Time in Seconds | Per cent Red | $\beta_0$ |
|---|---|---|---|---|---|
| 19.5 | 48.7 | 1.33 | 91.5 | 28.7 | 0.57 |
| 22.5 | 47.5 | 1.20 | 102.5 | 28.2 | 0.52 |
| 35.5 | 43.4 | 0.87 | 114.5 | 25.6 | 0.51 |
| 52.5 | 37.5 | 0.73 | 151.5 | 20.3 | 0.48 |
| 62.5 | 35.6 | 0.65 | 191.5 | 16.6 | 0.48 |
| 71.0 | 33.1 | 0.62 | 211.5 | 14.4 | 0.46 |
| 87.5 | 29 6 | 0.58 | | | |

[1] Trans. Faraday Soc., 19, 636 (1926).

In the following table are given the results obtained for the same electrolyte concentration, but with a different sol preparation.

TABLE II

Coagulation of gold sol (Sol 16) by 0.001068 N $BaCl_2$ at 25° C.

| Time in Seconds | Per cent Red | $\beta_o$ | Time in Seconds | Per cent Red | $\beta_o$ |
|---|---|---|---|---|---|
| 45 | 28.4 | 1.17 | 80 | 20.5 | 0.91 |
| 60 | 25.2 | 0.99 | 90 | 20.0 | 0.82 |
| 70 | 22.2 | 0.96 | 120 | 16.9 | 0.71 |

TABLE III

Coagulation of gold sol (Sol 8) by 0.000596 N $BaCl_2$ at 25° C.

| Time in Seconds | Per cent Red | $\beta_o$ | Time in Seconds | Per cent Red | $\beta_o$ |
|---|---|---|---|---|---|
| 10 | 70.0 | 1.18 | 58.5 | 45.0 | 0.50 |
| 20 | 58.7 | 0.91 | 60 | 47.5 | 0.45 |
| 21 | 57.5 | 0.93 | 120 | 31.2 | 0.39 |
| 30 | 55.0 | 0.70 | 180 | 26.2 | 0.27 |
| 40 | 5.12 | 0.60 | | | |

It will be seen from the above results that $\beta_o$ instead of remaining constant, falls regularly as the reaction proceeds. In order to work at an electrolyte concentration that will permit of the reaction being of measurable speed at 80° C., it has been necessary to choose a condition not closely approximating to rapid coagulation at 25° C. The fall in $\beta_o$ will be discussed more fully later.

*Measurements of the velocity of coagulation at* 80° C.

The data of Tables IV, V and VI refer to the same sols as do Tables I, II and III respectively.

TABLE IV

Coagulation of gold sol (Sol 22) by 0.001068 N $BaCl_2$ at 80° C.

| Time in Seconds | Per cent Red | $\beta_o$ | Time in Seconds | Per cent Red | $\beta_o$ |
|---|---|---|---|---|---|
| 13.5 | 37.8 | 2.79 | 20.0 | 30.9 | 2.39 |
| 18.0 | 33.4 | 2.43 | 34.0 | 25.9 | 1.70 |
| 19.5 | 32.8 | 2.29 | 38.5 | 23.1 | 1.68 |

TABLE V

Coagulation of gold sol (Sol 16) by 0.001068 N $BaCl_2$ at 80° C.

| Time in Seconds | Per cent Red | $\beta_o$ | Time in Seconds | Per cent Red | $\beta_o$ |
|---|---|---|---|---|---|
| 10 | 36.6 | 3.92 | 30 | 21.9 | 2.27 |
| 15 | 32.5 | 3.02 | 40 | 16.9 | 2.15 |
| 20 | 27.8 | 2.69 | | | |

TABLE VI

Coagulation of gold sol (Sol 8) by 0.000596 N $BaCl_2$ at 80° C.

| Time in Seconds | Per cent Red | $\beta_o$ | Time in Seconds | Per cent Red | $\beta_o$ |
|---|---|---|---|---|---|
| 10 | 51.2 | 2.40 | 40 | 32.5 | 1.13 |
| 14 | 47.5 | 1.93 | 50 | 27.5 | 1.09 |
| 30 | 40.0 | 1.16 | 59 | 23.7 | 1.07 |

## Discussion

Anderson, in considering the results of his experiments, says that the constancy of $\beta_o$ is quite good in the region approximating to rapid coagulation; but a close examination of the results shows that the variation which does exist in his results is regular. In fact, as in the case of the results obtained in the present research, the values of $\beta_o$ fall steadily.

It will be recalled that the equation from which $\beta_o$ is calculated is

$$v_1 = \frac{v_o}{(1 + \beta_o t)^2}$$

$$\text{i. e. } \beta_o = \frac{1}{t}\left(\sqrt{\frac{v_o}{v_1}} - 1\right)$$

Thus the value of $\beta_o$ can be obtained by plotting $\left(\sqrt{\frac{v_o}{v_1}} - 1\right)$ against time and taking the tangent to the resulting curve. This has been done with the present results, and it is found that the curve is a straight line, and hence $\beta_o$ calculated in this manner is a constant. The significance of the fact that the line does not pass through the origin will be discussed later.

An example of the type of curve obtained at 25° and 80° C respectively on plotting $\left(\sqrt{\frac{v_o}{v_1}} - 1\right)$ against time is given on the graph. The corresponding data are given in the following tables. In column one will be found the time in seconds ($t$), in column two the percentage red ($v_1$) remaining after time $t$, as found by comparison in the Hatschek wedge, the third column contains the value of $\left(\sqrt{\frac{v_o}{v_1}} - 1\right)$, while in the last column is the value of $\beta_o$ obtained by measuring the slope of the straight line. This value we will term $\beta'$.

TABLE VII

Data of Table I

Coagulation of gold sol (Sol 22) by 0.001068 N $BaCl_2$ at 25° C

| Time in Seconds | Per cent Red | $\left(\sqrt{\frac{v_o}{v_1}} - 1\right)$ | $\beta'$ | Time in Seconds | Per cent Red | $\left(\sqrt{\frac{v_o}{v_1}} - 1\right)$ | $\beta'$ |
|---|---|---|---|---|---|---|---|
| 19.5 | 48.7 | 0.43 | | 91.5 | 28.7 | 0.87 | |
| 22.5 | 47.5 | 0.45 | | 102.5 | 27.9 | 0.92 | |
| 35.5 | 43.4 | 0.52 | | 114.5 | 25.6 | 0.97 | |
| 52.5 | 37.5 | 0.63 | 0.34 | 151.5 | 20.3 | 1.22 | 0.34 |
| 62.5 | 35.6 | 0.67 | | 181.5 | 16.6 | 1.45 | |
| 71.0 | 33.1 | 0.74 | | 211.5 | 14.4 | 1.63 | |
| 87.5 | 29.6 | 0.84 | | | | | |

TABLE VIII

Data of Table IV

Coagulation of gold sol (Sol 22) by 0.001068 N $BaCl_2$ at 80° C

| Time in Seconds | Per cent Red | $\left(\sqrt{\frac{\nu_0}{\nu_1}}-1\right)$ | $\beta'$ | Time in Seconds | Per cent Red | $\left(\sqrt{\frac{\nu_0}{\nu_1}}-1\right)$ | $\beta'$ |
|---|---|---|---|---|---|---|---|
| 13.5 | 37.8 | 0.63 | 1.05 | 20.0 | 30.9 | 0.80 | 1.05 |
| 18.0 | 33.4 | 0.73 | | 34.0 | 25.9 | 0.96 | |
| 19.5 | 32.8 | 0.75 | | 38.5 | 23.1 | 1.08 | |

The data of Tables II, III, V and VI were plotted in a similar manner, and in each case a straight line was obtained. The results are summarised in Table IX

TABLE IX

| Table | Sol preparation | Temperature | $\beta'$ |
|---|---|---|---|
| II | 16 | 25° C. | 0.54 |
| V | 16 | 80° C. | 1.56 |
| III | 8 | 25° C. | 0.28 |
| VI | 8 | 80° C. | 0.84 |

We will now proceed to the question of the influence of temperature on the coagulation. It has previously been deduced on the basis of the Smoluchowski theory that

$$\frac{\beta_2}{\beta_1} = \frac{\eta_1 T_2}{\eta_2 T_1}$$

where $T_1$ and $T_2$ denote the respective temperatures on the absolute scale, at which the reactions are carried out; $\eta_1$ and $\eta_2$ are the viscosities at the temperatures $T_1$ and $T_2$ respectively; and $\beta_1$ and $\beta_2$ are the Smoluchowski constants at the corresponding tempera tures. Since the sols contain only 56 milligrams of gold per litre, their viscosities have been assumed to be that of the medium, water.

At 25° C. $\eta_{298} = 0.4981$
At 80° C. $\eta_{353} = 0.199$

From this follows the relationship

$$\frac{\beta_{353}}{\beta_{298}} = \frac{.498 \times 353}{.199 \times 298}$$

or

$$\frac{\beta_{353}}{\beta_{298}} = 2.964$$

Employing the values of the Smoluchowski constants $\beta'$ obtained from the slope of the respective straight lines, we can evaluate the ratio $\beta'_{353} \div \beta'_{298}$. These will be found in Table X. In column one will be found the preparation number of the gold sol; in column two the concentration of barium chloride;

columns three and four give the observed values of $\beta'$ at 25° C. and 80° C. respectively, the ratio of which is contained in column five; while in column six is the calculated value.

TABLE X

| Sol preparations. | Concn. of $BaCl_2$ in mols/litre | $\beta'_{298}$ | $\beta'_{353}$ | $\frac{\beta'_{353}}{\beta'_{298}}$ Obs. | $\frac{\beta_{353}}{\beta_{298}}$ calc. |
|---|---|---|---|---|---|
| 8 | 0.000596 | 0.28 | 0.84 | 3.00 | 2.96 |
| 16 | 0.001068 | 0.54 | 1.56 | 2.89 | 2.96 |
| 22 | 0.001068 | 0.35 | 1.05 | 3.00 | 2.96 |

The close agreement between the observed and calculated values of the ratio points quite definitely to the conclusion that the increase of the velocity of coagulation of gold sol with temperature is entirely due to the change in the viscosity of the medium; this is more particularly so, since the ratio appears to be independent of both the sol preparation and of the concentration of coagulating electrolyte; provided the latter approximates to that required for a rapid coagulation.

*The significance of the "zero discrepancy"*

It will be seen from the graph that if the straight line obtained on plotting $\left(\sqrt{\frac{\nu_o}{\nu_1}} - 1\right)$ against time be extrapolated back it does not pass through the origin, but cuts the time axis at a point corresponding to a negative time. This is what is meant by the phrase zero discrepancy. The discrepancy is due to the fact that, though over the major portion of the reaction the velocity of coagulation is constant, during a short initial period the velocity is enhanced. In other words, a fraction of the primaries coagulate much faster than do the majority of the particles; the difference between their actual time of coagulation and the time for an equal number of primaries (coagulating with the mean velocity) to become completely coagulated, being equal to the distance cut off on the time axis by the extrapolation of the curve.

It has already been mentioned that in a paper by Anderson it is suggested that "incomplete coagulation exists as a consequence of unequal, and in some cases, therefore, of excessive charge on the primary particle." Such inequality of charge will also necessitate a fraction of the primaries carrying a charge below the mean. The velocities of the coagulations studied in the present instance, though approximating to rapid, are actually in the region in which $\beta_o$ is dependent on electrolyte concentration. Hence on addition of electrolyte the particles will be partially discharged and will coagulate with a velocity characteristic of their residual charge. The bulk of the particles carrying the mean charge will coagulate with the mean velocity but those primaries which originally carried a charge less than that mean will be more completely discharged and consequently will coagulate with a velocity greater than the

mean velocity, hence producing the enhanced velocity at the beginning of the reaction.

A fuller investigation of this point, from the theoretical aspect, will be given in a later paper.

## Summary

1. A short survey of investigations bearing on the Smoluchowski equation has been given.

2. Using the method of Hatschek, colorimetric determinations of the velocity of coagulation of gold sol by barium chloride have been carried out at 25° C. and at 80° C.

3. It is concluded from these measurements that the increase of the velocity of coagulation with temperature is entirely due to change of the viscosity of the medium.

4. The shape of the $\left(\sqrt{\frac{\nu_o}{\nu_1}} - 1\right)/t$ curves is interpreted as indicating that the initial primary particles of the sol are unequally charged.

*Muspratt Laboratory of Physical and Electro-chemistry.*
*University of Liverpool.*
*June 26, 1926.*

# NOTE ON THE SIGNIFICANCE OF THE VARIATION IN THE SMOLUCHOWSKI COAGULATION COEFFICIENT ($\beta$)

BY MAUD GARNER

It is generally accepted that the manner in which the addition of electrolyte brings about the coagulation of a sol is by reduction of the repulsive forces between the particles in consequence of neutralisation of their charges due to adsorption thereon of ions of opposite sign. On the theory of Smoluchowski,[1] it is assumed that, not only do primaries react with one another, but that secondaries can further react with primaries and with one another to give teriaries and other complexes. From probability considerations Smoluchowski deduces a formula for rapid coagulation i. e. a rate so great as to be independent of further increase in concentration of electrolyte, namely

$$\nu_1 = \frac{\nu_0}{(1 + \beta_0 t)^2}$$

where

$\nu_0$ = the initial number of primary particles.

$\nu_1$ = the number of primary particles remaining after time $t$ and $\beta_0 = 4\pi D\rho\nu$.

where

$\rho$ = the radius of the sphere of attraction of a primary particle.

and D = the diffusion constant, as given by Einstein's equation namely,

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi r\eta}$$

where

$r$ = the radius of the particle.

and $\eta$ = the viscosity of the medium.

In attempting to extend his equation to the region in which the velocity of coagulation varies with electrolyte concentration Smoluchowski assumes that, owing to incomplete discharge of the electrical double layer, the attractive forces of the particles are not at their maximum and hence only a fraction of the collisions result in union. A probability factor $\xi$ is introduced to allow for this, the resulting equation being:—

$$\nu_1 = \frac{\nu_0}{(1 + \xi\beta_0 t)^2}$$

$\xi$, being a function of the residual nett charge on the particle, will be a constant throughout the course of coagulation, assuming the particles are equally charged; in other words,

$$\beta = \xi\beta_0 = \text{a constant.}$$

[1] Z. physik. Chem., 92, 129 (1917).

where $\beta_0$ is the constant for rapid coagulation. Hence for non-rapid coagulation the Smoluchowski equation becomes,

$$\nu_1 = \frac{\nu_0}{(1+\beta t)^2} \qquad \text{or} \qquad \beta = \frac{1}{t}\left(\sqrt{\frac{\nu_0}{\nu_1}} - 1\right)$$

It is to be understood that in calculating $\beta$ from experimental data the Smoluchowski equation just given is employed and time is reckoned from zero. This mode of calculation is to be distinguished from the graphical method in which $u$ is obtained by taking the tangent to the curve obtained on plotting $\left(\sqrt{\frac{\nu_0}{\nu_1}} - 1\right)$ against time. In the subsequent text the coefficient calculated from the Smoluchowski equation, time being reckoned from zero, will be denoted by $\beta$; while the value of the coefficient obtained by the graphical method will be termed $\beta'$. If the coefficient is referred to in the general sense, i. e. if no specific mode of calculation is implied, then it will be termed the "Smoluchowski coefficient."

It has been suggested by Anderson[1] in order to account for incomplete coagulation at very low concentrations of electrolyte, that the primary particles of a sol are *un*equally charged. If this is assumed, then some mode of distribution of the charges must be imagined. While allowing for diversity of charge, it is to be expected that the vast majority of particles will possess charges at, or about, a mean value, the number of particles carrying any particular charge rapidly falling off as that charge diverges from the mean. Hence, if the number of particles be plotted against charge, it is probable the curve will somewhat resemble the Maxwellian distribution curve.

Such being the case, the resulting coagulation will comprise a number of simultaneous reactions, each characterised by a different probability factor. Consequently the observed Smoluchowski coefficient will equal ($\xi$ mean . $\beta_0$). But the low charged particles, in consequence of their greater probability of inelastic collision, will, as the reaction proceeds, coagulate more quickly than those particles carrying a higher charge. This decrease in the number of low charged particles in the system will produce a corresponding decrease in the value of $\xi$ mean. Since, however, the majority of particles carry a charge approximating to the mean value, $\xi$ mean will rapidly become constant. Furthermore, this constancy of $\xi$ mean will persist until the greater part of the sol has coagulated, after which it will fall to the value characteristic of the highly charged particles.

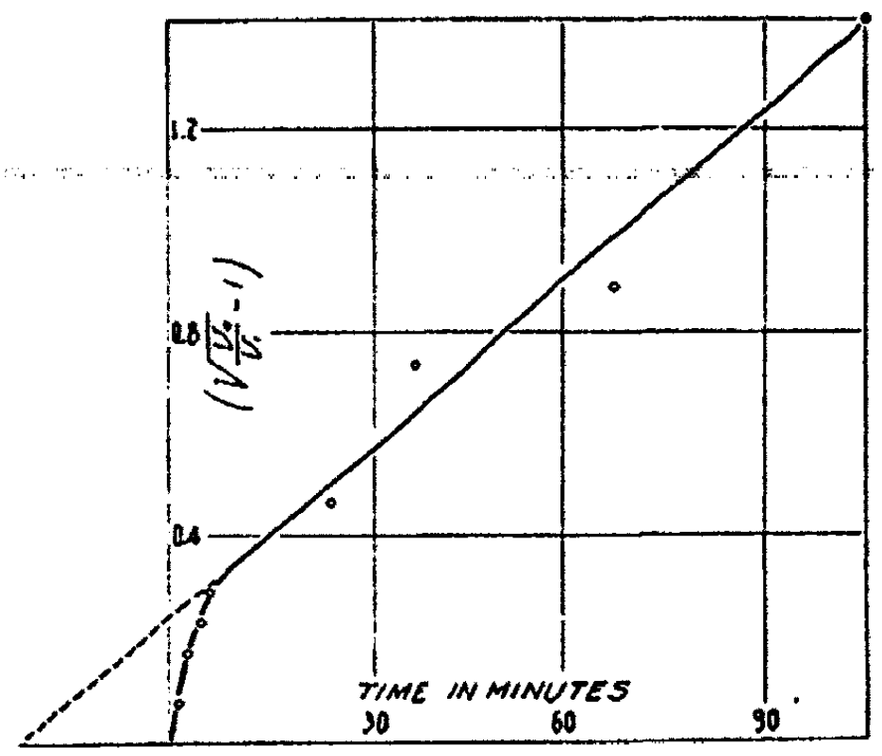
It will be seen from the equation

$$\beta = \frac{1}{t}\left(\sqrt{\frac{\nu_0}{\nu_1}} - 1\right)$$

that the Smoluchowski coefficient is the tangent to the curve $\left(\sqrt{\frac{\nu_0}{\nu_1}} - 1\right)$ against time. Therefore the slope of the curve will vary in a similar manner

[1] Trans. Faraday. Soc., 19, 623 (1924).

to $\xi$ mean. In other words, the value of $\beta'$ will fall rapidly at the beginning of the reaction to a constant value which will persist over the major portion of the coagulation, a further decrease in the value of $\beta'$ manifesting itself towards the end of the reaction. In consequence of the initial decrease in the slope of the curve, if the linear portion be extrapolated back the line will not pass through the origin, but will cut the axis at a negative time. Thus while the reaction proceeds with a constant velocity over the major portion of its course, this is not revealed by the Smoluchowski coefficient $\beta$ calculated from zero time, on account of the zero discrepancy.



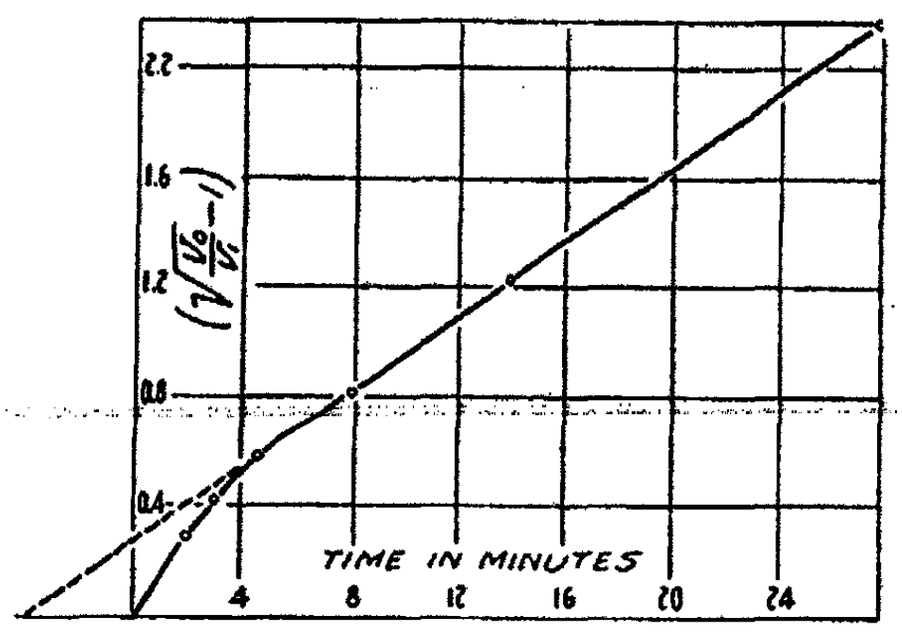

GRAPH I

The experiments described in the preceding paper on the rate of coagulation of gold sol by barium chloride at 25°C will now be considered. Relatively high concentrations of electrolyte were employed in order to coagulate the sol at a rate approximating to truly rapid coagulation. $\beta'$ was found by the graphical method to be constant over the portion or the reaction examined; but an initial fall in the Smoluchowski coefficient was indicated in every case by a "zero discrepancy" of about fifty seconds.

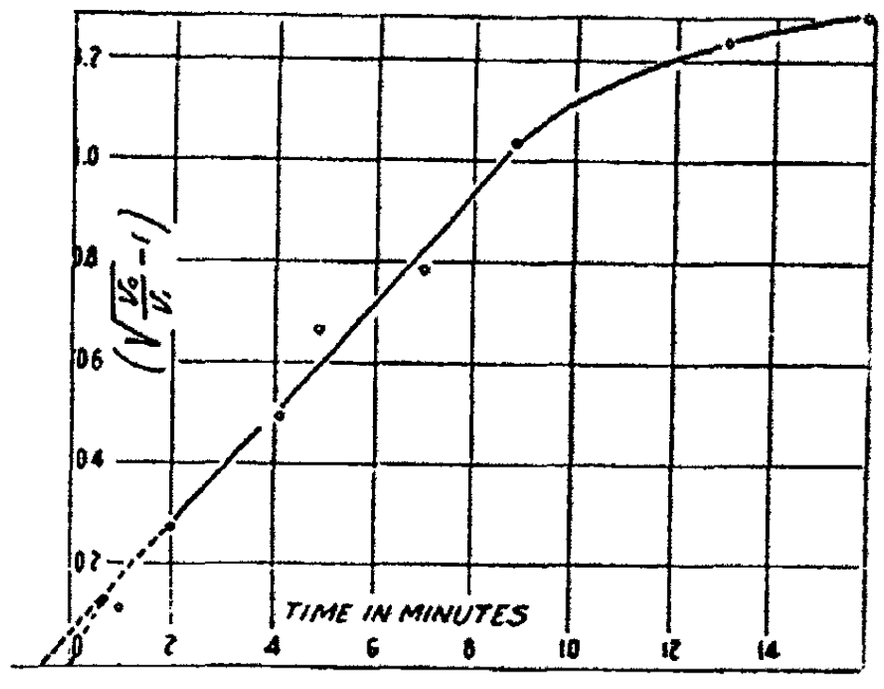
From the data of two experiments carried out by Anderson on the coagulation of gold sol by a slightly higher concentration of barium chloride than that employed in the above experiments, $\left(\sqrt{\frac{v_0}{v_1}}-1\right)$ has been calculated by the writer and plotted against time. It is found that $\beta'$ is constant over the portion of the reaction examined, but in these cases also the lines do not pass through the origin, there being a "zero discrepancy" of about five seconds.

Anderson also measured the velocity of coagulation of gold sol at low electrolyte concentrations. Graph I has been plotted from his data on the rate of coagulation of gold sol by 0.001N barium chloride. The initial fall

in $\beta'$ is well marked, and the zero "discrepancy" is large, namely twenty-two minutes. The curves referring to coagulation by 0.00847N and 0.0508N hydrochloric acid are similar.




GRAPH II




GRAPH III

Graph II, for which the data of Hatschek[1] on the coagulation of gold sol by 0.0075N hydrochloric acid, have been employed, depicts the same type of curve.

The data of Mukherjee and Papaconstantinou[2] on the coagulation of gold sol by 0.00075N barium chloride, have been employed in plotting Graph III. This curve demonstrates the final fall in the value of $\beta'$.

[1] Trans. Faraday Soc., 17, 499 (1921).
[2] Phil. Mag. (6) 44, 305 (1922).

It appears, therefore, that on the assumption that the primary particles of a sol are unequally charged, *qualitative* predictions can be made concerning the behaviour of the Smoluchowski coefficient in the region in which the rate of coagulation varies with electrolyte concentration.

**Summary**

On the assumption that the initial primary particles of a metallic sol are *un*equally charged, the behaviour of the Smoluchowski coefficient during coagulation in the region in which the rate of coagulation varies with electrolyte concentration is predicted and is found to be in agreement with experiment.

*Muspratt Laboratory of Physical and Electro-chemistry.*
*University of Liverpool.*
*June 26, 1926.*

# A GEL OF METALLIC PLATINUM*

BY ARTHUR F. BENTON

Although numerous inorganic substances, mainly metallic oxides and arsenates, have been obtained in gel form, apparently no hydrogel of a metal has ever been described. That such a system is a possibility, however, is evident from the fact that Börjeson[1] has prepared a gel from a sol of metallic cadmium dispersed in ethyl alcohol. Presumably most metals are incapable of forming the highly hydrous precipitates which gel formation ordinarily requires. With platinum, however, the conditions are more favorable, for this metal when finely divided (platinum black) is known to adsorb water very strongly. It is the purpose of this note to describe the conditions under which a gel of metallic platinum was actually obtained.

In the course of some work on the adsorption of gases by catalytic agents, it was desired to prepare a sample of platinum black with a large surface area. This was accomplished by slowly adding 1500 cc. of a boiling solution of sodium chloroplatinate containing about 27 g. of platinum per liter to an equal volume of a boiling 5% solution of sodium formate. The platinum thus precipitated settled rapidly for the most part, owing to the high concentration of electrolytes present. These were then gradually removed by washing the precipitate repeatedly by decantation, using 600-700 cc. of boiling water each time. The first five washings all remained opaque even after standing indefinitely, but only the second and third contained a high concentration of colloidal platinum. After standing undisturbed for two days, the sol obtained in the second washing was found to have been transformed in part to gel, about 50-60 cc. of the latter being formed. The supernatant sol remained completely opaque.

The gel thus obtained was a shiny, black substance, apparently homogeneous throughout its extent, and showing the elastic properties characteristic of jellies. It also exhibited the phenomenon of syneresis, for on relieving the hydrostatic pressure on the gel by pouring off the supernatant sol, water at once began to exude from it. Although the volume of water thus obtained constituted a large fraction of the total volume of the gel, the latter did not undergo any considerable contraction. It is noteworthy that the synerized liquid was clear water, rather than a colloidal solution of platinum, a fact which indicates the fineness of the gel structure.

Analysis of the gel after standing ten days in a covered beaker showed 3.1% platinum by weight (equivalent to 2.1% by volume), and 0.048% of sodium chloride. The mol ratio of water to platinum was, therefore, 24 to 1 at that time. Before undergoing the syneresis the ratio was probably about 40 or 50

*Contribution No. 28 from the Cobb Chemical Laboratory, University of Virginia.

[1] Cf. Harrison: "The Physics and Chemistry of Colloids and Their Bearing on Industrial Questions," Report of a General Discussion held jointly by the Faraday Society and Physical Societies of London, Oct. 25, p. 55, (1920).

to 1. The supernatant sol contained 0.47 g. of sodium chloride and about 1 g. of platinum per liter.

The gel was apparently stable indefinitely at room temperature. Samples of it contracted greatly on drying, whether at 100° or in a desiccator at ordinary temperature, but retained their general form. This substance obviously belongs to the class of rigid gels, typified by silica gel, since the drying process is irreversible even when carried out at room temperature. No visible structure could be detected under the microscope, either before or after drying.

Since the literature contains numerous references to the preparation of platinum black and colloidal platinum by reduction methods, it is perhaps pertinent to suggest a reason why a gel of this metal has not been described hitherto. It seems probable that this is due to the fact that platinum sols have usually been formed directly by reduction, rather than by reduction with precipitation, followed by peptization. Only relatively dilute sols can be obtained by direct reduction, because if one starts with concentrated solutions a precipitate results and not a sol. In the present case a large quantity of very finely divided platinum was brought into colloidal solution with a relatively small quantity of water, and a sol thus obtained sufficiently concentrated to undergo transformation to gel. Nevertheless there was doubtless a particularly favorable conjunction of circumstances, such as electrolyte concentration, etc., because an attempt to duplicate the gel produced only a highly gelatinous precipitate.

Although a mol ratio of 40 or 50 to 1 represents a relatively concentrated gel in comparison with those which have been obtained with many other substances, nevertheless it seems remarkable that metallic platinum can hold so much water in a solid structure. Its ability to do so is probably attributable to the tendency of this metal, when finely divided, to form filaments or chains of particles. When concentrated platinum sols are allowed to stand, such structures can frequently be observed, usually forming fern-like branches up to several millimeters in length. Under favorable conditions these branching filaments probably extend gradually throughout the sol, or at least throughout the lower, more concentrated part of it, forming a structure which has the elasticity of a typical jelly, and which is capable of retaining large quantities of water, partly mechanically and partly by adsorption. While all gels need not necessarily possess the same type of structure, it is noteworthy that the weight of the evidence appears to favor a similar structure for the majority of inorganic jellies.[1]

## Summary

The formation of a hydrogel of metallic platinum is reported, and its properties, composition and structure are briefly discussed.

*University, Virginia.*

[1] Cf. Bogue: "The Theory and Application of Colloidal Behavior," 1, 377-389 (Chapter by Weiser) (1924).

# THE STABILITY OF DIAZO-BENZENE CHLORIDE SOLUTIONS.*
# I. THE REACTION OF DIAZO-BENZENE CHLORIDE WITH WATER.

BY H. A. HOLDEN PRAY**

## Introduction

Considering the immense importance of the diazo compounds as intermediates in the industrial production of azo dyes, as well as the interest which the decompositions of these compounds hold from the theoretical viewpoint, there have been surprisingly few studies made of the kinetics of their reactions. Hausser and Muller[1] were the first to determine the velocity of the decomposition of diazo salts with water. They followed the reaction by measuring the volume of nitrogen evolved at definite time intervals. The decomposition of the diazo salts derived from a number of different amines was studied in this way. When appropriate values were substituted in the equation for a monomolecular reaction, somewhat diminishing values for K were obtained, although of sufficient constancy to indicate that the reaction is a monomolecular one. The original concentration of the diazo salt was found to have no effect upon the magnitude of K, another indication that the reaction is monomolecular.

Another series of experiments was performed by Hantzsch[2] who followed the rate of reaction by the method used by Hausser and Muller, and, in one or two cases, by titrating with standard alkali the acid formed during the course of the reaction. He showed that excess of hydrochloric acid has absolutely no effect on the rate of the reaction of a number of different diazo compounds with water and that, as Hausser and Muller had observed, changing the initial concentration of the diazo salt does not change the magnitude of the velocity constant. On the basis of the fact that the reaction of the different diazo bodies with water appeared to be monomolecular, and also on the basis of the chemical properties which these bodies were known to possess, Hantzsch proposed a theory for the mechanism of the typical diazo reactions. According to this theory, the diazonium salt becomes first an addition compound, this then becomes a syn-diazo compound from which the final products of the decomposition are formed.

$$\begin{array}{l} Ar \\ | \\ N \equiv N \\ | \\ Cl \end{array} + \begin{array}{l} R \\ | \\ \cdot \\ | \\ H \end{array} \longrightarrow \begin{array}{l} Ar \quad R \\ | \quad | \\ N \equiv N \\ | \quad | \\ Cl \quad H \end{array} \longrightarrow \begin{array}{l} Ar \quad R \\ | \quad | \\ N = N \end{array} + HCl \longrightarrow Ar - R + N_2 + HCl$$

*Contribution from the Laboratory of General Chemistry, the University of Wisconsin.

**The work included in this paper is taken from the thesis presented by H. A. Holden Pray in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin. This investigation was conducted under the supervision of Professor J. H. Walton.

[1] Hausser and Muller: Bull. (3), 7, 721 (1892); Compt. rend., 114, 549, 669, 760, 1438, Bull., 9, 353, (1893).

[2] Hantzsch: Ber., 33, 2517 (1900).

The formation of the addition compound is presumably instantaneous as is the decomposition of the syn-diazo body. Criticism of this theory of the diazo reactions will be reserved for a later paper.

Cain and Nicoll have determined the reaction velocity, and hence the relative stability of water solutions of a long series of diazo salts of the benzene[1] and of the naphthalene series.[2] The temperature coefficients for the decomposition of several of the diazo compounds in water solution have also been determined by these investigators.[3]

In another investigation, Cain[4] demonstrated that, when an excess of hydrochloric acid is added to a solution of diazo-benzene chloride in water, no change in the velocity of the decomposition results. An excess of sulfuric acid increases the stability of the solution somewhat, a fact which this experimenter attributes to the dehydrating action of concentrated sulfuric acid. An excess of sodium acetate causes coupling of the phenol with the undecomposed diazo compound and a consequent drop in the monomolecular constants. More startling, however, is the observation that equivalent solutions of diazo-benzene chloride, sulfate, nitrate, and oxalate decompose at the same rate.

Shortly after the publication of the results of Cain's work, a paper appeared by Lamplough[5] in which the gasometric method used by Cain was shown to be inaccurate. This, Lamplough showed to have been due to the fact that, when a solution from which a gas is liberated is not agitated, a very high degree of supersaturation of the gas in the solution results. "The reaction resembles a monomolecular one for a limited range when measured by the rate of evolution of the gas from a still solution, and it is this resemblance which has been measured by Cain and Nicoll and other investigators." The velocity constants obtained when the reaction mixture is agitated are somewhat higher than those of Cain and Nicoll although much more constant.

It was at this point that the present investigation was undertaken, with the object in view of making a study of the effect of foreign substances upon the velocity of the reaction of diazo-benzene chloride with water.

## Experimental

*Preparation of Reagents*—A dilute solution of diazo-benzene chloride was prepared by the method used by Cain and Nicoll.[6] For each run, 8.87 g. of freshly distilled aniline were dissolved in three times the theoretical amount of hydrochloric acid (22.5 c.c. of hydrochloric acid of sp. gr. 1.12), the solution then somewhat diluted with water, and an equivalent amount of sodium nitrite (100 c.c. of a solution containing 65.8 g. per liter), added. This was

[1] Cain and Nicoll: J. Chem. Soc., **81**, 1412 (1902).
[2] Cain and Nicoll: J. Chem. Soc., **83**, 206 (1903).
[3] Cain and Nicoll: J. Chem. Soc., **83**, 470 (1903).
[4] Cain: Ber., **38**, 2511 (1905).
[5] Lamplough: Proc. Camb. Phil. Soc., **14**, 580 (1908).
[6] Cain and Nicoll: J. Chem. Soc., **81**, 1412 (1902).

carried out at 0° and the whole diluted to 1000 c.c. The resulting solution contained 12.46 g. of diazo-benzene chloride, and for every mol of this substance one mol of sodium chloride and one of hydrogen chloride.

The inorganic salts used were the purest obtainable, and no attempt was made to purify them.

The gelatin used was obtained from the Eastman Kodak Co., and was of the grade known as "de-ashed isoelectric gelatin, purified by electro-dialysis."

The dextrin and egg-albumin were obtained from Merck and Co.

*Apparatus and Methods*—Specially designed reaction vessels, having a capacity of about 80 c.c. were used. Thirty c.c. of the diazo solution were pippetted into these flasks and diluted to forty c.c. with water or with a solution of the substance whose effect upon the reaction was being investigated. The flasks were then suspended in a thermostat by means of a specially-designed shaking device, and connected by means of capillary tubing to the gas burettes. The burettes were of 100 c.c. capacity, provided with leveling tubes, and also supported in the same thermostat, which was provided with a plate glass window. The reaction was allowed to proceed until the reacting solution had attained the temperature of the thermostat (usually 10 or 12 minutes) after which the "zero" reading on the burettes was recorded. At definite time intervals, measured by a stop-watch, the volume of nitrogen evolved was recorded. The reaction was considered to be ended and the final volume recorded when, after one hours time, the volume suffered no change. If during an experiment the barometric pressure underwent any appreciable change, appropriate corrections were applied.

From the data so obtained, the values of A and x in the equation

$$K = \frac{1}{t} \ln \frac{A}{A-x}$$

were calculated and substituted in the equation. For convenience. the value $K_s$, which is $0.4343\ K \times 10^4$, will be used in this paper. As an illustration, the sample data sheet given in Table I will serve.

TABLE I

The Decomposition of Diazo-benzene Chloride at 40°.

| Time in minutes | Burette Reading | x | A-x | $K_s$ |
|---|---|---|---|---|
| 0 | 20.5 | 0 | 67.3 | |
| 4 | 26.8 | 6.3 | 61.0 | 107. |
| 9 | 34.0 | 13.5 | 53.8 | 106. |
| 15 | 41.3 | 20.8 | 46.5 | 107. |
| 20 | 46.7 | 26.2 | 41.1 | 107. |
| 30 | 55.7 | 35.2 | 32.1 | 107. |
| 40 | 62.6 | 42.1 | 25.2 | 107. |
| 50 | 68.1 | 47.6 | 19.7 | 107. |
| 60 | 72.6 | 52.1 | 15.2 | 107.5 |
| End | 87.8 | 67.3 | | |
| | | | Mean | 107.0 |
| | | | Duplicate | 107.1 |

*Order of the Reaction and Temperature Coefficient*—The data of Table I will also serve to confirm the results of previous investigators in regard to the order of the reaction. The excellent constancy of $K_s$ as calculated from the equation for a monomolecular reaction indicates that the reaction is apparently monomolecular. It may be noted, however, that if the reaction which is being measured were bimolecular the constants calculated by this method would still appear monomolecular due to the fact that one of the reactants (water) is present in large excess. The values obtained for the temperature coefficient of this reaction are in perfect accord with those obtained by Lamplough.

*The Effect of Various Soluble Salts*—In an attempt to find a catalyst (more especially a negative catalyst) for this reaction, the rate of decomposition of diazo-benzene chloride was followed in the presence of a number of foreign substances. In each case, either 10 c.c. of a saturated solution, or 10 c.c. of a solution containing 2 g. of the foreign substance were added to 30 c.c. of the diazo solution, and the rate followed as before. Table II gives the results obtained.

TABLE II

The Effect of Foreign Substances upon the Velocity of Decomposition of Diazo-benzene Chloride.

| Added Substance | $K_s$ at 40° | Added Substance | $K_s$ at 40° |
|---|---|---|---|
| KCl | 106.5 | Na Citrate | 172. |
| $K_2SO_4$ | 105. | K Oxalate | 108. |
| $KNO_3$ | 104. | $Na_2B_4O_7$ | 108. |
| Na Formate | 105. | $KBrO_3$ | 85. |
| Na Succinate | 172. | KBr | 108. |
| $AlCl_3$ | 106.4 | $AsCl_3$ | 114. |
| $FeCl_3$ | 110. | $SbCl_3$ | 105. |
| $NiCl_2$ | 103. | $MgCl_2$ | 106. |
| $CoCl_2$ | 102. | $AuCl_3$ | 104. |
| $CuCl_2$ | 104. | $FeCl_2$ | 101. |
| $CdCl_2$ | 101. | $CeCl_2$ | 103. |
| $MnCl_2$ | 103. | $NH_4CNS$ | 110. |
| $HgCl_2$ | 105. | $VCl_3$ | 105. |
| $ZnCl_2$ | 106. | Glycerine | 106. |
| $SrCl_2$ | 106. | Strychnine | 103. |
| $CaCl_2$ | 106. | Quinine | 102. |
| LiCl | 100. | Morphine | 104. |
| $BiCl_3$ | 102. | Papaverine | 106. |
| $CrCl_3$ | 102. | $Na_2HPO_4$ | 270.—188. |
| $PtCl_4$ | 101. | $(NH_4)_6Mo_7O_{24}$ | 22.0 |

It is evident that of the foreign substances introduced, very few have any marked effect upon the velocity constant. Sodium phosphate, sodium succinate, and sodium citrate cause abnormal constants by increasing the extent to which "coupling reactions" take place. Diazo-benzene chloride reacts with phenol with the formation of a dye in the presence of these substances, which results in a decrease in the concentration of the diazo-benzene chloride without a corresponding increase in the volume of nitrogen. This is evidenced by the deep color developed by the reaction mixture, and by the fact that from one half to one third of the diazo nitrogen is not evolved from the solution.

Ammonium molybdate, as the value in Table II indicates, exerts a marked retarding effect upon the velocity of the decomposition. The effect was found to be dependent upon the concentration of the molybdate and upon the concentration of the hydrochloric acid present. The retardation is offset by increasing the concentration of hydrochloric acid. Table III shows the relation which exists between these three factors, and the results are illustrated graphically in Figure 1.

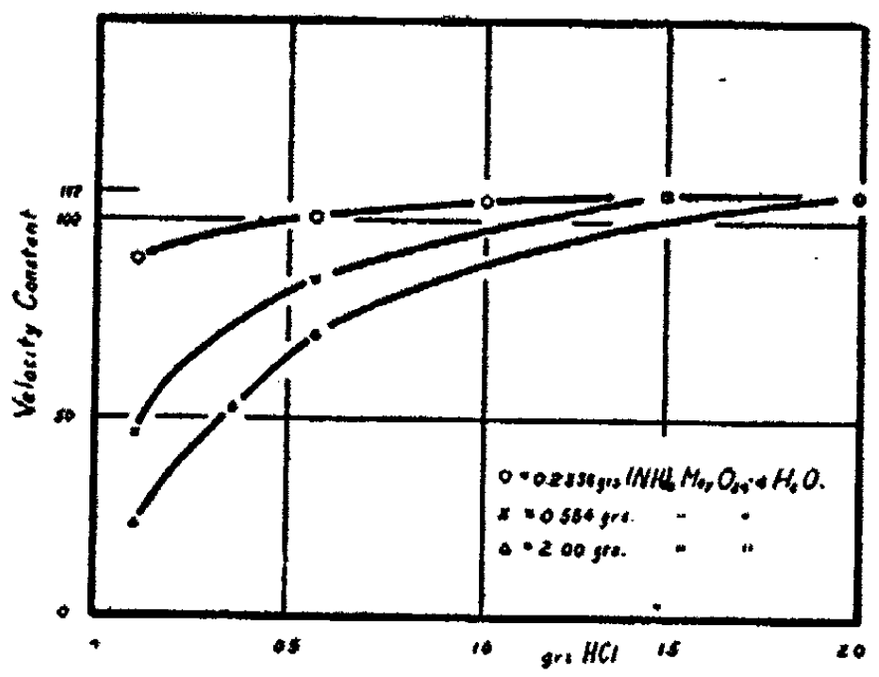



FIG. 1

Such a relation indicates the formation of a diazo-benzene molybdate which is more stable than the chloride. In the presence of molybdic acid, the diazo-chloride would react to form the diazo-molybdate just as sodium chloride under the same circumstances would react to form sodium molybdate, the sodium and diazonium salts having been shown to be very similar as to their behavior in solution.[1] The extent to which the molybdate is formed will obviously depend upon the relative concentrations of molybdic and hydrochloric acids present. If the diazo-molybdate is much more stable than the chloride, the observed relation between velocity constant, molybdate concentration, and hydrochloric acid concentration is explained.

[1] Hantzsch: Ber., **28**, 1740 (1895); Hantzsch and Danziger: **30**, 2529 (1897); Hantzsch and Davidson: **31**, 1612, (1898).

TABLE III

The Decomposition Velocity of Diazo-benzene Chloride in the Presence of Ammonium Molybdate and Hydrochloric Acid at 40°

| grams of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ | grams of HCl | $K_s$ |
|---|---|---|
| 0.2336 | 0.0132 | 90.0 |
| 0.2336 | 0.5722 | 101. |
| 0.2336 | 1.0412 | 105.7 |
| 0.2336 | 1.5100 | 107.6 |
| 0.5840 | 0.0132 | 45.4 |
| 0.5840 | 0.5722 | 85.0 |
| 0.5840 | 1.5100 | 107.0 |
| 2.00 | .00132 | 22.5 |
| 2.00 | 0.3540 | 53.7 |
| 2.00 | 0.5722 | 71.0 |
| 2.00 | 2.00 | 106.8 |

Several attempts were made to prepare a solution of pure diazo-benzene molybdate and to determine the stability of such a solution. These were unsuccessful because of the insolubility of molybdic acid, and, as Krause and Krauskopf[1] have demonstrated, the extreme ease of hydrolysis of aniline molybdate in water solution and its extreme insolubility in organic solvents such as alcohols, acids, etc. Diazo-molybdates derived from certain other amines have, however, been prepared.[2]

*The Effect of changing the Viscosity of the Solvent*—The fact that the decomposition of diazo-benzene chloride in water solution is a homogeneous reaction involving the liberation of a gas from a liquid, led to a study of the effect of the viscosity on the rate of the reaction. Very concentrated solutions of calcium and magnesium chlorides were used to increase the viscosity of the medium in which the reaction takes place. The diazo solution was made more concentrated than before and diluted to the same concentration as that

TABLE IV

The Effect of Viscosity of the Solution upon the Velocity of the Reaction of Diazo-benzene Chloride with Water at 40°

| Added Substance | Conc. of Added Subst. in g. per liter | Relative Viscosity | $K_s$ |
|---|---|---|---|
| None | | 1.192 | 107.0 |
| $MgCl_2$ | 281.25 | 1.828 | 100.8 |
| $MgCl_2$ | 375.0 | 2.238 | 95.2 |
| $MgCl_2$ | 468.75 | 2.798 | 89.7 |
| $CaCl_2$ | | 2.130 | 91.2 |
| $CaCl_2$ | | 5.045 | 71.0 |
| $CaCl_2$ | | 9.180 | 59.7 |

[1] Krause and Krauskopf: J. Am. Chem. Soc., 47, 1689 (1925).
[2] Morgan and Alcock: J. Chem. Soc., 95, 1319 (1909).

previously used by addition of varying amounts of these solutions of calcium and magnesium chlorides and water. In the accompanying graph (Fig. 2), $K_s$ at 40° is plotted against the relative viscosity of the reaction mixture. The results are also collected in the following table.

An examination of the data will show that increase in viscosity, whether produced by the addition of calcium chloride or magnesium chloride, causes a decrease in $K_s$. The magnitude of this decrease is, however, not the same in the two cases. It is evident then, that the increase in viscosity is not the only factor involved. Indeed, it may not be one of the factors, although the similarity in the general trend of the two curves indicates that viscosity is in part responsible for the retardation in velocity.

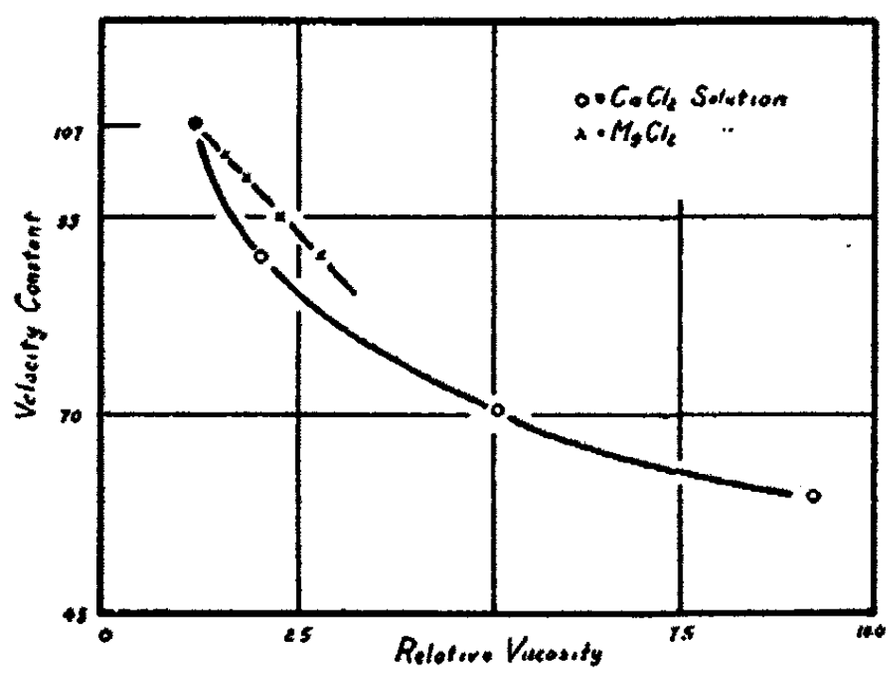



FIG. 2

*The Effect of Certain Colloids*—A recent paper by Findlay and Thomas[1] indicates that the kinetics of reactions involving the liberation of a gas from a solution cannot be studied by the gasometric method in the presence of colloids because of the protective action which these colloids exert upon the minute colloidal gas bubbles formed during such reactions. Certain colloids inhibit the coagulation of these colloidal gas bubbles and consequently affect the rate at which the gas is liberated from solution. Solutions of the colloids used by Findlay and Thomas were prepared, and their effect upon the decomposition of diazo-benzene chloride in aqueous solution determined. From Table V, it is evident that these colloids have no effect upon the rate at which nitrogen is liberated from the solution.

[1] Findlay and Thomas: J. Chem. Soc., **125**, 1244 (1924).

TABLE V

The Effect of Colloids upon the Velocity of the Decomposition of Diazo-benzene Chloride

| Temp. | Added Colloid | $K_s$ |
|---|---|---|
| 30° | None | 25.0 |
| " | 2% Gelatin | 25.0 |
| " | 1% Gelatin | 25.0 |
| " | 0.5% Gelatin | 24.5 |
| 30° | 0.01% Gelatin | 25.0 |
| 40° | None | 107.0 |
| " | 2% Dextrin | 107. |
| " | 1.5% Dextrin | 105. |
| " | 1.0% Dextrin | 108. |
| " | 2.5% Starch | 109. |
| " | 1.5% Starch | 109. |
| " | 2% Agar | 104. |
| " | 1% Agar | 104. |
| " | 2% Egg Albumin | 105. |
| " | 1% Egg Albumin | 106. |

## Discussion of Results

The reaction of diazo-benzene chloride with water is a remarkable one in that a catalyst has not been found that will either increase or decrease the rate at which the reaction proceeds.

That there is no quantitative relation between the viscosity of the medium in which the reaction takes place and the velocity of the reaction is not surprising. Several investigators have brought forward evidence that the viscosity of the medium may be a factor in determining the speed of a reaction. Buchböck,[1] in studying the rate of hydrolysis of carbonyl sulfide in neutral salts solutions, pointed out that the greater the viscosity of the solution, the greater the retarding effect. He later repeated the work,[2] and concluded that the velocity of the decomposition of thiocarbonic acid is inversely proportional to the viscosity of the solution. According to Raschig,[3] who investigated the reactions of monochlor amine in ammoniacal solution, the velocity of the reaction involving the evolution of nitrogen can be suppressed by substances that increase the viscosity, and increased by those that decrease the viscosity of the solution. On the other hand Arrhenius[4] found the velocity of inversion of cane sugar to be accelerated by the addition of salts which both raise and lower the viscosity, and Reformatski[5] found the velocity of hydrolysis of methyl acetate was not influenced by high concentrations of gelatin or agar

[1] Buchböck: Z. physik. Chem., 23, 123 (1897).
[2] Buchböck: Z. physik. Chem., 34, 229 (1900).
[3] Raschig: Verh. Ges. Naturforscher, 2 I, 120 (1907).
[4] Arrhenius: Z. physik. Chem., 36, 284 (1888); 28, 317 (1899).
[5] Reformatski: Z. physik. Chem., 7, 34 (1891).

agar. Bohnson,[1] in a study of the decomposition of hydrogen peroxide by sodium iodide in mixed solvents, concluded that whatever relation there may be between viscosity of the solvent and velocity of reaction it is quite overbalanced by other and greater influences.

The fact that there is no quantitative relation between the viscosity of the calcium chloride and magnesium chloride solutions and the rate at which diazo-benzene chloride decomposes in them, indicates that here too, other influences are involved. Both salts are known to be highly hydrated in solution. Sulfuric acid has been shown to retard the velocity of the decomposition when present in high concentration. The dehydrating action of these two salts may be, either wholly or in part, responsible for the observed retardation.

Findlay and Thomas[2] followed the decomposition of hydrogen peroxide by iodide ion in the presence of gelatin, starch, dextrin, albumin, and peptone by two methods. The results obtained by the titration of hydrogen peroxide with permanganate showed these colloids have no effect upon the velocity of the decomposition. When the reaction was followed by the gasometric method however, all of these colloids appeared to retard the velocity. Since they have no effect upon the velocity of the chemical reaction involved, as shown by the titrimetric method, they must affect the rate at which gas is liberated from the solution. That is, in the case of a reaction involving the liberation of a gas, and taking place in homogeneous solution, they conclude that the velocity of the chemical reaction can be determined from the volume of gas evolved only when no colloids are present in the reaction mixture. They also followed the decomposition of nitrosotriacetonamine by hydroxyl ion by the gasometric method, and found similar retarding effects in the presence of the same colloids. This compound decomposes into phorone and nitrogen. The gas liberated in this case is the same as that liberated in the decomposition of diazo-benzene chloride. If the retardation of the decomposition of nitrosotriacetonamine catalyzed by hydroxyl ions in the presence of colloids is a matter of the protective action of the added colloid, the same effect should be observed in the decomposition of diazo-benzene chloride. Such is not the case, the reaction velocity being entirely independent of the added colloid.

## Summary

(1). The effect of a number of foreign substances upon the velocity of the decomposition of diazo-benzene chloride with water has been determined. A catalyst for the reaction has not been found.

(2). Evidence has been obtained in favor of the fact that diazo-benzene molybdate solutions are much more stable than those of the chloride, nitrate, sulfate, etc.

---

[1] Bohnson: J. Phys. Chem., **24**, 677 (1920).
[2] Findlay and Thomas: J. Chem. Soc., **125**, 1244 (1924).

(3). The effect of altering the viscosity of the medium in which the reaction takes place has been studied. There is no apparent relation between the viscosity of the medium and the velocity of the decomposition.

(4). The colloids gelatin, dextrin, starch, agar, and egg albumin have been found to affect in no way either the velocity of the reaction or the rate at which evolution of the gas bubbles takes place from such solutions.

*Madison,*
*Wisconsin.*

# STUDIES IN PHOTOCHEMICAL TECHNIQUE. PART III

## The Quartz Mercury Lamp in Use

BY P. W. CUNLIFFE, R. G. FRANKLIN, R. E. W. MADDISON AND L. REEVE

The use of the quartz mercury lamp in this laboratory, extending over a period of several years, has resulted in a collection of data which is now presented primarily to illustrate the points discussed in the previous papers of this series.[1]

The technique of the measurement of energy distribution has already been described in the second paper, and it appears necessary only to state that the burners employed were all made by the Hewitt Electric Co., London. The working conditions and ages of the lamps are given in Table I, while the percentage of the total radiation emitted by each line in the wave length range examined, namely, 248$\mu\mu$-579$\mu\mu$, is recorded in Table II.

Although the mercury spectrum contains lines of shorter wave length than 248$\mu\mu$, the spectrometric apparatus which was used did not give any certain indication of their presence. A consideration of the optical system shows that this could not be due to the quartz whose absorption in the ultra-violet is inappreciable for wave lengths greater than 220$\mu\mu$. The mirror incorporated in the spectrometer, however, possesses marked absorption in this region of short wave length, (see graph in second paper of this series p. 724) and to this may partly be attributed the non-detection of these lines. With a perfectly new lamp any slight indication of the lines disappeared after about 50 hours burning. (cf. Part 1 of this series, p. 54.)

It has been stated in an earlier paper that the radiation passing a 1 cm. quartz-water cell in the region 579$\mu\mu$-1400$\mu\mu$ is considerable (see figures quoted in Part II. p. 726.) but as the means for carrying out the necessary measurements were, unfortunately not available, the energy distribution measurements are to this extent incomplete, and cease with the yellow line at 579$\mu\mu$.

Considering the results given in the tables, it is seen that the intensity of the short ultra-violet radiation, 289$\mu\mu$-248$\mu\mu$, is considerably reduced during the first 500 hours of the life of the lamp. (For example, the lamps 2d, 5, 6 and 7 of Table II.) While this loss is not as rapid with the lines below 248$\mu\mu$, it is sufficiently great to necessitate a redetermination of the energy distribution every 200 hours (say) when quantitative work is carried out in this region. (cf. Part I, p. 55.) The valuable property of the mercury arc as a radiator of short wave lengths is thus attended by this inconvenience, but pending the discovery of a more permanent source it would appear that its continued use is necessary, proper precautions being observed.

An interesting result, which has since been confirmed, is presented by Lamp 2, which was accidentally broken after being in use for about 500 hours.

[1] J. Phys. Chem., 29, 39, 713 (1925).

TABLE I

| Lamp No. | Measurement | Pattern of Lamp | Age | Volts | Amps | Diam of Diaphgram | Remarks |
|---|---|---|---|---|---|---|---|
| 1. | a. | Straight | New | 64.5 | 3.7 | 1 cm. | Two lenses and water screen in front of spectrometer |
| | b. | " | 35 hrs. | 74 | 3.7 | 1 cm. | (ditto) |
| | c. | " | Immediately after b. | 73 | 3.75 | Not used | Bull burner placed immediately in front of spectrometer slit; no lenses and no water screen |
| 2. | a. | Old bulb pattern. | | 66-70 | 3.8 | " | (ditto) |
| | b. | " | | 70 | 3.75 | 1.8 cm. | Disposition as in 1a |
| | c. | " | 500 h. from first use. | 72 | 3.7 | | Lamp broken after 500 h.: repaired and E. D. then taken |
| | d. | " | 1000 h. from first use. | 72 | 3.7 | | |
| 3. | a. | Straight | 20 hrs. | 130 | 4.5 | Not used | Disposition as in 1a |
| | b. | " | 50 hrs. | 146.5 | 4.6 | " | (ditto) |
| 4. | | " | Almost new | 62 | 4.2 | | |
| 5. | | " | 1100 hrs. | 66 | 4.2 | 1 cm. | " |
| 6. | | " | 550 hrs. | 66 | 4.4 | " | " |
| 7. | a. | U-pattern | 12 hrs. | 146 | 2.0 | " | " |
| | b. | " | 146 hrs. | 146 | 2.0 | " | " |

TABLE II

| Wave Length | Measurement No. 1a. | 1b. | 1c. | 2a. | 2b. | 2c. | 2d. | 3a. | 3b. | 4. | 5. | 6. | 7a. | 7b |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 248 | 2.3% | 2.4% | 3.0% | 2.1% | 1.9% | 0.9% | — | 1.3% | 1.7% | 0.5% | — | — | 1.6% | — |
| 254 | 6.6 | 4.6 | 5.6 | 4.3 | 3.5 | 2.2 | 1.1 | 3.6 | 3.2 | 2.7 | 1.85 | 2.1 | 3.9 | 2.7 |
| 257 | 0.9 | 0.8 | 0.8 | 0.7 | 1.0 | — | — | 0.3 | — | — | — | — | — | — |
| 265 | 3.9 | 3.3 | 4.5 | 4.4 | 4.2 | 1.9 | 1.1 | 2.9 | 2.7 | 2.4 | 1.75 | 1.5 | 3.1 | 2.4 |
| 270 | 0.6 | 0.6 | 0.7 | 0.7 | 0.7 | 0.5 | 0.3 | 0.4 | 1.0 | 0.5 | — | — | — | — |
| 275 | 0.5 | 0.4 | 0.4 | 0.2 | 0.2 | 0.3 | 0.3 | 0.3 | 0.3 | 0.2 | — | — | — | — |
| 280 | 1.8 | 1.5 | 2.0 | 1.3 | 1.1 | 1.0 | 1.1 | 1.6 | 1.4 | 1.4 | — | 1.3 | 1.9 | trace |
| 289 | 0.3 | 0.2 | 0.3 | 0.3 | 0.3 | 0.8 | 0.6 | 0.4 | 0.4 | 1.2 | — | — | 1.0 | trace |
| 297 | 1.7 | 1.4 | 2.1 | 1.9 | 1.7 | 1.8 | 1.1 | 2.2 | 2.2 | 2.2 | 1.6 | 1.9 | 2.8 | 2.1 |
| 303 | 4.3 | 4.5 | 5.6 | 5.4 | 5.2 | 5.0 | 2.9 | 3.9 | 4.1 | 5.6 | 2.75 | 4.1 | 5.5 | 4.8 |
| 313 | 11.3 | 8.6 | 10.8 | 11.2 | 10.2 | 13.4 | 8.1 | 8.2 | 9.2 | 14.5 | 6.9 | 7.8 | 12.1 | 10.7 |
| 334 | 1.0 | 1.1 | 1.3 | 1.3 | 1.1 | 0.6 | 0.5 | 1.0 | 1.8 | 0.6 | 1.1 | 1.1 | 1.7 | 1.3 |
| 365 | 18.4 | 18.8 | 21.5 | 22.3 | 18.6 | 19.5 | 19.8 | 21.9 | 20.4 | 22.1 | 18.0 | 19.1 | 18.6 | 19.1 |
| 405 | 7.1 | 6.9 | 6.5 | 7.9 | 7.4 | 7.8 | 8.7 | 7.3 | 7.7 | 7.5 | 7.8 | 6.9 | 7.7 | 8.8 |
| 435 | 12.2 | 12.9 | 11.8 | 13.6 | 14.7 | 14.5 | 16.5 | 10.9 | 11.0 | 11.3 | 15.1 | 15.2 | 10.6 | 12.4 |
| 546 | 12.9 | 14.4 | 10.4 | 11.9 | 14.6 | 14.9 | 18.8 | 14.6 | 15.0 | 12.9 | 22.1 | 20.6 | 14.6 | 18.1 |
| 579 | 14.0 | 17.2 | 12.5 | 10.3 | 13.4 | 14.9 | 18.8 | 18.7 | 17.8 | 14.1 | 21.0 | 18.5 | 14.9 | 18.1 |

The lamp was repaired by a process involving the heating of the whole burner in a furnace, and identical with that employed in the manufacture of a new lamp. The energy distribution 2c was taken immediately after the repair of the lamp, that is 500 hours from its first use, and again 500 hours after repair, or 1000 hours from its first use. The figures in 2c contain higher values for the ultra-violet and indicate that the lamp was behaving like a new one, although actually 500 hours old; while the figures in 2d are about normal for a lamp 1000 hours old. The treatment received by the lamp during the repair thus gave a temporary rejuvenation but did not increase its life beyond the normal. For this lamp the percentage decrease in the intensity of the lines has already been given. (Part I. p. 54.)

It may be stated that the usefulness of the mercury lamp does not diminish uniformly, and the time when it may be said to be of no further value for photochemical purposes arrives suddenly. An approximation to the useful life of a lamp is 1000 hours, but occasionally one will last longer, as is seen with Lamp 5 which lasted about 1400 hours. As the burner ages, the silica tube connecting the two electrodes become coated with a brown film, which has been attributed to various causes, e. g., the disintegration of the electrodes. Recently it has been stated[1] that the film disappears and the full activity of the lamp may be restored by heating the tube in a Bunsen flame. The production of this film undoubtedly influences the intensity of the radiation emitted by the lamp and it would be of interest to determine the effect of the heat treatment on the energy distribution and on the total energy.

The change in the energy distribution of one lamp (No. 4), produced by an increase in the power consumed is shown in the following table.

TABLE III

| Wave length | Relative intensity with applied voltage of | |
|---|---|---|
| | 62 volts | 65 volts |
| 365 | 100 | 100 |
| 546 | 85.2 | 92 |
| 5F9 | 85.2 | 95.7 |

(There was no material change in amperage)

The remainder of the lines were hardly altered either in relative or un absolute intensity, the whole effect being in agreement with that previously observed.

An idea of the absolute magnitude of the energy in a beam from the quartz mercury lamp may be gathered from the following table which refers to Lamp 2c, disposed as described in Part II (pp. 715-724 and Figs. 1 and 6b) and burning under the conditions given in Table I.

[1] Baker and Carlton, J. Chem. Soc., **127**, 1922 (1925).

The figures are for the energy in the beam emerging from the water cell.

TABLE IV

| Aperture before lamp | Intensity |
|---|---|
| 1.8 cms. | 21.57 H.K. |
| 1.4 " | 17.73 " |
| 1.0 " | 11.63 " |

One of the objects in presenting the data in this paper is to give a general idea of the magnitude to be expected in the energy values of definite wave lengths in the radiation from the quartz mercury arc lamp. The individuality of the lamps and the importance for quantitative photochemical work of accurately determining in absolute units (ergs per sq. cm. per sec) the intensity of a given wave length with the lamp burning under well defined conditions are emphasised.

The authors gratefully acknowledge the helpful criticism and advice given by Prof. A. J. Allmand, M.C., D.Sc. under whose direction the work was carried out. One of us (P. W. C.) acknowledges his indebtedness to the British Cotton Industry Research Association for the award of a bursary, and the others similarly acknowledge the grants made them by the Advisory Council of the Department of Scientific and Industrial Research.

*University of London,*
*King's College.*
*July 27, 1926*

## NEW BOOKS

**The Kinetics of Chemical Change in Gaseous Systems.** *By C. N. Hinshelwood. 24×16 cm; pp. 204. New York and London: Oxford University Press, 1926. Price: $4.25.* The author has "sought to give a continuous account of those phenomena of chemical change which offer some prospect of interpretation in terms of the kinetic theory." The book is therefore confined to the kinetics of gaseous reactions whether homogeneous or occurring at the surfaces of solids or liquids. The treatment is brief but it is wonderfully logical and crystal clear. The author is to be congratulated on the attainment of his objective, a "true perspective of the whole field of inquiry."

The introductory chapter outlines the chief conclusions from the kinetic theory pertinent to gaseous reactions, root mean square velocity, mass of gas striking unit area in unit time, distribution of speeds, collision number and free path, size of gas molecules. It discusses types of motion as revealed by heat capacity data, the failure of classical theory and the postulates of quantum theory to account for the failures. The chapter concludes with a general discussion of the nature of chemical union and of the exceptional condition which molecules are capable of assuming under the influence of varying agencies. "It is seen to be probable that, before a molecule can undergo chemical change involving the formation of non-polar linkages, energy must be communicated to it either by collision or by radiation. This is called activation. . . . Where a simple rearrangement of polar linkages occurs, no activation can be needed. . . . A reaction between hydrochloric acid and sodium thiosulphate is not truly ionic . . . because there is formation of free sulphur and this process necessitates the rearrangement of non-polar linkages within the thiosulphate ion itself."

In the second chapter the distinguishing characteristics of homogeneous bimolecular reactions are displayed. The dependence of time of half change on the concentration is chosen as the principal criterion and linear variation of log k with 1/T is displayed in both homogeneous and heterogeneous reactions. The molecular statistics of bimolecular processes are set forth and the ratio of effective collisions to total collisions is set equal to $e^{-E/RT}$, whence E is calculable and is shown to be identical with the value obtained from the Arrhenius equation, $d \log k/dt = E/RT^2$. These several features are illustrated with six homogeneous bimolecular gas reactions. Photochemical kinetics are introduced to show how they lead to the newer work of Bodenstein and his colleagues on the kinetics of collision between bromine atoms, and on the thermal decomposition of phosgene which apparently involves collision of phosgene with chlorine atoms. The formation of hydrogen bromide, thermally and photochemically, apparently both involve the same sequence of changes.

The general theory of energy of activation is discussed in Chapter III. It is concluded that "it is possible to account for the rate of bimolecular reactions quantitatively by assuming that the collision process is the actual activating process and that the kinetic energy of the molecules is transformed at the moment of collision to internal energy of vibration or energy corresponding to a higher quantum state of electrons. . . . It can equally well be assumed that the molecules are activated before collision by radiation or by collisions which have not led to reaction, and it is not possible to tell definitely which methods of activation are actually operative. We require data of greater accuracy and more information about the influence of orientation of the colliding molecules or the effectiveness of the impact. . . . The best proof of the real significance of the energy of activation lies in the demonstration of the fact that the higher the activation energy, the higher is the temperature necessary for the attainment of a given rate of change.

Termolecular reactions are few and it is shown (Chap. IV) that their energy of activation must be small. Since the publication of this volume, Hinshelwood and Hutchinson have added one example to the sole example of a unimolecular reaction discussed in Chap. V, namely the decomposition of nitrogen pentoxide. The new reaction is the decomposition of acetone. The authors think that they have measured the rate of its dissociation into $CO + 2(CH^3)$. There is a possibility that they have really measured the rate of thermal

decomposition of ketene. The principal interest of this new example is that it strengthens the argument in Chapter V which attempts to show that activation by collision is about $10^6$ times too slow for the unimolecular process and also that a monochromatic radiation theory is inadequate to explain such unimolecular processes. Hinshelwood concludes that some extended radiation theory is necessary or that reaction chains are possible.

An extended discussion of the adsorption theory of gas kinetics at surfaces is given in Chapter VI. The form in which it is developed is essentially that of Langmuir, the concept of a saturation adsorption, with the extension to the cases in which the adsorbing surface is not homogeneous and in which different types of adsorption may be involved. He demonstrates, with a convincing list of examples, how the apparent order depends on the extent of adsorption of the reactants and on the desorption of the products and shows how the true order can be learned. As an example of $2A \longrightarrow A_2$, for which (p. 147) he says a particular case has not been discovered, it may be pointed out that Langmuir found that the combination of hydrogen atoms in contact with a heated wire was bimolecular.

The final chapter is devoted to activation in heterogeneous reactions. The temperature coefficient here gives only the apparent energy of activation. Hinshelwood shows that the true energy of activation is related to this apparent value by the expression

$$E_{app} = E_{true} + \lambda' - \lambda$$

where $\lambda'$ is the energy of desorption of the products and $\lambda$ is the energy of adsorption. He concludes, erroneously, from the early data of Taylor and Burns that $\lambda$ will generally be small compared with E. The newer data of actual measurements of Taylor and Burns are showing that, in catalysed processes, these are frequently of the same order of magnitude as E and such data are giving quantitative bases for the explanation of catalytic mechanism. Hinshelwood's concept of a particular unstable phase for decomposing formic acid moecules (pp. 182-183) is unnecessary if we assume that all oxide catalysts are dual in nature having positive ions as dehydrogenation catalysts and negative ions as the loci of dehydration change. The book concludes with a consideration of the nature of the action of surfaces, firstly in respect to non-uniformity, next as to spatial configuration and as to orientation of adsorbed molecules and finally as to the nature of the change induced in the reactant by its association with the catalyst. The author thus brings us to the point where "the stream of inquiry divides into several parallel channels which have not yet been explored to their confluence." To all those who would embark on such a voyage of exploration this volume is an indispensable portion of the kit. It could very profitably be read by all students of physical chemistry.

*Hugh S. Taylor*

**Concerning the Nature of Things.** *By Sir William Bragg. 21 + 15 cm; pp. xvii+249. New York and London: Harper and Brothers, 1925. Price: $3.00.* This is an American edition of the Christmas Lectures given at the Royal Institution in 1923-24. These popular lectures for the young are done very well in England. We have nothing corresponding to them and consequently very few people who could do them because such lectures are not easy to give. The individual lectures are entitled: the atoms of which things are made; the nature of gases; the nature of liquids; the nature of crystals (3)-diamond, ice and snow, metals.

"I have said that all atoms are in motion, and that there is a constant struggle between some form of attractive force which would draw all the atoms together and this motion which would keep them independent. The existence of an attractive force which we here take into account as something very important does not at first seem to be reconcilable with the atomic structure we have just considered, because in this we supposed that the outer shells of electrons would prevent the atoms from coming too close to one another. It is a difficult point, because both views are certainly correct. It is, no doubt, our present ignorance of the nature of these forces that prevents us from arriving at a clear understanding. We have seen how it can happen that when two atoms approach each other at great speeds they go through each other, while at moderate speeds they bound off each other like two billiard balls. We have to go a step further, and see how, at very slow speeds of ap-

proach, they may actually stick together. We have all seen those swinging gates which, when their swing is considerable, go to and fro without locking. When the swing has declined, however, the latch suddenly drops into its place, the gate is held, and after a short rattle the motion is all over. We have to explain an effect something like that. When the two atoms meet, the repulsions of their electron shells usually cause them to recall; but if the motion is small and the atoms spend a longer time in each other's neighborhood, there is time for something to happen in the internal arrangements of both atoms, like the drop of the gate-latch into its socket, and the atoms are held. It all depends on some structure of the atom which causes a want of uniformity over its surface, so that there is usually a repulsion; but the repulsion will be turned into attraction if the two atoms are allowed time to make the necessary arrangements, or even if at the outset they are presented to each other in the right way. We shall see later several very interesting examples of this effect," p. 48.

"There are three stages in the arrangements of matter: the single atom as we find it in helium gas; the molecule as it is studied by the chemist; and the crystal unit which we now examine by X-ray analysis. To take an example, there are the *atoms* of silicon or of oxygen. The *molecule* of silicon dioxide contains one unit of silicon and two units of oxygen, arranged, no doubt, in some special way. Lastly, there is the substance quartz, of which the *crystal unit* consists of three molecules of silicon dioxide, arranged, again, in a special fashion which we now know has a certain screw-like character. The quartz crystal contains an innumerable multiplication of these units. Each of the units has all the properties of quartz, and, in fact, is quartz; but a separate molecule of silicon dioxide is not quartz. For example, one of the best known properties of quartz is its power of rotating the place of polarization of light, and this property is associated with the screw which is to be found in the crystal unit. It takes three molecules to make the screw," p. 134.

"Ice when it forms quietly on a water surface exposed to the sky crystallizes in a form analogous to that of the snow crystal, all the six-sided figures being horizontal. That it does so is not generally very obvious, though in books on Arctic exploration pictures are to be found of table ice breaking up into six-sided vertical columns, like the basalt columns of the Giant's Causeway. It is also said that when the ice on a lake breaks up, it first divides into vertical columns, which for a time hold one another up; when, however, the ice begins to move, the collapse is rapid and the lake clears quickly.

"In the accounts given by Antarctic explorers, it is especially mentioned that the ice on fresh-water lakes was found to be divided into six-sided prisms, all standing upright on the surface. The planes of separation were marked by lines of air bubbles. On the sea ice the formation of the crystals led to an expulsion of the salt which was deposited in the spaces between the crystals, and sometimes squeezed out above the top surface. The prisms were free from salt inside, and fairly fresh water could be obtained if the outside layers were first melted off. They were clear crystals, through which an observer might look at the rocks underneath as through tubes," p. 182.

"In the case of the cube there are four ways of thinking of the arrangement of the layers; there is a layer perpendicular to each diagonal of the cube, and, as a cube has four diangonals, there are four sets of layers. This does not mean that the atoms in any one layer are specially tied together in that layer; merely that one can sort out the atoms of the crystal into this kind of layer in four different ways.

"Now it turns out that these layers are of very great importance in respect to the properties of the metal crystals built on the close-packed cubic plan. Gold, silver, copper, aluminium, and other metals like them can be drawn into wires, rolled into sheets, and beaten into various shapes. They are, as we say, ductile, and their ductility is one of the characteristics that make them so useful. They can be bent and pulled into all sorts of convenient forms. It seems possible to make a metal flow like treacle. Gold can be hammered into leaves so thin that the metal in a sovereign will cover a large field: the others can be beaten nearly as thin. Cups and vessels of all sorts, chains and ornaments, and innumerable useful things are made by taking advantage of this singular property of ductility. The first thing that we should like the X-ray to explain for us more clearly, if we can make them do

so, is that feature in their structure which accounts for this most valuable property. We should also like to understand the inner meaning of the hardening and other changes that are due to 'cold-working,' as it is called—that is to say, to hammering or straining the metal when it is cold. And what is annealing, the softening and relief from strain that heat brings about? Why are all these things so obvious in the case of a metal, while they do not appear in, for instance, diamond or rock salt or quartz?"

"Gold leaf is very thin, as we have seen. It is even transparent, but it absorbs part of the spectrum of light that passes through it, allowing a greenish light to filter through. It is yellow when viewed by reflected light, as we know. It is very curious that when it has been heated to a dull red it becomes permanently transparent, and white by reflected light. Faraday was very interested in this fact; he suggested as a partial explanation that the thin layer of gold broke up, the metal gathering itself together in little heaps, and that the light went through the holes that were left. Sir George Beilby has made many experiments, and added considerably to the information we have in regard to the behavior of this and other substances when heated in the same way. If there are holes in the heated leaf, they are exceedingly small, he says, beyond the power of the microscope to see. Now the X-rays have something to say on this point. When gold leaf is examined by their aid, it is found that it consists of masses of cubic crystals of gold all lying with faces parallel to the leaf. They are not necessarily cubes, of course. They consist, like ordinary salt, which is cubic, of rectangular blocks of all sizes. They must be exceedingly thin blocks, and no doubt their thickness is far less than their width or length. When the leaf has been heated, the blocks are piled up anyhow, perhaps gathered together to some extent in heaps, as Faraday supposed, even if they are too small to be seen by the microscope; and perhaps this is the reason why gold and silver leaf become transparent when heated. Why gold should be green when looked through is a mystery. But we do see that the heating of the gold has spread out the crystal blocks so that they all lie with one face in the leaf surface, and that heat has destroyed this amount of regularity of arrangement," p. 231.

"It very often happens that the addition to a metal of quite a small quantity of a second metal, or even of a non-metal, causes a notable increase in hardness, p. 240. "Let us take one of the simpler cases—for example, that in which the addition of a small quantity of aluminium to copper produces an increase in hardness. The X-rays show that the structure of the copper crystals remains the same, except that here and there an aluminium atom takes the place of a copper atom. Now the weakness of the crystal lies, as we have seen, in the fact that one part slides on another part along a certain plane. This plane is now no longer even: there is a scattering of aluminium atoms in it, and we can readily suppose that the slipping has become more difficult, and that we have here the cause of hardening. There is a remarkable effect which makes us think we are right in supposing so. The atoms of aluminium must strain the structure of the copper crystal, because the copper will not take up more than a certain number. If an alloy is made containing more than about 10 percent of aluminium, the X-rays tell us that the copper crystals are broken up altogether, and a new structure is formed. The alumnium atoms must be distorting the copper crystal, and this fits in very well with the fact that it hardens the copper. On the other hand, when nickel is added to copper the atoms of the former replace the atoms of the latter to any extent; evidently they can slip into the places of the copper atoms without straining the copper crystals at all. And in this case there is no hardening effect, which is just what we should expect. It is only when we push in atoms which really strain the copper crystal and make its planes uneven that the hardening is brought about. We have jammed the sliding planes.

"In the case of steel the action is the same kind, but here the carbon atoms that are the cause of the hardening do not replace the iron atoms, but are forced into the empty spaces between them. We can easily see that this may distort the iron crystal, and as before prevent the movement along a plane of slip. Once again there is a limit to the amount of the alloying substance: only a small percentage of carbon can be introduced into the iron without breaking up its ordinary simple structure.

"The problems of iron and steel contain, however, many more complications than this. We have only to ask what happens when more carbon is put in than the iron structure can carry, and we find we have a new problem. Among other things, a new crystal appears, formed of molecules, each containing three atoms of iron and one of carbon; it is known as cementite. The new crystals are very hard and unyielding, and in form are like needles. Their presence hardens the iron very greatly and makes it difficult to work. A beautiful example of its effect on steel is to be found in the old swords that once made their way from India through Damascus into Europe. Damascus steel was greatly valued for the excellence of its qualities. Fine specimens are to be seen in the Wallace Collection; they show the characteristic wavy pattern which has always been looked on as evidence of genuiness. When examined under the microscope the lines of the pattern are seen to consist of multitudes of dots, forming a sort of Milky Way in the steel. These dots are the tiny crystals of cementite. As Colonel Belaiew tells us, the steel when it was first made was most difficult to work. The smith, with his little furnace, would heat the steel red hot, but after he had struck but a few blows and made a slight impression on the steel, the momentary softening had gone. The hardness due to the cementite crystals had only been removed for an instant. More heating, a few more blows, and slowly the steel became less rigid. In fact, the cementite crystals were changing their form. They were becoming less like needles, gathering themselves together into more rounded shapes, and as they did so the steel became more pliable. At last the fine Damascus steel was reached, so strong and yet so elastic. It is very likely that much of the keen edge that these swords would take was due to the presence of the very hard particles embodied and held in the softer iron. The edge would be like a saw with extremely fine teeth. In the trial of skill between Saladin and King Richard which Walter Scott describes in *The Talisman*, the former threw a gossamer veil into the air and severed it by drawing his scimitar across it, a fine test of keenness and of skill. Richard, on the other hand, used his sword like an ax, and clove in two an iron bar, the mace of one of his knights. This also was a test requiring great qualities in the steel, but or the part of the man the skill lay more in the power to strike a terrific blow than in delicacy of touch," p. 241.

Since no one is omniscient, it is not surprising to find Sir William nodding at times. "A very curious feature of the soap bubble is its reluctance to join up with another bubble. If we blow a bubble on a ring, we may take a second bubble and knock it against the first with force, one would think, enough to break them. But the bubbles bounce from one another like india-rubber balloons. Perhaps the explanation lies in the fact that in both cases the outer layer consists of those ends of the molecules which, as we saw before, have very little tendency to associate with other molecules or parts of molecules. There is no tendency for the one bubble to coalesce with the other when the two are pressed together, because the parts that come first into contact do not attract each other." The adsorbed air film has been overlooked completely.

It is a little misleading to say, p. 242, that the copper crystals are broken up altogether and that a new structure is formed when more than ten percent of aluminium is added to copper. What actually happens is that some new crystals are formed in addition to those containing about ten percent of aluminium.

This is a delightful book.

*Wilder D. Bancroft*

**Hexosamines and Mucoproteins.** *By P. A. Levene. 24 x 15 cm; pp. x + 163. London and New York: Longmans Green and Co., 1925. Price: $3.75.* For the present most physical chemists will be interested only in portions of this book.

"The problem of mucoproteins and of the so-called glucoproteins, more than that of any other tissue component, is intimately connected with that of hexosamines. The original interest in mucoproteins, as well as in hexosamines, may be attributed to theories connecting the glucosidic structure of proteins with the capacity of proteins to take up the place of carbohydrates in the economy of the animal organism. As the result of more modern work the mechanism of sugar formation from proteins has been explained more accurately. It

was shown that even without preformed sugar the protein molecule contains components which in the organism may be transformed into sugar. On the other hand, it was found that the function of the nitrogenous sugars is different from that of simple sugars. As yet it is not possible to define accurately the rôle which hexosamines play in the animal organism. Only an approximate estimate can be formed, and that on the basis of the distribution of the tissue elements containing hexosamine. The most striking example is chitin. The rôle of chitin as an architectonic element is so evident that it scarcely needs to be pointed out. The similarity of its function to that of cellulose is striking. It is peculiar that whereas cellulose, the architectonic element of the plant, is nitrogenfree, chitin, which, in the lower forms of animal life, takes the place of celloluse is a product of the condensation of a nitrogenous sugar. In the higher animal forms, amino sugars are constituent parts of the skin, the skeleton, the connective tissue, the serous and mucous membranes, in a word all of those tissues which preform either an architectonic or a protecting function. It is then not surprising that nitrogenous sugars do not possess the same tendency to burn in the organism as do the ordinary sugars. Thus the direction of interest of the biologist in regard to nitrogenous sugars has changed but the interest has remained, or perhaps has even increased, since it was discovered that their distribution in the animal tissue is wide," p. 1.

"Theoretically hexosamines permit of a greater number of isomers than the corresponding hexoses, for the reason that to every hexose five hexosamines are possible according to the position of the amino group. Fortunately the nitrogenous sugars thus far discovered in nature have the structure of 2-aminohexoses. Synthetically were prepared hexoses with an amino group also in positions 3 and 6, as well as one 1-amino-2-ketohexose (aminofructose," p. 11.

Many of the properties of the sugars can be studied with advantage on hexonic acids for the reason that in these acids the symmetry of the carbon atom (1) has dissapeared and thus their molecules represent structurally simpler systems.....Amino hexonic acids, as sugar acids generally, represent a very convenient material for the study of relationships which exist between configuration and optical behavior.

"There was another reason which attracted the interest of the author of this monograph to the synthesis of 2-hexosaminic acids, namely, their relationships to simple amino acids. Since all simple hexonic acids are readily converted into caproic acid, it seemed that 2-aminohexonic acids could also be transformed into the corresponding simple amino acids, and this reaction seemed to hold out the promise of correlating the configurations of amino acids with those of sugars. Indeed, Neuberg recorded a successful reduction of chitosaminic acid to 2-aminocaproic acid (normal leucin). Unfortunately, Wildman and the writer did not meet with the same good fortune and the product they obtained was always amino hydroxycaproic acid which, besides, was optically inactive. The same result was obtained with several other 2-aminohexonic acids. Some day the experimental difficulties of the problem will perhaps be overcome," p. 26.

"Biologists and often even chemists referred to aminohexoses as substances occupying an intermediate position between carbohydrates and proteins. This assumption inferred that the nitrogenous sugars were capable of functioning in the organism either as carbohydrates or as proteins. It was a disappointment, particularly to the physiologist that this expectation was not borne out by experiments. Chitosamine was found to act differently from ordinary carbohydrates. The animal organism possesses a certain mechanism which brings about a condesation of the unconsumed simple sugars into glycogen. Only when the quantity of ingested sugar is exceedingly large, is part of it eliminated in the urine. The sugar which is neither eliminated nor burned is stored up in the form of glycogen. On the basis of this fact it was reasoned that every substance which leads to an increase in the stored glycogen is being transformed in the organism into glucose. Applying this test to chitosamine, it was found that it did not function glycogenetically," p. 61.

"A curious incident should be recorded in connection with the preparation of the *a*- and *β*-isomers of this sugar. When chondrosamine hydrochloride was isolated the first time on hydrolysis of chondroitin sulphuric acid, it had a specific rotation of + 129.5°, reaching an equilibrium at + 95°. A few years later the specific rotation of the same sample was

measured and found + 125°. A sample chondrosamine obtained from another source 15 minutes after the substance was brought into solution, had a specific rotation of + 115°, and an equilibrium rotation of + 96.4°. Thus these two samples were evidently the α-forms. Subsequently when the natural sugar was prepared on the larger scale the hydrochloride invariably crystallized in the β-form. The synthetic chondrosamine also crystallized in the β-form. This is a very peculiar occurrence, particularly as the β-isomer is the common form for only a few of the simpler sugars. However, this occurrence in not unique. It is well known that α-mannose could not be prepared in spite of many efforts, but after it was once obtained by the present author it became impossible in his laboratory to recrystallize the β-isomer without changing it into the α-form. On the other hand, in the case of other sugars, such as glucose and galactose, one can obtain at will either one or the other isomer.

"Eventually a method was found to prepare the α- and the β-isomers of chondrosamine hydrochloride. The rate of mutarotation of each of the isomers was measured and the initial rotation of each form was obtained by extrapolation," p. 20.

*Wilder D. Bancroft*

**The New Physics.** *By Arthur Haas. Translated by Robert W. Lawson. 19 + 14 cm: pp.. Ix + 165. New York: E. P. Dutton and Company. Price: $2.50.* The chapters are entitled: the electromagnetic theory of light; molecular statistics; the electron theory; the quantum theory; the theory of the chemical elements; the theory of relativity and gravitation.

"In consequence of the magnificent advances made in theoretical physics since the beginning of the twentieth century, our views on natural phenomena have undergone a complete transformation. . . Our conception of nature has been beautifully extended, and at the same time simplified and unified.

"This most recent development of physics. so revolutionary and yet so successful, was aided by two theories which originated in the latter half of the nineteenth century, each of which represented a great advance in an endeavour to obtain uniformity in physics. The first of these theories, due to Maxwell, identified the phenomena of light with those of electricity, and thus converted optics into a branch of the science of electricity. The other theory explained the phenomena of heat by assuming a continuous motion of the smallest particles composing bodies, and thus the science of heat became a branch of mechanics. At the same time, this latter theory clearly showed the extraordinary fruitfulness of the atomistic principle. At the end of the nineteenth century the extension of Maxwell's theory led to the electron theory. This theory enabled us to regard electricity as the primordial constituent of all things, and to recognize in the small electrical charges the building stones of matter. The quantum theory, which constitutes an extension and a development of the atomistic principle, has been pre-eminently successful, especially in the interpretation of spectra, and it has supplied us with valuable information on the internal structure of the atoms of the chemical elements. The theory of relativity brought about an entirely new conception of the nature of space and time, of motion and of matter, and from a generalization of the theory of relativity we have been led to the modern theory of gravitation, which also yields important information on cosmological questions," p. 1.

"As to whether or not a physicist detects fluctuations in density will thus depend solely on the smallness of the volume chosen for his molecular statistical considerations. From an objective point of view, molecular fluctuations of density will be unimportant for all processes in which distances of about a hundred thousandth of a millimetre are too small to be of moment for the process. On the other hand, for those processes in which such small (or not appreciably greater) distances have to be taken into account, the effect of the molecular fluctuations must make themselves manifest. The passage of a ray of light through a gas belongs to this class of phenomena. The value of the quantity that characterizes the optical behavior of a gas, i.e. the so-called refractive index, depends on the density of the gas. Fluctuations in the density must therefore result in fluctuations in the value of the refractive index.

"The great progress made in theoretical atomistics since the beginning of the twentieth century is due largely to Smoluchowski. He recognized that such fluctuations of the re-refractive index in the atmosphere are responsible for the blue colour of the sky. The correctness of this interpretation has been established without doubt by different interesting experiments. In fact it was possible, on the basis of Smoluchowski's theory to calculate the size of the molecules from optical measurements on the colour of the sky, and the results are in good agreement with those obtained by quite different methods. The phenomenon of the blue of the sky has been known since the beginning of mankind, and yet we are indebted to modern physics for recognizing in it a brilliant empirical confirmation of the atomistic hypothesis, devised long ago on purely philosophical grounds by the genius of a Grecian thinker," p. 35.

"In 1907, two years after he founded the idea of light quanta, Einstein discovered an additional very important field of application of the quantum hypothesis, in the theory of the specific heat of solid bodies. By the specific heat of a substance we understand the amount of heat that must be supplied to 1 grm. of the substance to raise its temperature by 1° C. In 1819 Dulong and Petit discovered an interesting relation between the specific heat of a solid element and its atomic weight. According to the so-called law of Dulong and Petti, the product of these two quantities, the atomic heat, should have the same value for all solid elements. This relation, a theoretical basis for which was given later, in is general well confirmed by experience. But even at the time of the formulation of the law, very large deviations from the law were noted in the case of several elements of low atomic weight, e.g. beryllium, boron, and particularly diamond. Later, the fact was established that, especially in the case of diamond, the specific heat decreases very much when the crystals are strongly cooled.

'The deviations from Dulong and Petit's law could not be explained by classical physics. But they certainly found a simple interpretation when Einstein applied the quantum principle to the theory of heat of solid bodies. In accordance with the classical ideas, Einstein assumed that the heat of solid bodies is based on the vibrations of their atoms, but he further assumed that the energy of these vibrations is made up of elements of energy in the sense of Planck's hypothesis, according to which these elements are proportional to the frequency. As a result of this assumption of Einstein, not only did the increase of the specific he. t at low temperatures become intelligible, but also the fact that even at room temperature appreciable deviations from Dulong and Petit's law occurs with elements, the atoms of which, being particularly light, vibrate very rapidly in consequence. Einstein's idea was subsequently developed by different scientists, in particular by Debye, who improved the theory of Einstein and thus brought into still better agreement with experience. In 1912, Debye's work led him to an important law, according to which the specific heat of a solid body is proportional to the third power of the absolute temperature at very low temperatures," p. 80.

"Positive and negative electrical charges now appear as the bricks of the universe. They are arranged in numerous ways into systems that we call atoms. The kind of arrangement determines the chemical nature of the atoms, the internal structure of which is regulated by quantum relations. The appearance of a mechanical mass follows from electrical properties. In consequence of their charge and motion, the electrons call forth an electromagnetic field, which is periodic in space and time. Space is therefore filled with electromagnetic waves of all possible frequencies. Only a very small part of the spectrum is revealed to the most perfect of the human dense organs, i.e. to the eye, as light. Totality phenomena, in which a large number of material individuals take part, are responsible for the phenomena of heat. Space and time, however, in which all processes appear to operate, are linked together to form a four-dimensional manifold, the geometry of which is manifested in the phenomena of gravitation.

"Thus the new physics reveals to us a picture of nature of great simplicity. In point of fact, it is not nature that is complicated, but only the path that led to the true knowledge of it. This path was complicated because it started off from the narrow limitations of the human senses, and because theoretical physics only gradually succeeded in liberating it from human points of view," p. 154.

*Wilder D. Bancroft*

**Relativity.** *By G. B. Jeffery. 19 + 13 cm. pp. vii + 150. New York: E. P. Dutton Company, 1924. Price: $2.40.* This book is written "to introduce the theory of relativity to students of science who are able to make some use of mathematics as an instrument of thought; but who may be not quite ready to face the mathematical analysis which is essential for the thorough exploration of the subject in all its ramifications." The chapters are entitled: introduction—Einstein's theory of relativity; the origin of the theory; the Michelson-Morley experiment and the Lorentz transformation; the laws of motion and of magnetism; the restricted principle of relatively and some consequences; the equivalence hypothesis; the four-dimensional continuum; the general theory.

"As I conceive the office of a professor, it is that he should stand before his students as the living representative of those great men who in the past have laboured in that branch of human knowledge which he has made his own; that by means of a reverent yet unflinching criticism he should strive to reveal the workings of these master minds, to the end that he may impart, not merely knowledge, but that more precious gift—the art of acquiring knowledge, the art of discovery. If we approach our task with this spirit, we shall find the key to the solution of much that is difficult and perplexing in our present knowledge, and the inspiration which will lead us on to further discoveries," p. 31.

"The young scientist can suffer from no greater fault than a misunderstanding of scientific genius. We are to apt to think that advance in scientific knowledge is reserved for those who, by reason of some special gift, are able for the first time in human history to see something which others have been blind to see. Now there is a measure of truth in this view, but it is important that we should see what that measure is, more particularly when we come to the conclusion, as most of us must quite young in life, that we are very ordinary people with no very special gifts. When that moment comes, it will depend upon our conception of the way in which science advances whether we go forward and play our part, such as it may be, in the progress of knowledge, or whether in despair we leave the matter to those more fortunate ones who have been predestinated for the work," p. 33.

"Relativity is commonly supposed to be a revolutionary theory. The theory has its roots in the very beginning of modern science, but it is nevertheless a revolutionary theory in that its acceptance commits us to a radical reconstruction of our most fundamental physical concepts. In attempting this task of reconstruction it is essential that we should understand the reasons which led to the formation of the older concepts, in order that, if these are eventually discarded, we may ensure that nothing of value is lost.

"Perhaps the most important lesson of the history of science is the abiding value of the result of a physical experiment carefully and accurately carried out under definite conditions. The chapter of scientific history with which we shall be most concerned is very largely the story of an always-changing theory based upon a growing body of unchanging experimental facts," p. 36.

*Wilder D. Bancroft*

**An Introduction to the Literature of Chemistry.** *By F. A. Mason. 18×12 cm; pp. 42. New York: Oxford University Press, American Branch, 1925. Price: 70 cents.* In the foreword W. H. Perkin says that "those employed in supervising research are only too well aware of the difficulty in familiarizing students with the way chemical facts are catalogued and with the method which must be adopted in order to find out whether a substance is known or not, if known, where an account of its preparation and properties is to be found. It will be a relief to those in charge of the everincreasing number of research students to be able to direct them to the clear introduction to the literature contained in the following pages, and Dr. Mason is to be congratulated on producing so valuable and convincing and at the same time so simple a work on this important aspect of the subject."

The reviewer hopes that the student will find this book as valuable as this introduction implies. Personally, he does not quite see why a student interested in looking up any special problem should read a biographical sketch of Sir Henry Roscoe, for instance, or Cohen's life of van't Hoff, to take another case. One does not see why Clibbens and Rivett should be cited under the phase rule and not Findlay.

*Wilder D. Bancroft*

91 A 217

1441

# THE COLOR OF THE RUBY

BY CHARLES W. STILLWELL

In 1837 Gaudin[1] found that by adding a small amount of green chromic oxide to aluminum oxide and fusing the mixture in an oxy-hydrogen flame, the color of the natural ruby could be reproduced. Since that time, and doubtless long before, it has been assumed that the ruby owes its brilliant color to a trace of chromium. This is justifiable because the natural ruby is known to contain a trace of this metal. On the other hand, chromium is also held responsible for the green color of the emerald.[2] The reaction of the average man of intelligence who is confronted with these facts is one of wonder, if he be of a tolerant nature; and one of ridicule and denial if he be intolerant. The attitude of investigators and authors in the field of precious stones has been open-minded to the point of neglect. Some[3] leave the matter completely up in the air as does Goodchild,[4] "Traces of ferric oxide, silica and oxide of chromium are found in even the purer varieties often and it is supposed (though it is by no means certain) that these substances, slightly varying in amount and proportion, give to the ruby, the sapphire and the other precious forms of corundum their beautiful colors on which the value so largely depends." Others[5] state the facts, as though firmly established, with the matter-of-factness of Kraus and Holden.[6]" "This green color [of the emerald] is thought to be due to a trace of chromium. As the red color of the ruby is also ascribed to the same element, it obviously must exist in different states of combination in the two minerals. Accordingly in minerals and chemical compounds chromium may produce either a green or a red to violet color." The authors who have been quoted represent fairly the attitude of the literature in general on this question. We have advanced to the point where we are willing to say definitely that the red color is produced by chromium. For the most part, however, we assert it glibly as though it were an everyday occurrence to color a substance red by adding a green coloring matter to it; and little progress has been made toward an explanation for this phenomenon.

The issue has bothered those of the ceramics industry in the form of the chrome-tin pink. They have been compelled through necessity to investigate some of the conditions under which chromic oxide causes a red or pink color in stannic oxide. The data which have been collected are voluminous and full of contradictory evidence. The results obtained are largely empirical

---

[1] Gaudin: Compt. rend., 4, 999 (1837).

[2] W. R. Cattelle: "Precious Stones," page 105 (1903); Kraus and Holden: "Gems and Gem Materials," page 124 (1925).

[3] G. F. Kunz: "Gems and Precious Stones," page 39 (1892); W. R. Cattelle: "Precious Stones," page 96 (1903).

[4] W. Goodchild: "Precious Stones," page 187 (1908).

[5] G. P. Merrill: U. S. National Museum Bulletin 118, 1.

[6] Kraus and Holden: "Gems and Gem Materials," page 124 (1925).

and bring us little nearer an explanation of the red color. As summarized by Bancroft[1] they do indicate several general conclusions. The red color is obtained when a comparatively low percentage of chromic oxide is added to stannic oxide or other white oxides or mixtures of white oxides; and as the chromic oxide content is increased the color changes to green, usually going through an intermediate brown. The point at which the color change occurs, in reference to chromic oxide content, is influenced by the particular oxide which is present. Finally, in a majority of cases at least, the formation of the red or violet color takes place in an oxidizing atmosphere while a reducing atmosphere produces the green.

The present investigation was undertaken for the purpose of determining the conditions under which chromic oxide imparts a ruby color to corundum as distinguished from those conditions causing a green coloration; and secondly to ascertain in what form or state of combination the chromium exists in corundum to produce the red color.

Possible explanations of this red or ruby color caused by the presence of chromium have been offered. It has been suggested[2] that it was due to colloidal chromic oxide present in the aluminum oxide, although no experimental evidence either for or against this view was furnished with the suggestion. It is at least a plausible theory, for we know that a change in the size of the particles of many metals is accompanied by a change in color, usually very striking.[3] Finely divided copper oxide has been prepared which is blue.[4] Scheetz[5] found that ferric oxide was yellow in the presence of alumina. Since the amounts and nature of the oxides to which the chromic oxide is added apparently affect the concentration at which the mixture changes from red to green, we might suppose, therefore, that these other oxides in some way stabilize colloidal chromic oxide.

In order to test this hypothesis, finely divided chromic oxide was prepared by electrical disintegration according to the method of Svedberg.[6] A high-tension oscillating arc was passed, under water, between two chromic oxide electrodes which had been prepared by fusing the powder in a convenient shape. The electrode disintegrated noticeably but tended toward a yellowish green color and at no point in the experiment was there any suggestion of red in the color of the particles formed. This yellowish color was found to be due to chromic acid. Finely divided chromic oxide was eventually prepared using the method described by Mott.[7] Carbon electrodes were set vertically and the metallic oxide placed in the lower, cup-shaped electrode. A 50 volt, 20 ampere direct current furnishes the arc, causing the oxide to volatilize and

[1] J. Phys. Chem., 23, 603 (1919).
[2] Hull: Trans. Am. Ceramic Soc., 4, 230 (1902).
[3] Bancroft: J. Phys. Chem., 23, 603 (1919).
[4] Schenk: J. Phys. Chem., 23, 283 (1919).
[5] J. Phys. Chem., 21 570 (1917).
[6] Svedberg: "Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe," page 424 (1909).
[7] Trans. Am. Electrochemical Soc., 34, 254 (1918).

deposit on the upper electrode. Mott found that the size of the particles deposited decreases as the distance from the arc increases. The results which he obtained with ferric oxide were first duplicated, a gradual change in color from red to yellow occurring as the distance from the arc increased. This agrees with the known fact that finely divided ferric oxide is yellow. When the experiment was repeated with chromic oxide, however, there was no color change evident except a paling of the green toward white, which is expected to accompany a decrease in the size of the particles and is noticeable when the green is ground in a mortar. It is evident from these results that finely divided chromic oxide is not red and that we must look for another explanation of the red color.

The results of some investigations of the chrome-tin pink, to which reference has already been made, suggest that the red color may be caused by the oxidation of chromic oxide to some higher oxide. This view has enjoyed considerable popularity in the past. Watts[1] states that with mixtures of chromic oxide and hydrous aluminum oxide ground together and calcined in an oxidizing flame, he obtained a pink color when there was 9.47 percent, or less, of chromic oxide in the final mixture. If the same mixture were calcined in a reducing flame a bright chrome green resulted. Seger[2] says that with mixtures of chromic oxide, stannic oxide and calcium oxide the red is destroyed by reducing conditions and reappears when oxidized. Rhead[3] notes a mixture colored by chromic oxide which gave a green in a fritt kiln and a red in a muffle kiln.

An attempt has been made to duplicate the results obtained by Watts. Hydrous aluminum oxide was precipitated from a solution of alum, dried at 140° C. and ground together with chromic oxide in the proper amounts to form a final mixture containing 90.6 percent of aluminum oxide and 9.4 percent of chromic oxide. This mixture was calcined at a temperature of approximately 1490° C. in an Ajax induction furnace. To ensure a strong reducing atmosphere, the mixture was placed in an alundum crucible which was in turn fitted into a piece of graphite. As a result, the furnace was filled with carbon monoxide throughout the run. Several trials were made with this mixture varying the temperature and the duration of the calcination, and in every case the resulting powder was of a distinct lavender or reddish lavender color: and there was not the least tendency toward a green. These results were independent of the method of cooling the powder. It could be removed when red hot and cooled in the air or it could be cooled to room temperature in the reducing atmosphere without any effect on the final color. There is a minimum temperature below which no reaction takes place, leaving the powder the original green color. This may be easily distinguished from a green which might be a product of the reaction, however, since a microscopic examination of the powder shows a mixture of green and white particles,

[1] J. Am. Ceramic Soc., **13**, 301 (1911).
[2] Trans. Am. Ceramic Soc., **4**, 230 (1902).
[3] J. Am. Ceramic Soc., **13**, 324 (1911).

different in appearance from the blended color resulting when the temperature is high enough to cause the reaction to take place. It is interesting to note that this diffusion of the lavender color into the white aluminum oxide takes place far below the melting point of either constituent. The same results are obtained as regards color in a reducing atmosphere if the mixture is completely fused. We have three samples of alpha aluminum oxide furnished by the Norton Company, containing roughly 0.5, 5.0 and 15.0 percent of chromic oxide respectively, with traces of other impurities. These were prepared by fusing the oxides in an electric arc, in which case the atmosphere is doubtless reducing. The samples are all of a bluish red or lilac shade, increasing only in saturation as the chromic oxide content increases. These results show that we do not obtain a green color with a reducing atmosphere necessarily; and it follows, of course, that an oxidizing atmosphere is not necessary to produce the red. It is equally true that with a reducing atmosphere we get a bluish-red color rather than a good ruby red and a possible explanation of this is offered later.[1]

It has been shown[2] that with solutions of chromic chloride and many other chromium salts, the color depends on the thickness through which light is transmitted or on the concentration of the solution. A chromic chloride solution goes from green to violet by transmitted light as the thickness of the solution transmitting the light is increased. If the thickness be kept constant and the concentration of the chromic chloride increased, the color of the solution changes from green to violet. The suggestion has been made that the red or lavender color caused by chromic oxide in aluminum oxide is similarly a concentration effect. This is impossible, however, since we find an increase in concentration of chromic oxide in aluminum oxide causing the color to change from bluish-red or red to green, while in the case of the solution it is just the reverse. It may also be seen from data given on page 1447 that mixtures of chromic oxide and aluminum oxide of identical composition may be either red or green depending upon the conditions under which they were prepared.

Recently the Norton Company has found that small amounts of chromic oxide color alpha alumina red or bluish-red, while the same percentage of chromic oxide always colors beta alumina green. This suggests the hypothesis that there may be two modifications of chromic oxide, one red or bluish-red and the other the usual green color; provided, of course, that the alpha and beta alumina have different crystalline structures.

The existence of beta alumina was first discovered at the Geophysical Laboratory and has been described by Rankin and Merwin.[3] The beta alumina used in our work is prepared by the Norton Company by adding sodium carbonate to the alpha alumina when it is fused. The analysis reported by the Norton Company for this product is as follows:

---

[1] Page 1454.
[2] Gladstone: J. Chem. Soc., 9, 145 (1857); 10, 79 (1858).
[3] J. Am. Chem. Soc., 38, 563 (1916).

| | Percent | |
|---|---|---|
| Sodium oxide | 5.45 | |
| Ferric oxide | 0.30 | |
| Silicon dioxide | 0.19 | |
| Titanium dioxide | trace | |
| Beta alumina | 100.0 | (i. e. all alumina is present in the beta form) |

The presence of the soda is evidently responsible for the formation of the beta alumina because the alumina reverts to the alpha form as soda is removed by heating. The beta alumina reported by Rankin was formed in the absence of soda and it is therefore not likely that it could be sodium aluminate instead of another form of alumina. To make sure of this point, however, an X-ray diffraction pattern of the beta alumina was made by the powder method of Davey[1] and compared with the diffraction pattern of sodium aluminate. The two are entirely different, which means that we are dealing with different crystal structures.

X-ray diffraction patterns were also taken of these samples obtained from the Norton Company:

| | |
|---|---|
| Alpha alumina | (white) |
| Beta alumina | (white) |
| Alpha alumin plus 5 percent chromic oxide | (bluish-red) |
| Beta alumina plus 5 percent chromic oxide | (light green) |

The spectrograms indicate that the crystal structure of the two forms are very different. Of course alpha alumina is known to be rhombohedral hexagonal and Rankin reported beta alumina as hexagonal; but the spectrogram shows it to be of a different form in the hexagonal system from that of the alpha. No additional differences in the pattern could be detected due to the presence of chromic oxide or to the resulting difference in color. This is to be expected, since according to Wyckoff[2] the powder method is not sensitive to less than ten percent of a foreign substance in the total.

A series of mixtures of varying proportions of alpha aluminum oxide and chromic oxide was prepared in order to determine the relation between the composition and the color; and the effect, if any, of either the composition or the color on the structure of the mixed crystal. The mixtures were prepared, throughout the entire range from 0 to 100 percent of chromic oxide, following the method used by Verneuil[3] in mixing the ingredients for his artificial rubies. Potassium aluminum sulfate and chromium potassium sulfate were dissolved in water in the proper proportions to yield the desired oxide mixture, precipitated with ammonia and the hydrous oxide precipitate washed, filtered, dried and calcined to remove the water. The powder thus formed has the advantage of being as nearly homogeneous as possible, as this is a necessary factor in

[1] General Electric Review, Sept. (1922).
[2] "Structure of Crystals," page 149 (1924).
[3] Ann. Chim. Phys., (8) 3, 20 (1904).

Verneuil's process. It was found to be very fluffy and easily blown away by the force of the blast, however, and so the mixtures finally used were made up by mixing aluminum oxide and chromic oxide directly. The matter of homogeneity is not so important in this work because the entire mass becomes fused and the entire sample is used, and hence no discrepancy in composition can occur.

An oxy-hydrogen blast lamp has been used in all the experiments recorded here to effect the fusion of the mixtures. A small pile of the powdered mixture is placed on an alundum slab and a very gentle oxy-hydrogen flame directed upon it. If this first step is done carefully, little powder is blown away by the force of the flame. A considerable portion of the pile will soon sinter together somewhat and the force of the flame may then be increased until complete fusion occurs, when the melt will become mobile and assume a spherical shape. Unless the heat becomes so intense that this molten sphere is flattened against the alundum by the force of the blast, no difficulty is encountered in removing the sphere from the slab when it cools and the surface of contact between the two is so small that there can be no appreciable contamination of the product by the slab. In general it was found convenient to prepare globules of the product of not more than two or three millimeters in diameter. The main objection to preparing larger samples by this method lies in the fact that if the mixtures be heated very much above the fusion temperature the chromic oxide begins to volatilize, and if a larger sample is taken, boiling occurs on the surface before the inner part has become fused. This takes place even with comparatively gradual heating. Since in all this work the composition of the product is assumed to be that of the mixture before fusion it is essential that any boiling during fusion be prevented. The following mixtures were prepared and fused:

| Percent $Al_2O_3$ | Percent $Cr_2O_3$ | Color of Product |
|---|---|---|
| 90 | 10 | red or bluish-red |
| 80 | 20 | red or bluish-red |
| 70 | 30 | red or bluish-red |
| 60 | 40 | green |
| 30 | 70 | green |

The red product of the first three mixtures was obtained by heating the powder with an ordinary blast lamp burning oxygen and hydrogen. The hot part of this flame was tested with a copper-borax bead and found to be an oxidizing flame. The bluish-red products were produced in the flame of a regular oxy-hydrogen burner which proved to be a reducing flame when tested with the copper-borax bead. It was found impossible to fuse the mixture containing seventy percent of chromic oxide with the means available, since apparently the melting point of the mixture increases as the chromic oxide content increases. To obtain a complete series under identical conditions, therefore, mixtures were made from chromic oxide identical with that used above and hydrous aluminum oxide which had been dried at 140° C. It was found that these mixtures fused more easily than those made up of the oxides directly.

but the resulting colors were approximately the same. Since the atmosphere in which the fusion takes place obviously makes a noticeable difference in the color of the product, another series was run, care being taken to control the atmosphere. The effect of chromic oxide content on the color of the product is summarized below:

| Percent of $Cr_2O_3$ in alpha $Al_2O_3$ | Color | |
|---|---|---|
| | Heated in oxidizing atmosphere. | Heated in Reducing Atmosphere. |
| 5.0 | red | bluish-red |
| 10.0 | red | bluish-red |
| 15.0 | red | bluish-red |
| 20.0 | red | bluish-red |
| 30.0 | red (slightly bluish.) | green |
| 45.0 | red (slightly bluish.) | green |
| 50.0 | green | green |
| 60.0 | green | green |
| 70.0 | green | green |
| 100.0 | green | green |

In the products containing 10, 15 and 20 percent of $Cr_2O_3$ the saturation of the red color increases with the increase of chromic oxide, but the hue or shade remains the same throughout.

A careful scrutiny of these results leads to several interesting and significant conclusions.

It is plain that we get the red color (for the present "red" is understood to include both the red and bluish-red. The occurrence of the bluish-red color is discussed later (on page 1454) for all mixtures up to and including twenty percent chromic oxide, regardless of the atmosphere in which the fusion is affected. Now, if the red color were due to a higher oxide of chromium, fusing a red mixture containing twenty percent of chromic oxide in a reducing flame should produce at least a small amount of the lower green oxide. We know that red and green mixed in the proper proportions will give a yellow effect[1] and we should therefore expect the color of the mixture fused in the reducing atmosphere to contain a certain yellow component and appear at least more orange than the corresponding mixture heated in the oxidizing atmosphere. It is obvious that it tends to change toward the blue rather than orange. For the same reason we should expect that heating a green mixture of, say sixty percent chromic oxide content in an oxidizing atmosphere would produce some of the higher red oxide with a consequent tendency towards yellow in the color of the mixture. There is no noticeable difference in the shade of the green products, however. It is evident, then, that the difference in color cannot be due to different degrees of oxidation of the chromium and it naturally follows that both the red and green colors are due to the presence of chromic oxide. In other words we have the same

[1] Rayleigh: Nature, 3, 234 (1871).

chemical compound differing in at least one physical property, that of color; and this is strong evidence of the existence of chromic oxide in two different modifications, one red and the other green.

There is an intermediate range from 30 to 45 percent of chromic oxide at least where either a red or a green color may be formed. At any definite concentration of chromic oxide within this range, therefore, either one of the modifications may be obtained but one must be stable and the other metastable.

In order to determine the effect of either color or chromic oxide content on the crystal structure of the products, X-ray diffraction patterns of several were made by the powder method. A casual inspection of the films made it immediately obvious that the axial ratios in the crystals were affected noticeably by the chromic oxide content and also by either the color or the conditions under which the fusion takes place—or both. Davey[1] has measured the axial ratio of alpha alumina as 2.726 and that of green chromic oxide as 2.754, both substances being of the same crystal form. The possibility of measuring quantitatively axial ratios lying between these two values and having the figures bear any significance was immediately abandoned and all the following statements concerning axial ratios are based on qualitative comparisons which were obtained very definitely by taking the X-ray patterns in suitably arranged pairs as indicated. The figures refer to the amount of chromic oxide in mixtures containing only chromic oxide and alpha alumina.

| | | | | | | |
|---|---|---|---|---|---|---|
| 1. | 0.5 | percent | red | 15.0 | percent | red |
| 2. | 15.0 | " | red | 15.0 | " | bluish-red |
| 3. | 15.0 | " | red | 30.0 | " | red |
| 4. | 30.0 | " | red | 30.0 | " | green |
| 5. | 30.0 | " | green | 60.0 | " | green |
| 6. | 30.0 | " | green | 45.0 | " | red |
| 7. | 45.0 | " | green | 45.0 | " | red |

Each film recorded two sets of lines, one for the mixture to the left, the other for the mixture to the right. The lines on both sets were arranged according to the same general pattern, indicating that the crystal forms of the two are the same. If the size of the crystals and their axial ratios were identical, each line would be at exactly the same distance from the zero point on the film as the corresponding line of the comparison pattern and we would see each line as the continuation of its mate on the other pattern. If the axial ratios of the two mixtures were different, however, some of the lines on the pattern of the crystal with the larger axial ratio would be shifted slightly toward the zero point. This latter condition was found to exist in certain of the films examined and by inspection it was possible to arrange these mixed crystals in the order of magnitude of their axial ratios. In the following table

[1] Phys. Rev., (2) 21, 716 (1923).

the composition of the crystal with the largest axial ratio, a value nearest to that of green chromic oxide, is placed at the top and the others in regular decreasing order.

| | | | | | |
|---|---|---|---|---|---|
| 1. | 60.0 | percent | chromic | oxide | green |
| 2. | 45.0 | " | " | " | green |
| 3. | 30.0 | " | " | " | green |
| 4. | 45.0 | " | " | " | red |
| 5. | 30.0 | " | " | " | red |
| 6. | 15.0 | " | " | " | bluish-red |
| 7. | 15.0 | " | " | " | red |
| 8. | 0.5 | " | " | " | red |

The difference between six and seven is very small compared to the magnitude of the difference between two and four, or three and five, for example.

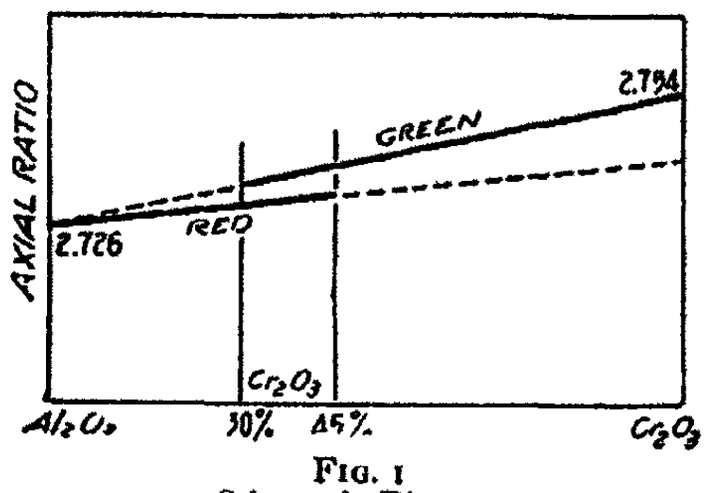



FIG. 1
Schematic Diagram

A study of these axial ratio relations offers a possible clue as to the conditions under which the red modification of chromic oxide will be formed in a given mixture and the conditions under which the green modification may occur in the same mixture. In Fig. 1 we have plotted axial ratios against composition. The curves, of course, do not represent absolute values of axial ratio but are constructed from the following qualitative deductions drawn from the tables above.

1. In the red crystals the axial ratio increases with chromic oxide content.

2. In the green crystals the axial ratio also increases with the chromic oxide content.

3. Since we are dealing with alpha alumina in both cases the curves must obviously meet at 100 percent alumina.

4. The quantitative values of pure alumina and pure green chromic oxide are fixed.

5. The approximate amount of divergence shown is justified by three of the qualitative observations: namely, the axial ratio of

30 percent green is greater than 30 percent red

45 percent green is greater than 45 percent red

30 percent green is greater than 45 percent red.

A consideration of the color change of samples of the various products as a whole and a microscopic examination of these same products finely powdered, make it evident that there is never a gradual change from red to green or from green to red. If both red and green existed in the same product and were intimately mixed, the color of the product should go through an intermediate brown or yellow color as the change from red to green, or vice-versa, occurred. It does not do this. Furthermore, the microscope does not reveal any brown or yellow particles in the powdered product. There is always a distinct, sharp change from red to green, or green to red, indicating that the red and green modifications do not occur in the same mixture at the same time. This is best explained by the assumption that in a mixture of a given composition the red form may occur normally at a lower axial ratio than the green and that there is a definite break in the axial ratio when one form changes to the other. This fact has been experimentally shown for mixtures containing between 30 and 45 percent of chromic oxide at least, and is also brought out by the curves in Fig. 1. We may assume, then, that, as chromic oxide is added to alumina, the red modification is normally formed up to thirty percent chromic oxide, and the axial ratios of the mixed crystals follow the red curve. At thirty percent, if the atmosphere in which the fusion is affected be reducing, we have a sharp change to the green modification accompanied by a break in the axial ratio of the crystal. Apparently the red form is stabilized by the alumina and, having an axial ratio more nearly equal to that of alpha alumina than has the green form, it occurs most readily at low concentrations of chromic oxide and would tend to form at any concentration. As the chromic oxide content is increased, however, there comes a point where there is not a sufficient amount of alumina to stabilize the red modification and so it jumps over into the green form. This change may be retarded to 45 percent chromic oxide instead of 30 percent, for reasons not definitely known, if the fusion be done in an oxidizing atmosphere. Above 45 percent of chromic oxide there is not a large enough proportion of alumina present to hold the chromic oxide in the red modification, and as it goes over into the green form the axial ratio relation jumps over on to the corresponding curve in the diagram. The portions of the curves filled in with solid lines have been qualitatively determined in these experiments. The conditions under which points on the dotted portion could be realized are not known as yet.

The red modification is of the same crystal form as alpha alumina. If it were not, new lines would appear in the diffraction pattern of a mixture containing as high as thirty percent chromic oxide which did not belong to the pattern of alpha alumina. Theoretically, then, red chromic oxide is isomorphous with alpha alumina and forms a continuous series of solid solutions with it. Green chromic oxide is also isomorphous with alpha alumina and forms a second continuous series of solid solutions with it. In practice, up to the present neither of these complete series has been realized and we cannot consider green chromic oxide as being isomorphous with alpha alumina in the usual sense. It forms solid solutions up to a certain point and then shifts over

to the red modification; so we really have a portion of each of the continuous series of solid solutions combining to form a discontinuous series. We have in this discontinuity definite evidence of the existence of a difference in a second physical property of the two modifications; namely, the axial ratios of the crystals. This clears up the apparently unreasonable behavior of chromic oxide toward alpha and beta alumina. It was found that alpha alumina had the same crystal structure as green chromic oxide, while beta alumina had a structure entirely different; and it was difficult to see why the normally green oxide should not dissolve green in the crystal which it most closely resembled. The answer is obvious when we know that there is a red modification of the chromic oxide which has a structure more nearly identical with that of alpha alumina than has the green. The reason why chromic oxide should dissolve in beta alumina as the green modification at low concentrations is not known. A study of the change in crystal structure and color with varying amounts of chromic oxide might throw light on this point.

Apparently at the alumina end of the curve the effect of a reducing atmosphere is not strong enough to pull the red modification over into the green. There is one possible instance in nature, however, where this may have been done. Mr. Sosman, of the Geophysical Laboratory, reports that the Oriental Emerald, the green form of corundum, is alpha alumina and not beta. This being the case, and if the color of the Oriental Emerald be due to chromic oxide, the axial ratio of the crystal must have been shifted to the curve for the green modification, either through peculiar conditions of formation or through the presence of a small amount of a third constituent which would cause a slight change in the crystal lattice without changing its form. We have not been able to find any analysis of this green corundum in the literature to confirm the presence of this third constituent. The color has been attributed by some to traces of iron and titanium which are said to produce yellow and blue respectively,[1] and by others to the presence of chromium.[2] There is no final evidence in proof of either conjecture, however, and the view that it is colored by the green modification of chromic oxide, because through some added influence its axial ratio has been brought within the range where the green modification may normally occur, is as justifiable as the other.

It was thought advisable, therefore, to investigate the possible effect of a third constituent on a mixture of alpha alumina and a small percentage of chromic oxide. This third constituent need not be of the same crystal form as the two oxides, provided it forms solid solutions with them. It has been shown in the case of several alloys especially, that a metal may dissolve in another of entirely different crystal form and in so doing shrink or stretch the lattice of the solvent up to a certain concentration, when the crystal lattice jumps over to that of the solute, which then becomes the solvent.[3] The same process is conceivable in the case here being considered.

[1] G. P. Merrill: U. S. National Museum Bull. **118**, 1.

[2] Kraus and Holden: "Gems and Gem Materials," p. 121 (1925); Doelter: Monatsheft, **29**, 1145 (1908).

[3] Bain: Chem. Met. Eng., **28**, 21 (1923).

In the case of aluminum and chromium oxides few oxides are available with a boiling point high enough to make them of any value in the method of fusing employed. When the powdered mixture is heated with the oxy-hydrogen flame the low boiling oxide tends to volatilize before the alumina and chromic oxide are fused. It was found that calcium fluoride or lime would change the color of a 97 percent alpha alumina and 3 percent chromic oxide from red to green, so the conditions accompanying this change were investigated.

When a mixture containing 30 percent calcium fluoride, 3 percent chromic oxide and 67 percent alpha alumina was fused, the product was green. It was found that the color changed from green through brown to red when the duration of the heating was increased. Since the melt boiled during the heating, the change of color was doubtless due to a decrease in the calcium fluoride content, the latter being lost by volatilization. It was found that approximately thirty percent of calcium fluoride was the least that would produce a green color if the oxides were mixed directly. If the initial mixture is made up of chromic oxide and hydrous aluminum oxide which has simply been dried, 10 percent of calcium fluoride will produce the green form. We know that the latter mixture fuses more readily and it is probable that because of this fact less calcium fluoride is volatilized before fusion is complete than with the straight oxide mixture. X-ray diffraction patterns were made of both of these green products compared with products containing the same amount of chromic oxide but no fluoride, namely,

3 parts $Cr_2O_3$; 87 parts $Al_2O_3.3H_2O$; 10 parts $CaF_2$ (green)
3 parts $Cr_2O_3$; 97 parts $Al_2O_3.3H_2O$ (red)
3 parts $Cr_2O_3$; 67 parts $Al_2O_3$; 30 parts $CaF_2$ (green)
3 parts $Cr_2O_3$; 97 parts $Al_2O_3$ (red)

The patterns show evidence of a compound being formed when the calcium fluoride is added. A new set of lines has appeared, although the alpha alumina lines are apparently still present and of greater intensity than the new lines. What is more, an inspection of the film makes it plain that these alpha alumina lines have been displaced in the direction to favor the formation of the green; that is, the crystal lattice has been stretched. The crystals are evidently in a state of change and the concentration of each form is rather low because it required an exposure of 2500 milliampere-hours to reproduce the lines of an intensity comparable with the intensity of the alpha alumina-chromic oxide half of the film obtained in 250 milliampere-hours.

It was found that by using lime instead of calcium fluoride the same color changes could be reproduced; but since the lime did not volatilize, the composition of the product after fusion could be known approximately. The following mixtures were fused in an oxidizing atmosphere.

| Percent $Cr_2O_3$ | Percent $Al_2O_3$ | Percent CaO | Color |
|---|---|---|---|
| 3.0 | 97.0 | 0.0 | red |
| 3.0 | 92.0 | 5.0 | reddish brown |
| 3.0 | 87.0 | 10.0 | brown |
| 3.0 | 82.0 | 15.0 | light green (almost colorless) |
| 3.0 | 72.0 | 25.0 | light emerald green. |

It is interesting to note that the progress of change from red (or bluish-red) to green differs in the two types of series investigated. In the first series, recorded in the table on page 1447, where the relative proportions of chromic oxide and alumina are varied, we have a sharp change from the red to the green color. An occasional grayish mixture examined under the microscope proves to be a mixture of bluish-red and green particles. These mixtures of color are rare, however, and occur only in those products whose composition approaches the value where the red normally changes to green. For the most part the products when examined under the microscope appear to be made up of all green or all red particles and these are a constant shade of red or green right up to the changing point regardless of the varying amount of chromic oxide in the mixture. There is no suggestion of an intermediate brown color in any case. With the lime series we get a gradual change of color from red through brown to emerald green. This is a natural progression since we know that a dilute mixture of green and red in the proper proportions will produce yellow by transmitted light.[1] Moreover, it has been found that in the system aluminum oxide-calcium oxide a compound of the formula $3CaO.5Al_2O_3$ is formed when 24.8 percent of lime has been added.[2] The solid then contains two phases; one the pure aluminum oxide and the other the compound. It is safe to assume that in the mixture containing twenty-five percent of lime we have practically the pure compound, and we can therefore state that chromic oxide colors this compound green. On the other hand, we know that the red modification of chromic oxide will occur in the alumina. We should expect intimate mixtures of these two substances, therefore, to behave the same as red and green chromium solutions and transmit a yellow or brown color when superimposed in the proper proportions.

Applying this argument to the first series (where the chromic oxide is varied), it would seem that an intermediate brown color was more to be expected than in the lime series. In the former we have a series of solid solutions while in the latter series we have two phases. One would expect that the homogeneity of the former would cause the color change to be more gradual. A gradual change would not be in keeping with the results which have already been recorded, however, It has been clearly shown that in the two component system $Al_2O_3$-$Cr_2O_3$, both forms of chromic oxide cannot coexist in the same product because of a discontinuity in the axial ratio of the mixed crystals in which they occur. Occasionally a product was found containing

[1] Rayleigh: Nature, 3, 234 (1871).

[2] Rankin and Wright: Am. J. Sci., 39, 1 (1915).

between 30 and 45 percent of chromic oxide which, when examined with the microscope, was found to contain a mixture of red and green particles. This is doubtless the result of slight local variations in the fusing atmosphere, however, because we know that between these limits of composition the form of chromic oxide which occurs is very sensitive to the fusing atmosphere.

Returning again to the discussion of the results given in the table on page 1447, it may be seen that the color of the products containing 20 percent or less of chromic oxide are affected slightly by the atmosphere in which the fusion takes place. The effect is comparatively slight, however. It is not a case of going from red to green at the lower concentrations as claimed by Watts[1] and others. The results agree with those found by Lecoq de Boisbaudran,[2] who found that his product tended toward a violet color when it was fused in hydrogen or mixed with a certain amount of sugar or some other organic substances; while when calcined in air it was red. It is interesting to note that the natural ruby occurs in shades varying from the rarest and most desirable "pigeon's blood" red to a lilac or violet red. We may well conclude that the atmosphere in which they were fused was responsible for this variation. Again, in the chrome-tin pink used in the ceramics industry we find the claim made that the source of the chromium affects the shade slightly.[3] This is improbable. It is much more reasonable to suppose that the atmosphere of the kiln varies slightly, thus causing a variation in color. Of course in some cases it is better to account for this on another basis. It is claimed, for example, by Purdy and Brown, that the chromium gives a redder product if it be added as potassium dichromate. It has been noticed in this work that if the mixture to be fused be made directly from the solution of alum and chrome alum by simply evaporating them to dryness, the resulting products of low chromic oxide concentration are more red than the corresponding ones prepared from the precipitated oxides. It is evident, then, that the presence of a very small amount of potassium oxide favors or intensifies the red color, and the addition of potassium dichromate would furnish this potassium oxide.

It will be shown, later in this paper, that chromous oxide is blue. The changing of the color of a mixture of chromic oxide and aluminum oxide from red to bluish-red in a reducing atmosphere suggests that a certain amount of the chromic oxide may be reduced to chromous oxide. This would account satisfactorily for the observed stretching of the crystal lattice by the reducing atmosphere. That is, the formation of chromous oxide in the crystal could have exactly the same effect on the size of the lattice as the addition of a third constituent would have. The shift of the lattice is due to the presence of chromic oxide and not to a change in the aluminum oxide. To check this, an X-ray diffraction pattern was made of two samples of aluminum oxide, one fused in a reducing atmosphere and the other fused in an oxidizing atmos-

[1] J. Am. Ceramic Soc., 13, 301 (1911).
[2] Compt. rend., 107, 468 (1888).
[3] Purdy and Brown: J. Am. Ceramic Soc., 11, 228 (1909).

phere. The lines of the two are absolutely parallel on the pattern. It is perfectly logical to assume that some chromous oxide is formed in the mixtures of higher chromium content which are green. The small amount of chromous oxide which is ordinarily formed would not affect the green color to a noticeable extent as it does the lighter and less saturated red color. If the explanation suggested be the correct one, it would seem as though a strong reducing agent should reduce the chromic oxide quantitatively and change the color of the alumina to a typical sapphire blue—the color of chromous oxide. No sample was heated in the oxy-hydrogen flame for more than five minutes and in that time no noticeable deepening of the blue color occurred. The sample referred to on page 1443, however, which was heated for about thirty minutes in a strong reducing atmosphere of carbon monoxide, was decidedly more bluish than those heated for only a few moments. There is a possible connection here with the results set forth on page 1447 in the table and the curves on page 1449. We know that the alumina is not influenced by the atmosphere but the chromic oxide is. Therefore, as the chromic oxide content of the mixture increases we should expect the mixture to become more sensitive to differences in the atmosphere in which the fusion is carried out. Starting with a small amount of chromic oxide in alumnia, the formation of any chromous oxide is strongly inhibited by the alumina, since the chromous oxide will necessarily have a different crystal structure than the alumina. It will be shown[1] that chromic oxide may be completely reduced to chromous oxide in a beryllium aluminum silicate which proved to be amorphous. As the amount of chromic oxide increases, however, the amount of oxide capable of being reduced increases and the proportional amount of alumina which tends to prevent this reduction decreases; and hence the mixture is more sensitive to changes in the atmosphere. The fact that the 30 and 45 percent chromic oxide mixtures even when heated in the oxidizing flame are sometimes slightly bluish-red points to this explanation as the logical one; since, with the crude method used to control the atmosphere, portions of the melt could well come under a reducing influence and would be apt to react to it in some degree within this sensitive range. This explanation, of course, is based on the assumption that chromous oxide has a greater stretching effect on the crystal lattice of alpha alumina than has chromic oxide. The assumption is substantiated by the qualitative observation that the mixture containing fifteen percent chromic oxide and fused in an oxidizing atmosphere to form a red product, has a slightly smaller axial ratio than the same mixture fused in a reducing atmosphere with the formation of a bluish-red product. In a word, the above discussion is simply another way of putting the conclusions already stated: that the alumina has a stabilizing effect on the red modification of chromic oxide up to a certain point, beyond which it is present in too small an amount to prevent the change into the green form. It goes one step farther, however, in suggesting why, within certain limits, the alumina may or may not be able to stabilize the red modification, depending on the condition of the atmosphere during the fusion.

[1] Page 1463.

It has long been known that the ruby, either natural or synthetic, turns green at a comparatively low temperature when heated and remains green as the temperature increases until it becomes red hot. On cooling, it goes through this same green stage and does not assume its characteristic red color until nearly cold.[1] No satisfactory explanation of this phenomenon has been offered and it remains as much of a mystery as ever. It cannot be a temperature reaction from a body transparent to red and absorbing green, because the color change occurs at too low a temperature. Of course several possible explanations at once come to mind in view of the results presented in this paper. We might assume that the chromic oxide is changed from the red to the green modification by an increase in the axial ratio of the alpha alumina as heat is applied. If this were the case, however, one would suppose that by quenching, the green modification would be retained. Quenching does not accomplish this. Furthermore X-ray powder data indicate that the only change which takes place when alpha alumina is heated, aside from a regular increase in intensity of all lines, is an abnormal decrease in the intensity of the line for the $(111)_1$ plane.[2] These facts also eliminate the possibility of beta alumina being formed at the higher temperature which is instable at ordinary temperatures.

In a further attempt to solve the riddle, the effect of cathode rays on the following samples was observed as they were heated.

1. Alpha alumina 0.5 percent chromic oxide (red)
2. Beta alumina 0.5 percent chromic oxide (green)
3. Alpha alumina (white)
4. Beta alumina (white)

Number one showed the typical ruby fluorescence spectrum[3] which persisted as the powder was heated to a dull red heat, although the lines gradually faded until only the brightest red line was faintly visible. At the same time the point of maximum brightness of the band shifted well into the green. Number two did not show any ruby lines but instead a red band (about $700\mu\mu$-$600\ \mu\mu$) and a green band (about $570\mu\mu$-$500\mu\mu$) approximately equal in intensity and extent. These bands gradually merged with a rise in temperature. Number three showed a green band ($580\mu\mu$-$500\mu\mu$) which gradually faded on heating. Number four also showed a green band, narrower and more intense than that of the alpha form. Neither showed any lines or bands in the red. Samples one and two were examined spectroscopically by Dr. Papish who reports the impurities as follows:

Alpha—Si, large trace; Mg, Fe, Na, Mn, traces.
Beta—Na, large quantity; Mn, Fe, Si, traces.

The only difference is that the red alpha sample contains a trace of magnesium which the beta does not contain. The significant difference in the spectra of

[1] Bauer: "Edelsteinkunde," page 334.
[2] Wyckoff: "Structure of Crystals," page 412 (1924).
[3] Crookes: Proc. Roy. Soc., 42, 25 (1887).

the two is that the alpha form gives the typical red lines of the ruby spectrum, while the beta form gives only a red band and no red lines. Hence there is nothing in the analyses to account for the absence of the red lines in the beta form spectrum and the presence of the red band. The difference in the spectra must therefore be due to a difference in the chromic oxide and adds weight to the evidence that it exists in two modifications. The results do not give any help on the problem of the change of color from red to green with an increase in temperature, however.

Although the reason for the red color in synthetic mixtures of aluminum oxide and chromic oxide is clear, there are facts in the literature concerning the natural ruby which seem to create the necessity for another explanation of its color. It has always been taken for granted that the color of the natural ruby was due to a minute trace of chromium—or some other oxide[1]; and no definite figures for the amount of chromium are given even in detailed analyses.[2] On the other hand, Verneuil uses 2.5 percent of chromic oxide in making artificial rubies to reproduce the color of the natural stone.[3] A small trace of chromium does not color aluminum oxide when the two are artificially fused together. Bordas[4] believes that the color of the natural stone has been intensified by the action of radium. He fused aluminum oxide containing a trace of chromium and found it to be colorless, but on exposure to radium bromide it turned rose colored. It is well known that the coloring power of a colloid is relatively high and it might be that the color of the natural ruby was due to colloidal chromium. The action of radium is generally counteracted by heat, and if radium were responsible for the color we should expect the ruby to bleach when heated. Furthermore, heat should bleach a stone colored by colloidal chromium, since it would tend to agglomerate the particles. A natural ruby was heated up to fusion without any fading of the color. When it actually began to fuse, fading occurred locally at the part of the stone in the hottest part of the flame. A microscopic examination of this area showed it to be pitted, indicating that boiling had occurred on the surface and that the fading was doubtless due to the volatilization of chromic oxide. A synthetic ruby containing between two and three percent of chromic oxide was prepared to duplicate as nearly as possible the intensity of color of the natural stone, and this was heated in the same way. The same amount of fading occurred in the same relative position of the stone and was apparently due to the volatilization of chromic oxide. A natural ruby crystal examined with the ultramicroscope showed no evidence of a colloidal suspension. It appears, then, that the cause of the color must be the same in both the synthetic and the natural rubies, and it follows that the coloring agent must be

[1] G. F. Kunz: "Gems and Precious Stones," p. 39 (1892).

[2] W. Goodchild: "Precious Stones," p. 187 (1908); Max Bauer: "Edelsteinkunde," p. 329; L. Smith: Ann. Mines (4) 18, 289 (1850); Pfeil: Centralbl. Min., 1902, 145.

[3] Ann. Chim. Phys., (8) 3, 20 (1904).

[4] Compt. rend., 145, 800 (1907).

present in equal amounts in the two to produce the same intensity of color. Accordingly, a spectroscopic analysis of a natural ruby was made with the following result:

Weight of sample 6.0 mg.
Actual weight of chromium between 0.01-0.1 mgs.
Estimated weight of chromium 0.04 mg.

Calculating this on a chromic oxide basis we find that the particular natural ruby which was analyzed certainly contained between 0.5 percent and 5.0 percent of chromic oxide, and the estimated content is 2.5 percent. This is far from the slight and supposedly undetectable trace of chromium which the ruby was thought to contain and shows without a doubt that the natural ruby is identical in this respect, as in all others, with the artificial stone. Incidentally, the spectroscopic analysis showed only a trace of iron and the published analyses of ruby report varying amounts of ferric oxide up to 1.5 percent. This leads one to suspect that the chromium was in some way mistaken for iron in the older analyses.

Another series of solid solutions which behaves in a manner similar to the solid solutions of alpha alumina and chromic oxides has recently come to our attention. In making photographic emulsions the practice is to add 5 percent of silver iodide to 95 percent of silver bromide. It has been noticed that the color of the resulting mixture is a darker yellow shade than either of the pure constituents, and until the present this has not been explained. Trivelli[1] made a crystallographic study of these solid solutions, however, and found that as silver iodide is added to silver bromide, the resulting mixed crystal is in the cubic system, which is the form of pure silver bromide. The addition of silver iodide shrinks the cubic lattice in proportion to the amount added. For a considerable intermediate range the results are uncertain. Silver iodide is hexagonal in the stable form and the mixed crystals containing seventy percent of the iodide, or more, assume this structure. It is known further that at about 140°C. the yellow, hexagonal silver iodide changes into an orange-red, cubic form.[2] Obviously the mixture containing 5 percent of silver iodide is of a deeper shade than the pure yellow iodide because the iodide is present in this mixed crystal in the cubic form. The silver iodide, then, is a substance which exists in two modifications; the form stable at room temperatures is hexagonal, the form stable above 140° C. but metastable at room temperatures, is cubic. This metastable, cubic silver iodide in this case is stabilized at ordinary temperature by adding to it a sufficient amount of another cubic substance, the silver bromide, whose crystal structure it more closely resembles than does the hexagonal, stable form. This case offers a beautiful analogy to that of the two chromic oxides and alumina. There we have a red form, metastable at ordinary temperatures but stabilized by the presence of a sufficient amount of alpha alumina, whose crystal form it re-

[1] Rec. Trav. chim., 42, 714 (1923).
[2] J. W. Mellor: "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 3, page 427.

sembles more closely than does the green chromic oxide. We have noticed that when the silver iodide changes over into the cubic form there is some change in color from yellow to a deeper yellow. Then, as the temperature rises, the color continues to change gradually to a deep orange. A mixed crystal having the composition 85 percent silver bromide and 15 percent silver iodide is of a deeper yellow than pure silver bromide; and it is also darker than the cubic form of silver iodide when it is at a temperature only slightly above the transition temperature. It is evident, then, that the silver bromide not only stabilizes the cubic form of silver iodide, but stabilizes it in the color which it would have at a temperature considerably above the transition temperature. It is impossible to preserve this deep orange color of the pure iodide by quenching. The behavior of zinc oxide toward heat offers a similar case. That changes to a yellow color as the temperature rises and this yellow cannot be maintained by quenching. The green color of the ruby, obtained by heating it, also cannot be preserved by quenching and it is very possible that when someone finds the explanation for the behavior of any one of these three substances toward heat they will have the answer for all three. At any rate, the behavior of the ruby in this respect is not unique.

Still another case of a series of solid solutions analogous to the aluminum oxide-chromic oxide mixtures is that of the discontinuous series of solutions of mercuric iodide and mercuric bromide. This has been studied by J. S. van Nest[1] and others.[2] Red, tetragonal mercuric iodide is stable at temperatures below 128°C., while yellow, rhombic mercuric iodide is stable above that temperature. Mercuric bromide is white, and rhombic in crystal form. Van Nest obtained an unbroken series of yellow mixed crystals of mercuric iodide and mercuric bromide varying in composition from zero up to 97% of mercuric iodide. That is, the yellow form, stable at high temperatures, is stabilized at ordinary temperatures by the presence of a sufficient amount of rhombic mercuric bromide whose crystal form it more closely resembles than does the red, tetragonal form. With less than 3% of the bromide, its influence is not sufficient to stabilize the high temperature form and only red crystals occur. It is evident that the analogy between this case and the alpha alumina-chromic oxide series is even more complete than the case of silver bromide and silver iodide to which reference has already been made. In the case of the silver halides we have merely a change in shade of the yellow color when the series of solid solutions is broken. With the mercuric halides, however, a marked change in color from red to yellow gives evidence of the break in the series. In the case of the aluminum oxide and the two forms of chromic oxide we have a change in color no less distinct from red to green. My attention was drawn to this case by Dr. D. T. Wilbur.

## Summary

The results of this section are as follows:

1. The red color imparted to alpha alumina by chromic oxide is not due to colloidal chromic oxide.

[1] "Beiträge zur Kenntniss der Quecksilberhalogenide" (1909).

[2] Mellor: "Treatise on Inorganic and Theoretical Chemistry," 4, 904.

2. It is not due to a higher or lower oxide of chromium.

3. It is not due to a change in the concentration of the chromic oxide as is the case with solutions of chromic salts.

4. The red color is due to a second modification of chromic oxide, of the same crystal structure as the green modification and alpha alumina, whose axial ratio is nearer to that of alpha alumina than is the axial ratio of the green modification. Therefore, the red modification tends to form when chromic oxide is added to alpha alumina and does form under ordinary conditions up to a certain point, beyond which the effect of the alumina is not strong enough to stabilize it.

5. The occurrence of the red or green modification depends on the value of the axial ratio of the mixed crystal. There is a discontinuity in the change of the axial ratio with change in chromic oxide content when one modification changes to the other. There is also a marked difference in the axial ratio of a mixed crystal containing the red form of chromic oxide and a crystal containing the same amount of chromic oxide in the green form. This change in axial ratio may be affected in two different ways.

a. By changing the chromic oxide content.

b. By a variation of the atmosphere in which the fusion is carried out, for mixtures containing between 30 and 45 percent of chromic oxide.

6. It has been indicated that the two modifications differ in at least three properties; namely color, axial ratio of the crystals, behavior when exposed to cathode rays.

7. The bluish-red color of some varieties of ruby is due to the reduction of a limited amount of the red chromic oxide to blue chromous oxide.

8. The chromic oxide content of the natural ruby has been determined as approximately two percent and the cause of the color of the natural ruby has thereby been shown to be the same as that of the artificial ruby.

9. The temporary change of color of the ruby to green on heating cannot be explained by any of the above results and must still be accounted for.

10. When there is no stabilization of the red modification, as in the emerald, a green color is obtained with very low concentrations of chromic oxide.

## THE SAPPHIRE

There is little agreement among investigators as to the cause of the blue color of the sapphire. Goodchild[1] assumes it to be due to a trace of chromium, as does Doelter;[2] although the latter finds that the behavior of sapphires when heated varies with their source, and therefore suggests that there may be more than one substance which causes the color. Cattelle[3] states that the color may be caused by the presence of iron; while Verneuil[4] and Merrill[5]

[1] "Precious Stones," page 187 (1908).
[2] Monatsheft, 29, 1145 (1908).
[3] "Precious Stones," page 101 (1903).
[4] Compt. rend., 151, 1063 (1910).
[5] U. S. National Museum Bull., 118, 1.

assert that it is the result of a trace of titanium. Kraus and Holden[1] give an analysis of both natural and artificial (Verneuil) sapphires, the former containing, in addition to aluminum oxide, 0.92 to 1.95 percent of ferric oxide, depending on the source, and less than 1.0 percent of silica. According to this analysis the natural stone contains no titanium. Verneuil has made analyses of natural sapphires from three sources and finds that they all contain from 0.03 to 0.06 percent of titanium dioxide. Bauer[2] says the cause of the color is unknown, but suggests[3] that it is probably due to either iron or chromium.

The first note in reference to the production of the blue color of the sapphire artificially seems to be that of Sainte Claire Deville[4] who was working on the preparation of artificial rubies by heating a mixture of aluminum fluoride, chromium fluoride and boric oxide in a platinum crucible. He remarks that a small amount of chromium gives the typical ruby red, while a slightly larger amount produces the sapphire blue. The blue is attributed by him to this change in chromic oxide content or "perhaps to the state of oxidation." With a larger amount of chromic oxide he gets green. He admits, however, that the difference in chromic oxide content between the red and blue products could not be detected by the ordinary analytical means. Ebelmen[5] obtained two kinds of crystals in preparing artificial rubies—the ruby crystals and a larger quantity of bluish needles. The chromium may have been the cause of this color. Fremy[6] notes the occurrence of some red ruby crystals, artificially prepared, which are blue in the middle; and others that are red on one side and blue on the other. Kunz[7] describes several specimens of natural corundum which are both red and blue.

The problem came up in this investigation when it was noticed that many of the alumina-chromic oxide mixtures which were fused contained an appreciable number of vivid sapphire blue particles when examined under the microscope. The conditions favoring the formation of the blue could not be definitely established, except for the fact that the higher amount of blue appeared most frequently in the mixtures containing from 15 to 30 percent of chromic oxide. It is as likely to appear in a product which has been fused in an oxidizing flame as in one which has been fused in a reducing flame. It seemed unique in that it was always in isolated fragments, never forming part of a red, or bluish-red or green fragment. Even when observed through the microscope in a large piece of the substance before it had been powdered, the blue would appear as a distinct and separate unit embedded in the lump which served as a matrix. The total amount of blue, estimated by counting the number of particles in the field of the microscope in a given sample, was

[1] "Gem Materials," page 100 (1925).
[2] "Edelsteinkunde," page 356.
[3] Bauer: Z. angew. Chem., **22**, 2177 (1909).
[4] Compt. rend., **46**, 764 (1858).
[5] Ann. Chim. Phys., (3) **33**, 34 (1851).
[6] Fremy and Verneuil: Compt. rend., **111**, 667 (1890).
[7] "Gems and Precious Stones," page 46 (1892).

probably never greater than one to two percent. The color and degree of its saturation were always the same— an evenly distributed cornflower blue— regardless of the relative amounts of aluminum oxide and chromic oxide in the original sample.

It might be assumed that this blue color is due to a trace of titanium dioxide in the materials which does not diffuse throughout the mixture, but whose particles simply dissolve in the alumina immediately adjacent to them. To test this, the following mixtures were made up and fused. The aluminum oxide used is the alpha alumina employed in the mixtures with chromic oxide in which the blue particles occur.

| Percent $TiO_2$ in $Al_2O_3$. | Color |
|---|---|
| trace | gray with faint bluish tinge. |
| 0.5 | bluish gray |
| 1.0 | grayish blue, smoky |
| 5.0 | grayish blue, smoky |

A microscopic examination of the particles of all these mixtures reveals a mixture of colorless, fairly transparent particles and particles varying in color as indicated in the table. There is no suggestion of the cornflower blue color and the titanium dioxide apparently diffuses more or less evenly throughout the mass, since there are no isolated blue crystals in the product. The isolated flashes of blue observed in the ruby are therefore not due to titanium dioxide. Moreover, the mere fact that artificial sapphires can be made with titanium dioxide does not mean that this oxide is the coloring medium in the natural stone. Fremy[1] made artificial sapphires by coloring aluminum oxide with cobalt, but nobody has suggested that cobalt colors the natural sapphire.

The fact that mixtures of aluminum oxide and chromic oxide of low chromic oxide content are red when fused in an oxidizing atmosphere and bluish-red when fused in a reducing atmosphere, offers the suggestion that the blue may be the result of a reduction. Mixtures of aluminum oxide containing varying amounts of chromic oxide up to thirty percent were fused in a reducing flame and held at the fusion temperature for varying lengths of time and cooled at different rates. None of these factors seemed to have any consistent effect on the number of isolated cornflower blue particles in the product. Cooling to room temperature in an atmosphere of hydrogen did not increase their number. It was found, as has been noted before, that the sample containing ten percent of chromic oxide which was heated for thirty minutes in the Ajax induction furnace in a strong reducing atmosphere was decidedly more bluish than the others, although it contained no more of the isolated blue particles. Duboin[2] gives a receipe for making a blue glass colored by chromium. He states specifically that the fusion must be carried on in a reducing atmosphere. This work of Duboin's was repeated and a greenish-blue product obtained.

[1] Fremy and Feil: Compt. rend., 85, 1029 (1877).
[2] Duboin: Ber., 31, 1977 (1898).

The blue color was next discovered in a mixture of beryllium oxide, aluminum oxide and silicon dioxide in the proportion in which they occur in the emerald, and containing one percent of chromic oxide. It was found, moreover, that the production of this blue color required a reducing atmosphere. An oxidizing atmosphere produced green and no blue. Furthermore, upon heating in the oxy-hydrogen flame, the globule was seen to boil and the amount of the blue formed depended on the duration of this boiling. By increasing the proportion of oxygen in the flame the boiling could be stopped, showing definitely that the apparent boiling was an evolution of oxygen or steam resulting from a reduction in the globule. A single globule was changed from green to blue to green several times over by alternating the conditions of fusion between a reducing and a oxidizing atmosphere. The change in color cannot be due to a change in composition; since, if it were, the colors could not be reproduced at will after the heating and possible volatilization had continued for some time. The effect of varying the amount of chromic oxide was investigated and it was found that the blue color, though more saturated, was obtained in mixtures containing up to fifteen percent of chromic oxide. We did not go beyond this point. A curious result of the method of heating was observed in all of these cases. The blue color appears to rise toward the flame—or toward the top of the globule. That is, the upper portion of any bead after fusion is blue and comparatively transparent and glassy compared to the lower portion, which is green and opaque and granular in appearance. It is natural that the part toward the flame should be affected first; but if the bead be turned over with the green side up we would expect to have the entire bead blue after fusing. This is not the case. The blue and green apparently change places and we have the new upper side blue and the lower side green. As a result, it is practically impossible to get a uniform blue bead. It can be done by heating the second side only momentarily, although in this case the bead does not have the glossy, transparent appearance. It might be done by heating simultaneously from both sides. These results show beyond a doubt that chromium can impart a typical sapphire blue color to certain oxide mixtures at any rate, and that this blue color is due to chromous oxide. Furthermore, X-ray diffraction patterns of the green and blue beryllium aluminum silicates show both to be amorphous. As suggested elsewhere in this paper,[1] the fact that the mixture is not crystalline may explain why it is so easy to reduce the green to the blue in this case.

To return to the occurrence of this sapphire blue color in the artificial ruby, we have the effect of the blue brought to notice in two distinctly different ways. First as the isolated, vivid blue particles occurring in either an oxidizing or a reducing atmosphere. At present, no adequate explanation of the formation of these blue crystals can be brought foward. Several possible reasons have been considered and found wanting. For example, the alpha alumina is known to contain a small amount of beta alumina, and the chromous oxide might dissolve in that. This is not likely for two reasons. Beta alumina when

[1] Page 1455.

fused changes to the alpha form because the soda, which apparently stabilizes the beta form, is driven off; and secondly, the samples of beta alumina containing chromic oxide obtained from the Norton Company are green. These are made in a reducing atmosphere and hence should have been at least a bluish-green if the above assumption were true. It might also be argued that the chromous oxide formed is soluble in the chromic oxide-aluminum oxide melt to only a limited extent and therefore separates out as a second phase. If this were so, however, we should expect to find these blue flashes only in those samples which were already bluish-red in color, indicating that they were saturated with respect to chromous oxide. As has been noted, the blue particles found just as frequently in mixtures which have been heated in an oxidizing flame and have a pure red body color. Furthermore, if it were possible for the chromous oxide to separate out in a second phase, there is no reason why the change should not go further. All we can say definitely in regard to these blue particles, then, is to point out that chromous oxide is known to be exactly that shade of blue, at least in beryllium aluminum silicate mixtures containing from 1.0 to 15.0 percent of chromous oxide; and that titanium dioxide does not color alumina in that manner or with the shade of blue described.

In the second place, we have the effect of blue coming in when the color of the complete mass of the globule is changed from red to bluish-red by a reducing atmosphere. This is a perfectly consistent occurrence and may be duplicated at will. As has already been stated, this change in color is doubtless due to the formation of a limited amount of chromous oxide. So far, it has been impossible to cause a complete change of the red chromic oxide to blue chromous oxide. The reduction may be effected in the case of the emerald where we have an amorphous beryllium aluminum silicate containing the chromic oxide as the green modification. This tendency for the red chromic oxide to turn blue at least makes it legitimate for us to assume that the natural sapphire is colored by chromous oxide under conditions which we have not as yet been able to duplicate. We also have here at least a plausible explanation to account for the color of purple corundum, the Oriental Amethyst. It may well be a partially reduced product, an intermediate step between the red ruby and the blue sapphire. Its color has been attributed by Merrill[1] to the presence of traces of chromium, giving the red, and titanium giving the blue component. This is on the assumption that the amethyst contains titanium—which is not known—and that titanium does cause the blue color of the natural sapphire. Neither of these facts is very probable.

A possible duplication of the conditions used by nature to form these various colored corundums has been sought from time to time in the use of X-rays and radium emanation. Bordas[2] and Escard[3] claim that a ruby subjected to radium emanation turns from red to violet to blue to green to yellow.

[1] U. S. National Museum Bull., 118, 1.
[2] Compt. rend., 145, 710 (1902).
[3] Lumière Elec., (2) 22, 401 (1913).

Doelter[1] in a detailed description of many individual stones exposed to radium, records two rubies which went from red to a purplish-red and one which became more red. The experimental results, therefore are not consistent enough to assume that the action of radium on the ruby has produced the natural sapphire. The discrepancy in results may be due in part to the fact that radium emanation of different intensities was used in different cases. Unfortunately the strength is not stated in every case. Lind and Bardwell[2] insist that the ruby is not changed noticeably when exposed to 200 milligrams of radium for a considerable period of time. Most of those who have investigated the matter agree that, under the influence of radium, the sapphire changes from blue to green to a final yellow color. Of these investigators, Doelter alone has noticed a difference in stones in this respect as well as in their behavior toward heat. He states that several small Ceylon sapphires exposed to radium for as much as fifteen days underwent no change in color and were not bleached by heat. We may conclude that these sapphires which are stable toward heat and radium are colored by some stable metallic oxide, while those which are not stable may be colored in some other way.

Several small Ceylon sapphires were procured and their properties investigated. It was found that they did not lose their color when heated—at least not permanently. They did seem to fade somewhat when heated, but were just as blue after they were cooled again. When heated up to the melting point in an oxidizing atmosphere the sapphire turned to a reddish brown color. This is an interesting but slightly ambiguous result. If the blue color were due to chromous oxide, the oxidation product should be red chromic oxide; whereas if the blue color were caused by a blue modification of ferro-ferric oxide, the oxidation product should be the reddish-brown ferric oxide.

A spectroscopic analysis of another of these same sapphires revealed a surprising lack of impurities of any kind in the alumina, there being present only a small amount of iron, possibly a trace of titanium, and no chromium.

A casual inspection of these sapphires makes it plain, even to the amateur, that there is not as much coloring matter in them as in the ruby of a corresponding size. One gets the impression that the ruby is well saturated with the red color; while the blue of the sapphire, although dark in shade, gives the impression that the coloring matter is spread out too thinly to be very efficient, and is therefore present in smaller amounts than the coloring matter of the ruby.

All this discussion makes it obvious that the real cause of the color of the natural sapphire is as much in the dark as ever—in fact, much more so than one would guess after reading the statements common in the literature. For sapphires not bleached by heat the color may be caused by chromous oxide, although it was not found in the particular one we analyzed. It may be due to a blue ferro-ferric oxide, or possibly to titanium. It is certain that those sapphires of a deep blue or cornflower shade could not be colored by titanium,

---

[1] Monatsheft, **29**, 1145 (1908).
[2] J. Franklin Inst., **196**, 375 (1923).

but the smoky blue stones may be. As for those sapphires which bleach when heated, all we can say is that it is very improbable that their color is due to any of the causes just mentioned.

## Summary

The results of this section are:

1. Alpha alumina colored by red chromic oxide turns bluish-red when fused in a reducing atmosphere due to the formation of some blue chromous oxide. It remains to determine under what conditions this reduction could be carried to completion, giving a sapphire blue corundum.

2. The blue crystals observed in preparations of artificial ruby may be colored by chromous oxide because

a. It has been shown that chromous oxide is exactly that shade of blue, at least when dissolved in beryllium aluminum silicate.

b. There is no other impurity present in the mixture used which would produce that shade of blue.

3. The cause of the blue color of the natural sapphire is not known. It is very probable that the color of all sapphires is not caused by the same impurity.

## Acknowledgment

It is discouraging to one who enjoys a diversity of interests to hear from all sides that only through a narrowing of attention may one hope to become accomplished in his chosen field. It has been the writer's privilege, however, to work under the guidance of one who insists—and whose reputation most certainly proves—that in general an ever broadening viewpoint will produce better results than a narrowing one. Professor Wilder D. Bancroft, by his sense of humor, his ability to see the things of life with true sense of proportion and his evident belief that one need not take himself or his work too seriously at the expense of everthing else in order to be a good scientist, has maintained and increased the writer's interest in chemistry and in science, and has given to him a guide on which to base his future efforts.

The writer also wishes to thank Professor C. C. Murdock and Mr. H. W. Russell for their aid and advice in procuring the X-ray spectrograms; and Profesor J. Papish for making the several spectrographic analyses.

*Cornell University.*

# RHYTHMIC DIURNAL BANDS OF GOLD AND PLATINUM IN SILICIC ACID GEL*

BY EARL C. H. DAVIES AND VICTORIAN SIVERTZ[1]

## Introduction

The directions of Harry N. Holmes[2] for rhythmic bands of gold are as follows.

"To 25 cc. of a mixture of equal volumes of 1.16 density water glass and 3 N sulphuric acid was added 1 cc. of a 1 per cent gold chloride. The solid gel formed in a day or two and was then covered with a saturated solution of oxalic acid (about 8 per cent). As the oxalic acid diffused into the gel the gold chloride was reduced. A wonderfully beautiful series of colored bands of colloidal gold developed, with sparkling golden crystals scattered throughout the gel. The upper layer of the first bands was red, the next blue and the next green. A comparatively clear gap below this series was followed by another red-blue-green zone. Usually after the first few rainbows the red was omitted. A dozen or more such complex bands in a test tube were not uncommon, the upper bands measuring about 1 cm. in depth."

The Svedberg[3] has shown that, when viewed by transmitted light, growing crystals of gold pass through the following color changes: red, blue, green, and then yellow. Although colloids diffuse through gels slowly or not at all, depending upon the size of particles and the openness of the gel, we were, nevertheless, curious to see if the red gold, first produced in the upper layer of Holmes' rainbow bands, gradually turned to blue as it diffused deeper into the gel. It was a sort of scheme for tagging crystals to see how they grew.

In fact early in 1922 one of the present authors became convinced that in the usual Liesegang ring formation the phenomenon could be explained by a mechanical theory of delayed diffusion similar to that of Holmes, but that particles being precipitated gradually grow in size until they fill the capillary-like spaces in the gel. Then these bands act as filters which collect the larger particles but through which the diffusing electrolytes or other smaller particles may pass.

If this is true that these particles do gradually increase in size until they become large enough to clog the capillary-like spaces, and if Holmes' rainbow bands were due to the Liesegang phenomenon, then it seemed that these rhythmic bands of colloidal gold might be ideal for following changes in size of particles. Thus as the oxalic acid diffused into the gel containing the gold chloride we might then expect the small particles of red gold to first appear. Then these same particles might continue to diffuse and become blue, unless and until they became large enough to fill the capillaries.

---

[1] For the use of the term "diurnal" cf. Emil Hatschek: Proc. Roy. Soc., 99A, 499 (1921).

[2] Holmes: J. Phys. Chem., 21, 709 (1917); J. Am. Chem. Soc., 40, 1187 (1918); "Laboratory Manual of Colloid Chemistry," pp. 95-100 (1922).

[3] Ostwald: "Theoretical and Applied Colloid Chemistry," 60 (1917).

With this in mind Holmes' directions were followed, but a strip of paper was glued on the tube so that an exact record of distances and colors could be made. The tube was carried around for frequent observation in bright light. Red gold was produced continuously until night, but only yellow gold during the night, whereas, in the morning, red gold again formed, even as we watched the gel in bright light. Between this last red zone and the colored gold of the previous day was a clear space of 1 cm. containing many sparkling, yellow gold crystals.

It was evident that these were not true Liesegang rings, because the latter should be formed by diffusion in a gel and in the dark as well as in the light. Since then hundreds of combinations have been tried with silicic acid gel varying from 0.7 N to slightly basic and with nitric, hydrochloric, sulphuric, and acetic acids used with the water glass in making the gel. Other reducing agents have been used in place of the oxalic acid, but in no case has it been possible to get the colored rhythmic bands, described by Holmes, except by a combination of changing light and diffusion.

Moreover we believe our experiments show that the gold crystals do not move from the places in which the nuclei of gold are first formed. It is the molecular gold oxalate which diffuses to these nuclei and it is not likely that Liesegang rings of gold will be made unless some gold salt is first obtained in rhythmic bands. Then the metal might be formed by a reduction of this salt.

Diurnal bands may be classified as real and pseudo. The real diurnal bands are illustrated by the experiment of Holmes. Later in this paper we give a general rule for their production as well as specific directions for making diurnal bands of colloidal platinum. The pseudo bands[1] are made much as a silhouette on a photographic plate. The portion of the gel exposed to bright light reduces. The portion of the gel, upon which the black shadow is cast, remains unreduced. Then instead of using a "developer" to remove the unreduced salt, the latter is allowed to diffuse, in the dark, into the reduced zones, where reduction continues in the dark. It is apparent that the multiplicity and beauty of the colors produced by the different degrees of dispersion of the gold would be fine for photographic reproduction of colors. We have previously shown[2] that the speed of reduction varies inversely with the wave length of light.

At least we have opened up an interesting field of clearly defined rhythmic bands and since, as long as our earth has existed, night has followed day we may look with interest among the products of nature's laboratory for rhythmic bands which may not have been understood or which may have been erroneously attributed to the Liesegang phenomenon.

When the reduction of the gold oxalate takes place in the dark there is apparently about one yellow crystal for each cubic millimeter of gel. Assuming that there are 200 atoms of gold in each colloidal particle of red gold we

[1] Bands were made instead of more intricate patterns in order the better to study their development.

[2] J. Am. Chem. Soc., 45, 2262 (1923).

would have about three trillion times as many particles of red gold as if the reduction had taken place, in the dark, to give yellow gold. It is, then, easy to understand how in the dark reduction can give crystals which grow through all the stages from single or double atoms up to the macroscopic yellow crystals without at any time appearing red or blue. The nuclei formed in the dark are so few that it would take a gel of the thickness of more than six times the distance around the earth to give the same intensity of red as would be produced, in bright sunlight, in a layer 0.1 mm. thick.

When the gold oxalate reduces in the dark we have found that it takes as long as about 50 days (Table II, tube 17) for complete reduction in the dark. This would make an average of about sixty five million molecules of gold oxalate decomposing in each cubic millimeter of gel in one second. Although this sounds big, such a reaction is really very slow. We believe that a relatively few scattered molecules of gold decompose in the dark and give nuclei of gold to which surrounding gold oxalate diffuses and is reduced at or very close to these nuclei. The latter gradually grow as more and more gold oxalate diffuses to them. The nuclei remain "in situ." There is no reason to suppose that the metallic gold migrates while it grows. It is not a case of "the rolling stone gathering the moss." The nucleus is the first stone of a structure built bit by bit into the finished crystal of yellow gold. Now this is just where we believe it differs from Liesegang rings. With the latter careful and continuous observation shows distinct evidence of growing particles being carried along until the pores are clogged. Sometimes the particles first precipitated are also peptized[1] and redistributed into secondary bands. On the other hand we believe that at least the gold and platinum nuclei remain "in situ" and develop by growth from the gold or platinum oxalate diffusing to these nuclei. Whether or not this is general for diurnal bands we hope to prove by work now in progress.[2]

The case of our diurnal bands is thus widely different from that of the usual Liesegang rings where growing crystals travel with the stream of diffusing electrolyte; for with our diurnal bands growth starts not at the time of chemical reaction between two different chemicals. The chemical reaction first takes place and gives a molecularly soluble substance like the gold oxalate. This diffuses to zones of lower concentration of gold oxalate but no clustering or growth takes place until light or some other factor causes nuclei of the new substance (the gold) to form. The nuclei then become the centers of zero concentration of gold oxalate toward which the latter diffuses.

Beside working out conditions for making the real and pseudo diurnal bands of platinum in silicic acid gel we have made very beautiful pseudo diurnal bands of red gold. The study of the photo-chemical after-effect in the reduction of the gold salt shows clearly that the reduction takes place before it becomes visible. The experiments on the aging of the gold oxalate-

[1] Davies: J. Am. Chem. Soc., 44, 2699 (1922).

[2] LeRoy V. Clark and one of the authors have recently made interesting diurnal bands in mercury salts and very pretty blue-green bands of ferro-ferricyanide. We hope to study these and other systems in more detail.

silicic acid gel show that the soluble oxalate salts, plus the auric chloride in the gel, cause more rapid reduction than when oxalic acid is used. Other experiments show that a gold oxalate-silicic acid gel 11 days old reduces from 2 to 13 times faster in bright sunlight than the same mixture does in the same bright sunlight but just after mixing and before setting has taken place. The lower value is for a gel with pH 0.05 while the latter had a pH of 0.39. Thus the "ripening" in the dark was greater with the gel of less acidity.

*Experimental.* Among the many combinations tried in continuous artificial light, in the dark, and in intermittent light, the following are typical.

*Red Gold in Silicic Acid Gel.* In 10 cc. of 3N HCl dissolve 0.25 g. of ammonium oxalate,[1] add 0.8 cc. of 1% gold chloride and stir into this mixture 10 cc. of water glass (d = 1.16). Cover with black paper and allow the gel to set for at least one day in a dark room. Quickly open it in bright sunlight and with a stopwatch record the time when color first appears. In bright sunlight the entire gel becomes a beautiful red in less than one minute.

An interesting and instructive modification of this is as follows. Before opening the above tube in sunlight have it covered with a grid of black paper which has been so cut that a 1 cm. slit alternates with a 2 cm. black covering throughout the length of the gel. Expose as before to bright sunlight until the red color appears at the openings. No red color will have been produced behind the 2 cm. zones which were left covered during exposure. The tube is placed in the dark for about 3 weeks, after which interval the covering is entirely removed and the gel exposed to bright sunlight. No red gold will appear in the "clear" zones. The width of the red zones and the distance between them depend upon the slits.

TABLE I

Reduction in sunlight of 0.0385% gold chloride in silicic acid gel, containing 0.111 weight molar oxalic acid and made with decreasing concentrations of HCl and increasing concentrations of water glass.

| pH | Acid normality of gel | cc. of 3N HCl in 20.8 cc. of gel | Water glass (d = 1.16) in 20.8 cc. of gel | ($T_o$) Minutes for red to appear before gel set | ($T_{11}$) Minutes for red to appear after 11 days in dark | $T_o/T_{11}$ |
|---|---|---|---|---|---|---|
| .05 | 2.085 | 15 cc. | 5 cc. | 11 min. | 4.9 min. | 2.24 |
| | 1.514 | 12 | 8 | 7.08 | 2.86 | 2.50 |
| .10 | 1.011 | 10 | 10 | 6.75 | 1.08 | 6.25 |
| .22 | 0.690 | 9 | 11 | 6. | .62 | 9.75 |
| .39 | 0.552 | 8 | 12 | 6.66 | .50 | 13.33 |
| 1.10 | | 7 | 13 | Reduced in the dark | | |

*Reduction to Red Gold is more rapid in the Gel than in the same Mixture before Setting.* A series of 6 gel mixtures was prepared with the chemicals shown in Table I. These were kept in the dark for 11 days. Then an exact duplicate of this series was made. The 12 tubes were then opened simul-

[1] Equimolecular concentrations of oxalic acid, potassium oxalate, or sodium oxalate may be used instead of the ammonium oxalate. Results will be similar but rates of reduction somewhat different.

taneously in bright sunlight and a record made of the time for the first appearance of red in each of these tubes. In every case the mixture which had stood for 11 days turned red more rapidly than the duplicate mixture which had just been prepared. The ratio, given in the last column of Table I, not only shows that reduction is more rapid after the gel has set, but that as the gel becomes less acid this effect of age and setting is more pronounced.

*Photochemical After-Effect beautifully illustrated by the System*

*Gold Oxalate-Silicic Acid Gel.* In order to study the preliminary action of light, preceding visible reduction, the following plan was adopted. Ten tubes of silicic acid gel were made. Each one contained 12.5 cc. of 3 N HCl, 12.5 cc. of water glass (d. = 1.16), 1 cc. of 1% gold chloride, and was 0.155 molar with respect to both oxalic acid and ammonium oxalate. They were allowed to set in the dark for about 24 hours, and were then placed (a black paper covering being on each tube) on a circular test tube rack at whose center was a 1000 watt Mazda light. This light was thus equidistant (25 cm.) from each tube. Rise of temperature due to the Mazda light was prevented by an electric fan, so that thermometers at different places along the rack showed practically room temperature. Now, the light being off, covers were removed from 9 tubes, leaving one control tube (no. 1, Table II) covered. Next the Mazda light was turned on and the time noted. At the end of 3 minutes one of the tubes (no. 2, Table II) was covered with black paper. After 4 minutes of exposure tube 3 was covered and so on until all tubes were covered by the end of 11 minutes.

Only tubes 9 and 10 showed any development of red gold during this first exposure. All tubes then remained in the dark for another 24 hours, whereupon reexamination showed interesting "photochemical after-effects" as follows. Tubes 6-10 had visibly reduced in the dark (table 2, column 3). For example, when put away after the first exposure to light tube 10 had only a streak of red gold along the side nearest to the Mazda light, but, in the dark, red continued to spread until, before the second exposure to light, the entire gel had become red. Furthermore tubes 2-5 were very interesting although they showed no visible reduction in the dark. This interest lies in the fact that they all had different initial exposures (3, 4, 5, and 6 minutes, respectively) and yet in the second exposure to light they all flashed red at exactly the same moment (7.16 minutes). The control tube (no. 1), which had not been exposed at all on the first day, required 9.5 minutes for the red flash.

We, therefore, conclude that light produces changes in the gel before the flash of color of red gold. The particles of gold are at first too small to disperse even the short waves of "visible" light but are nevertheless steadily growing from the moment that light strikes the gel. Examination for dispersion of ultraviolet rays would almost certainly reveal these tiny crystals before the eye can see the red. During exposure to light there is a slight syneresis which leads us to also believe that the light affects the gel as well as the gold oxalate.

## Table II
### Photochemical After-Effect in the System Gold Oxalate-Silicic Acid Gel

| Tube no. | Appearance after first exposure to 1000 watt Mazda at 25 cm. | Appearance before second exposure, but after 24 hours in the dark following first exposure. | Appearance after second exposure to 1000 watt Mazda, 24 hours after first exposure. |
|---|---|---|---|
| 1 | Not exposed | Clear | Red in 9.5 min. |
| 2 | Clear after 3 min. | Clear | Red in 7.16 min. |
| 3 | Clear after 4 min. | Clear | Red in 7.16 min. |
| 4 | Clear after 5 min. | Clear | Red in 7.16 min. |
| 5 | Clear after 6 min. | Clear | Red in 7.16 min. |
| 6 | Clear after 7 min. | Gold crystals | |
| 7 | Clear after 8 min. | Small red spot | Red color became uniform |
| 8 | Clear after 9 min. | Red spot | |
| 9 | Red spot after 10 min. | One side red | |
| 10 | Red spot after 11 min. | All red | |

*Stability with Age of the System Gold Oxalate-Silicic Acid Gel.*

*Red, Blue, or Yellow Gold made in Gel of Identical Composition but of Different Age when exposed to Light.* Gels used for the experiments on aging were made 0.116 molar with oxalic acid or one of its salts, except that tubes 17 and 18 (table 3) contained no oxalate when made. Each tube also contained 10 cc. of water glass (d. = 1.16), 10 cc. of 3 N HCl, and 0.8 cc. of 1% gold chloride. The mixture was allowed to "set" in the dark under uniform conditions. The times recorded in column 3 (Table III) for tubes 1-16 are from the moment of mixing. Tubes 1, 5, 9, 13 were exposed simultaneously to sunlight on day 8 so that results in column 5 give a good comparison of the rates of reduction when oxalic acid is replaced by one of its salts. Thus column 5 shows that after 8 days tube 1 required 50 seconds exposure before any red color appeared, whereas, nos. 5, 9 and 13 required only 20 seconds. Therefore the oxalate salts were all faster than the oxalic acid. On day 21 (tubes 2, 6, 10, 14), upon simultaneous exposure to bright sunlight, tube 2 (oxalic acid present) became red in 47 seconds, tube 6 (ammonium oxalate present) became blue in 47 seconds, while in tube 10 (sodium oxalate present) and in 14 (potassium oxalate present) the dark reaction had already reduced all the gold oxalate to sparkling yellow crystals so that even a 2 hour exposure to bright sunlight gave no further reduction. On day 28 (nos. 3, 7, 11, 15) only tube 3 (oxalic acid present) had sufficient unreduced gold oxalate to give further change in sunlight, and it became blue after 34 seconds exposure. At the end of 37 days even the gel with oxalic acid present (no. 4) gave only a light blue coloration in 50 seconds.

Tubes 17 and 18 were similar to the others except that the original gel contained no oxalate and had been allowed to set for 3 days before the saturated oxalic acid was poured over the gel. The time is from the beginning of diffusion of the acid. At the end of 44 days tube 17 showed so little reduction in the dark that red was produced upon 45 seconds of exposure to sunlight,

while tube 18 had, during 111 days, passed over the possibility of forming the blue gold and had completely reduced in the dark to sparkling, yellow crystals of gold.

TABLE III

Stability with Age of the System Gold Oxalate-Silicic Acid Gel

| Tube no. | The oxalate in gel. | Age of gel before exposure. | Appearance before exposure[1] | Time for visible reduction in bright sunlight. |
|---|---|---|---|---|
| 1 | $H_2C_2O_4$ | 8 days | Clear | Red in 50 seconds. |
| 2 | " | 21 " | A few yellow crystals | Red in 47 " |
| 3 | " | 28 | " | Blue in 34 " |
| 4 | " | 37 | " | Light blue in 50 sec. |
| 5 | $(NH_4)_2C_2O_4$ | 8 | Clear | Red in 20 seconds. |
| 6 | " | 21 | Some yellow crystals | Blue in 47 " |
| 7 | " | 28 | " | No change in 2 hours. |
| 8 | " | 37 | " | No change in 2 hours. |
| 9 | $Na_2C_2O_4$ | 8 | Clear | Red in 20 seconds. |
| 10 | " | 21 | Some yellow crystals | No change in 2 hours. |
| 11 | " | 28 | " | No change in 2 hours. |
| 12 | " | 37 | " | No change in 2 hours. |
| 13 | $K_2C_2O_4$ | 8 | Clear | Red in 20 seconds. |
| 14 | " | 21 | Many yellow crystals | No change in 2 hours. |
| 15 | " | 28 | " | No change in 2 hours. |
| 16 | " | 37 | " | No change in 2 hours. |
| 17 | Sautrated oxalic acid | 44 | Some yellow crystals | Red in 45 seconds. |
| 18 | diffusing into gel | | | No change in 2 hours. |

*Black Diurnal Bands of Platinum.* In order to show that diurnal bands are not peculiar to gold oxalate, we made silicic acid gels with varying amounts of nitric, hydrochloric, sulphuric, and acetic acids, respectively (Table IV). Gels made with each kind of acid were of three different normalities, determined by titration just after mixing. Congo red was the indicator, except that for the acetic acid mixtures phenolphthalein was used. With each acid one mixture was about .66 N acidity, while one was about .02 N basic, and the third mixture was about .247 N basic. This basicity is indicated in the table by the negative sign.

In order to study the reduction in continuous light, accompanying diffusion a sample of each of these 12 gels was put at 28 cm. from two 100 watt Mazda

[1] We have observed that the speed of the dark reaction increases with rise of temperature.

lights, which were put in a dark room with their tips together, at the center of a circular rack of 28 cm. radius. Above each gel was a saturated solution of oxalic acid. These gels were left in continuous light for 3 weeks and observed frequently. Except in the gels strongly acid with nitric and hydrochloric acid, reduction accompanied diffusion and there were no regular bands. Duplicate gels, kept in the dark, did not become black during this same 3 weeks They were kept at the same distance of 28 cm. from the light but were covered with black paper. Therefore diffusion minus light gave no bands.

In order to study the reduction in intermittent light, accompanying diffusion, other samples of these same gel mixtures were also put at 28 cm. from the two Mazda lights but were left covered with black paper for from 3 to 21 days. The exact times are shown in Table IV (column 5). Tubes to be exposed to light on a given day were all exposed simultaneously at 25 cm. from a 1000 watt Mazda such as is used in a Balopticon. All the gels which had been reduced in the continuous light had duplicates which became black, in the light from the 1000 watt Mazda, in from 35 minutes to about 2 hours. These latter tubes, after reduction, looked just about the same as if they had been in continuous light. They became black down to the end of the zone of diffusion of the oxalic acid.

In order to study the results of diffusion of the oxalic acid, accompanied by reduction in ordinary light conditions of the laboratory, other duplicates of these 12 different gel mixtures were placed in an east window. The result of this combined action of diffusion and intermittent light was that every tube which became black in continuous light had a duplicate, in the window,

TABLE IV

Reduction, at 25 cm. from a 1000 watt Mazda, of silicic acid gels, containing .385% platinic chloride and into which saturated oxalic acid was diffusing. Also the reduction of similar gels in the dark, and at 28 cm. from two 100 watt Mazdas furnishing continuous light for 3 weeks.

| Acid | 3N acid per 26 cc. of gel | Water Glass (d. = 1.66) per 26 cc. | Normality of mixture (− sign means basic) | Days in dark | Appearance after reduction | Min. for reduction to begin | Effect of continuous light |
|---|---|---|---|---|---|---|---|
| $HNO_3$ | 12.5 cc. | 12.5 cc. | 0.656 | 4, 14 | no change | none | none |
| $HNO_3$ | 2 | 4.17 | −0.02 | 4, 12 | black | 104, 117 | black |
| $HNO_3$ | 2 | 8.35 | −0.247 | 3 | black | 50 | not run |
| HCl | 12.5 | 12.5 | 0.675 | 4, 14 | no change | none | none |
| HCl | 2 | 4.17 | −0.0167 | 4, 12 | black | 102, 117 | black |
| HCl | 2 | 8.35 | −0.248 | 3 | black | 38 | not run |
| $H_2SO_4$ | 12.5 | 12.5 | 0.652 | 4, 14 | black | 78, 95 | black |
| $H_2SO_4$ | 2 | 4.17 | −0.0116 | 4, 12 | black | 93, 93 | black |
| $H_2SO_4$ | 2 | 8.35 | −0.246 | 3 | black | 50 | not run |
| $HC_2H_3O_2$ | 12.5 | 12.5 | 0.658 | 4, 14, 21 | black | 61, 61, 35 | black |
| $HC_2H_3O_2$ | 2 | 4.17 | −0.019 | 4, 12 | black | 95, 58 | black |
| $HC_2H_3O_2$ | 2 | 8.35 | −0.246 | 3 | black | 47 | not run |

which gave black, diurnal bands. However, the gel which was .658 normal with acetic acid gave the best bands. There was a black band for each day. The bottom of each black band became more intensely black during the following night, due to the upward diffusion of the platinum salt into it during the night. In order to get uniform, horizontal bands it is necessary to either slowly rotate the tubes during the day, or else to reflect the light toward the back, as well as the front, of the tube. Striations will result if there are clouds or shadows. When a saturated solution of ammonium oxalate replaced the oxalic acid above the gel, black bands were also obtained. This is clearly a case analogous to the similar but colored rhythmic bands of colloidal gold.

*Directions for making Diurnal Bands of Platinum.* In 10 cc. of 3 N acetic acid dissolve 0.2 g. of oxalic acid. Add 0.8 cc. of 1% platinic chloride and in the dark stir into this mixture 10 cc. of water glass (d. = 1.16). Allow the tube to set in the dark for 3 days. Quickly open it in bright sunlight and with a stopwatch record the time when black first appears. As a modification of this experiment, make up the gel as before, except that no oxalic acid is used. Allow the gel to set for 3 days, then put 5 cc. of saturated oxalic acid[1] solution into the test tube above the gel. Place this tube in a window where it will be subject to changing light. Watch each day for new bands.

Also, as above in the case of gold oxalate, exposure through a grid, followed by several days in the dark, will give characteristic permanent bands of colloidal platinum, separated by nearly clear zones.

*Theory of Formation of Diurnal Bands.* The explanation for the rhythmic, diurnal bands obtained by Holmes with gold and by us with platinum is as follows. Suppose the oxalic acid or oxalate salt is added to the silicic acid-gold chloride, or platnium chloride, gel in the morning and the tube is placed in the ordinary laboratory. During the day a band grows because the gold oxalate or platinum oxalate is formed by the diffusion of the oxalate into the gel, and the light causes rapid reduction. At night gold oxalate or platinum oxalate is also formed by diffusion but the "dark reaction" to give metallic particles is so slow that this oxalate diffuses into the band formed during the previous day, for, in this latter zone, there is a nearly zero concentration of this oxalate. In these latter zones reduction occurs even in the dark. Thus when morning comes it finds little gold or platinum oxalate in the "clear" zones. The clarity and width of these zones depend both upon the rate of diffusion and also upon the ease with which the gold oxalate or platinum oxalate reduces in the dark.

The formation of the diurnal bands seems from our work to be quite general whenever: 1. There is in a gel a substance (A) and there is put upon the gel another substance (B) which diffuses into the gel and reacts to produce a third substance (C), that can diffuse through the gel, but which slowly decomposes in the dark to form a fourth substance (D), whenever the latter reduction is greatly catalyzed by light. Such a tube will give rhythmic

[1] Concentrated solutions of ammonium oxalate, sodium oxalate, or potassium oxalate may replace the oxalic acid. Results will be similar but rates of reduction different.

diurnal bands if placed in the ordinary room where darkness alternates with daylight. 2. Or there may be in a gel a substance (C) which slowly decomposes in the dark to form crystals (D), but much more rapidly in light, and which will itself diffuse through the gel but produces a substance (D) that will not diffuse through the gel. Such a gel will give pseudo diurnal bands by exposing to bright sunlight through a grid of black paper and then placing the tube in the dark for several days. Rhythmic slits give rhythmic bands.

## Summary

1. Simulated, rhythmic, diurnal bands of red, colloidal gold were obtained in a silicic acid gel containing 10 cc. of 3 N HCl, 10 cc. of water glass (d. = 1.16), 0.8 cc. of 1% gold chloride and 0.2 g. of oxalic acid, whenever exposure to light through a grid with rhythmic openings, was followed by several more days in the dark.

2. The system gold oxalate-silicic acid gel shows remarkably interesting photochemical after-effects when preliminary light exposure of different durations, not sufficient for visible reduction, is followed by 24 hours in the dark and then a second exposure.

3. Red, blue, or yellow gold was made in different tubes of gel of identical composition but of different age when exposed to light. Freshly prepared gel gave red gold, an older gel gave blue gold and a still older gel gave yellow gold.

4. Reduction to the red gold is more rapid in the gel than in the same mixture before setting.

5. Diurnal bands of platinum were produced in ordinary light when oxalic acid or one of its soluble salts diffused into a silicic acid gel containing: 10 cc. of 3 N acetic acid, 10 cc. of water glass (d. = 1.16) and 0.8 cc. of 1% platinic chloride. Continuous light for 3 weeks caused reduction to black but gave no bands.

6. Pseudo, rhythmic, diurnal bands of platinum were made in a silicic acid gel containing: 10 cc. of 3 N acetic acid, 10 cc. of water glass (d. = 1.16), 0.2 g. of oxalic acid, and 0.8 cc. of 1% platinic chloride, whenever exposure to light through a black grid with rhythmic openings was followed by several more days in the dark.

7. Diurnal bands result from the light reduction of alternate zones, followed by diffusion.

*Morgantown, W. Va.*
*July 5, 1926.*

# THE STABILITY OF DIAZO-BENZENE CHLORIDE SOLUTIONS.*
## II. THE REACTION OF DIAZO-BENZENE CHLORIDE WITH CERTAIN ORGANIC HYDROXY SUBSTANCES.

BY H. A. HOLDEN PRAY**

### Introduction

Although the products of the reaction of a large number of the diazo compounds with the different organic hydroxy substances have been determined, no study of the kinetics of these reactions has ever been made.

Remsen and Palmer[1] investigated the reaction of para diazo ortho toluene sulfonic acid with ethyl alcohol and found that the reaction follows two courses. Thus

$$(1)\quad R - N = N - X + R' - OH \longrightarrow R - O - R' + HX + N_2$$
$$(2)\quad R - N = N - X + R' - OH \longrightarrow RH + R'O + HX + N_2$$

where R and R′ represent hydrocarbon radicals and X an acid radical. In other words, the reaction may take place in either or both of two ways—with the formation of an ether or of a hydrocarbon or a mixture of the two. Both products were found to be formed in the case which they investigated. According to Hantzsch and his co-workers[2] diazo-benzene chloride reacts with methyl alcohol to yield anisole quantitatively. Diazo-benzene chloride with ethyl alcohol gives almost quantitative yields of phenetol, slight traces of benzene being formed. With primary and secondary propyl alcohols, the same compound reacts as with ethyl and methyl alcohols, the two propyl-phenyl ethers being formed with no trace of propyl aldehyde or acetone. Amyl alcohol with diazo-benzene chloride gives in part amyl-phenyl ether and in part valeric aldehyde and benzene. Benzyl alcohol gives mostly benzaldehyde and benzene, and only a very small amount of benzyl ether. Glycerine is analogous to propyl alcohol, giving the mono-ether entirely.

Orndorff[3] has demonstrated that with formic and acetic acids, diazo-benzene nitrate reacts quantitatively with the formation of phenyl esters. Para-diazo-toluene sulfate and para-diazo-benzene sulfonic acid react with acetic acid in the same way, yielding the corresponding esters quatitatively. Meldola[4] found that the same reaction takes place when certain diazo com-

---

*Contribution from the Laboratory of General Chemistry, the University of Wisconsin.

**The work included in this paper is taken from the thesis presented by H. A. Holden Pray in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin. This investigation was conducted under the supervision of Professor J. H. Walton.

[1] Remsen and Palmer: Am. Chem. J., 8, 243 (1886).

[2] Hantzsch and Jochem: Ber., 34, 3337 (1901); Hantzsch and Vock: 36, 2061 (1903).

[3] Orndorff: Am. Chem. J., 10, 368 (1888).

[4] Meldola: Ber., 21, 601 (1888).

pounds of the naphthalene series react with acetic acid. In all of the examples so far studied, diazo compounds react with acids with quantitative formation of the corresponding esters. Thus:

$$R - N = N - X + R'COOH \longrightarrow N_2 + HX + R'COOR$$

where R and R′ represent hydrocarbon radicals, and X represents an acid radical.

A determination of the velocity of the reaction of diazo-benzene chloride with the various alcohols and acids was undertaken with the expectation that the results would throw some light upon the mechanism of the decompositions of the diazo compounds.

## Experimental

*Preparation of Reagents*—The solid diazo-benzene chloride was prepared by the method of Hantzsch and Jochem.[1] 22 g. of aniline hydrochloride were suspended in 60 c.c. of glacial acetic acid. The mixture was cooled by immersing the container in ice water and, while the mixture was vigorously stirred by means of an electrically driven stirrer, 25 g. of amyl nitrite were slowly added from a dropping funnel. To precipitate the diazo salt from the cold solution of diazo-benzene chloride in glacial acetic acid, twice its volume of anhydrous ether was added drop-wise from the dropping funnel. It was found that the precipitation must be carried out very slowly, or the diazo compound would separate from the solution as a tarry liquid instead of the desired white crystalline precipitate. The diazo-benzene chloride was then filtered off and washed with anhydrous ether to remove acetic acid. The solid salt could be preserved for several days by keeping it under anhydrous ether.

The alcohols used were very carefully dried by refluxing several hours over lime and redistilling from the same substance.

Acetic acid was crystallized from the ordinary commercial glacial acetic acid by cooling, the crystals were then drained off and distilled.

Formic acid was dehydrated by the method of Schlesinger and Martin.[2]

Propionic and butyric acids were obtained from the General Chemical Company, and as they gave no color reaction with copper sulfate, were considered to be sufficiently dry.

*Apparatus and Methods*—The apparatus was the same as that used in a previous investigation.[3]

In preference to weighing each sample of the diazo salt on the balance, it was measured in a capsule whose capacity was found to be approximately 0.3 g. The amount of salt used could be calculated from the volume of nitrogen gas evolved. A capsule of the dry diazo-benzene chloride was introduced into the reaction flasks which contained 40 c.c. of the solvent. The flasks were

[1] Hantzsch and Jochem: Ber., 34, 3337 (1901).
[2] Schlesinger and Martin: J. Am. Chem. Soc., 36, 1589 (1914).
[3] Pray: J. Phys. Chem., 30, 0000 (1926).

introduced into the thermostat and shaken. After allowing the reacting solutions to come to the temperature of the thermostat, burette readings were taken and appropriate values substituted in the equation

$$K = \frac{1}{t} \ln \frac{A}{A-x}.$$

$K_s$ which is 0.4343 $K \times 10^4$, will be used for convenience in tabulating the results.

*Order of the Reactions.* The constancy of $K_s$ and the independence of $K_s$ upon the initial concentration of the diazo-benzene chloride indicate that the reactions are monomolecular or pseudo-monomolecular. Table I will serve to illustrate this in the case of one of the alcohols used. The constants obtained for all of the alcohols and acids used were as constant or more so than the example given.

TABLE I

The Decomposition of Diazo-benzene Chloride in Iso-butyl Alcohol at 30°

| Time in minutes | Burette Reading | x | A-x | $K_s$ |
|---|---|---|---|---|
| 0 | 11.6 | 0 | 57.6 | — |
| 5 | 15.1 | 3.5 | 54.1 | 53. |
| 15 | 21.5 | 9.9 | 47.7 | 54. |
| 20 | 24.3 | 12.7 | 44.9 | 54. |
| 30 | 29.6 | 18.0 | 39.6 | 54. |
| 40 | 34.2 | 22.6 | 35.0 | 54. |
| 50 | 38.3 | 26.7 | 30.9 | 54. |
| 70 | 45.2 | 33.6 | 24.0 | 54. |
| End | 69.2 | 57.6 | — | |
| | | | Mean | 54. |
| | | | Duplicate | 54. |

The mean constants are the same when the original concentration of the diazobenzene chloride is reduced to half the value used in the above experiment, and therefore the original concentration of the diazo solution does not determine the magnitude of the velocity constant. The reaction is apparently monomolecular then by two criteria. It may be noted, however, that if the reaction measured were bimolecular, it would appear monomolecular by both of these criteria because of the fact that one of the reactants, in this case isobutyl alcohol, is present in enormous excess.

*Relative Reaction Velocities.* The relative reaction velocities of diazobenzene chloride with various alcohols and acids, determined as described above, are tabulated in Table II. The values given are the mean of two or more determinations for each solvent.

TABLE II

The Decomposition of Diazo-benzene Chloride in Various Alcohols and Organic Acids

| Solvent | $K_s$ at 20° | 30° | 40° | 50° |
|---|---|---|---|---|
| Methyl Alcohol | 11.3 | 53.5 | 227. | — |
| Ethyl " | 11.3 | 53.5 | 218. | — |
| N-propyl " | — | 52.0 | 204.2 | — |
| Iso-propyl " | — | 69.0 | 288. | — |
| N-butyl " | — | 50.0 | 201. | — |
| Iso-butyl " | — | 54.0 | 208. | — |
| Amyl " | — | 46.3 | — | — |
| Allyl " | — | 41.7 | — | — |
| Benzyl " | — | — | 153.0 | — |
| Formic Acid | — | 18.6 | 73.1 | — |
| Acetic Acid | — | 18.7 | 82.0 | 333.0 |
| Propionic Acid | — | 18.9 | 82.0 | 297.0 |
| Butyric " | — | 23.0 | 102.0 | — |
| Di-chlor Acetic Acid | — | — | 53.1 | — |
| Water | — | 25.0 | 107.0 | 404. |

From this table it is evident that the reaction with alcohols is without exception much faster than the reaction with either acids or water. The reaction with acids is somewhat slower than with water. The reaction with benzyl alcohol is slower than with the other alcohols, but it must be remembered that in this case the reaction proceeds mainly with the formation of the hydrocarbon, whereas with the other alcohols the corresponding ethers are the primary products. With amyl alcohol both hydrocarbon and ether are formed, and examination of $K_s$ for this reaction shows it to lie between the values obtained for methyl alcohol (an ether forming alcohol) and benzyl alcohol (a hydrocarbon forming alcohol). With those exceptions, the similarity between the values of $K_s$ for the different alcohols is very striking. The same is true of the acids. Formic and acetic are known to form only the ester with diazo-benzene chloride. At 30°, $K_s$ for these two reactions is practically identical. With propionic and butyric acids the product formed is unknown, but is presumably the corresponding ester. The values of the constants for all four of them are strikingly close.

*Temperature Coefficients.* The effect of temperature upon these reactions is summarized in Table III, the temperature coefficients having been calculated from the data of Table II. The table shows the temperature coefficients of all of the reactions to be rather high and to vary markedly with the temperature. The values are not the same for the various reactions.

TABLE III
Temperature Coefficients

| Solvent | $K_{30°}/K_{20°}$ | $K_{40°}/K_{30°}$ | $K_{50°}/K_{40°}$ |
|---|---|---|---|
| Methyl Alcohol | 4.73 | 4.22 | |
| Ethyl " | 4.73 | 4.05 | — |
| N-propyl " | — | 3.92 | — |
| Iso-propyl " | — | 4.17 | — |
| N-butyl " | — | 4.02 | — |
| Iso-butyl " | — | 3.85 | — |
| Formic Acid | — | 3.93 | — |
| Acetic " | — | 4.38 | 4.06 |
| Propionic " | — | 4.33 | 3.62 |
| Butyric " | — | 4.43 | — |
| Water | — | 4.24 | 3.77 |

*Methyl Alcohol—Water Mixtures.* Since diazo-benzene chloride is soluble in and reacts with both methyl alcohol and water, it was thought that a study

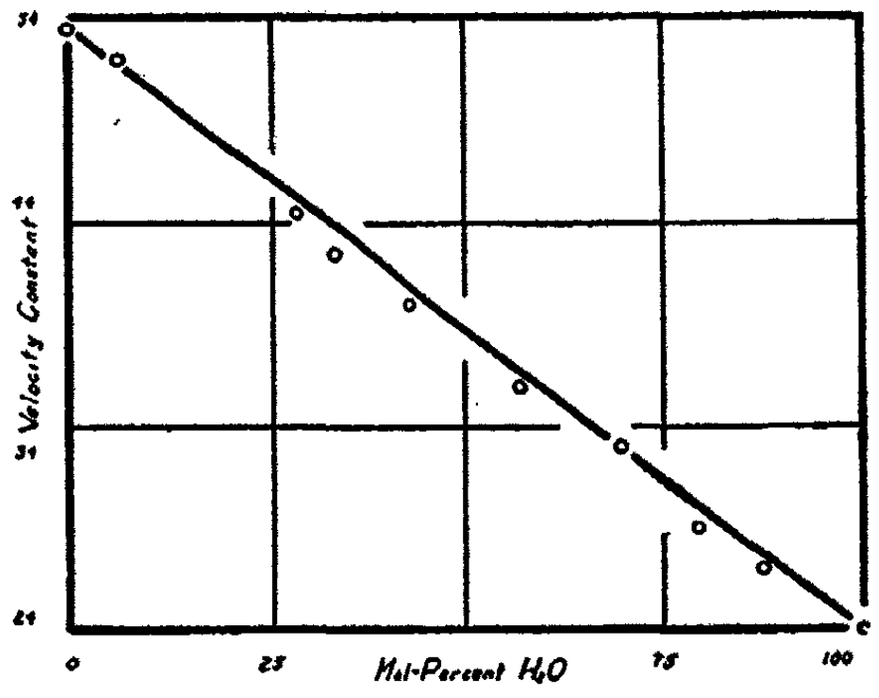



FIG. 1
Methyl Alcohol-Water Mixtures

of the decomposition in the mixed solvent might prove interesting. Such a study was made. $K_s$ at 30° was determined for solutions of diazo-benzene chloride in alcohol-water mixtures of various composition. The results are shown in Table IV, and graphically in Figure 1.

TABLE IV
The Decomposition of Diazo-benzene Chloride in Methyl Alcohol-Water Mixtures at 30°

| Mol % Water | $K_s$ | Mol % Water | $K_s$ |
|---|---|---|---|
| 0 | 53.5 | 57.1 | 36.0 |
| 5.43 | 52.0 | 69.0 | 33.0 |
| 27.6 | 44.5 | 78.8 | 29.0 |
| 32.3 | 42.6 | 87.0 | 27.0 |
| 42.6 | 40.0 | 100.0 | 24.0 |

In the figure, $K_s$, plotted against the mol per cent of water, is within the limits of experimental error a straight line function. This indicates that both the alcohol and water reactions are going forward in these mixtures, and that the extent to which the diazo compound reacts with either water or alcohol is dependent only upon the relative number of molecules of alcohol and water present. Thus, the reaction is not a selective one, or the variation in $K_s$ with changing mol per cent of the constituents of the solvent would not be a straight line function.

A single mixture of acetic acid with water was also used. This mixture contained 24 mol per cent of acetic acid and $K_s$ for the decomposition of diazo-benzene chloride in this solvent was found to be 22.6. This value falls, within the limits of experimental error, upon the mixture line as in the case of methyl alcohol-water mixtures. The fact that the velocity of the decomposition in acetic acid is so close to that in water, makes a determination of the velocity in the mixed solvent difficult.

*The Solubility of Diazo-benzene Chloride in Various Solvents.* It was thought highly desirable to find a solvent for diazo-benzene chloride in which the diazo salt is stable, or in which it decomposes at a very slow rate. If such a solvent could be found, the true order of the reaction with water and alcohols could be determined by introducing equivalent amounts of the diazo salt and the other reactant and following the decomposition as before. It was found to be insoluble in benzene, toluene, ether, carbon tetrachloride, chloroform, heptane, nitro-benzene, benzo-nitrile, anisole, nitromethane, acetone, methyl-ethyl ketone, ethylene chloride, ethylene bromide, trichloro-ethane, N-butyl bromide, N-butyl ether, diethyl malonate, methyl salicylate, methyl acetate, oleic acid, furfural, furane, furfuryl acetate, and methyl fuorate. It is somewhat soluble in furyl alcohol, pyridine, and quinoline. However, in these solvents the addition of water or alcohol does not cause the liberation of nitrogen, the diazo compound apparently being combined with the solvent in such a way that the ordinary diazo reactions cannot take place. It is soluble in arsenic trichloride, phosphorus oxychloride, and selenium oxychloride. In these solvents the diazo compound is quite unstable, and consequently they are not suited to the purpose. In arsenic trichloride, it was found to decompose at exactly the same rate as in water. The product of the reaction is unknown.

It is apparent that diazo-benzene chloride is soluble only in such substances as it would be expected to react with. Thus it dissolves in water, acids, and alcohols with presumably the immediate formation of solvates. That pyridine and quinoline react with the diazo salt is evident from the fact that water will not liberate nitrogen from a solution of the salt in these solvents. That such highly reactive substances as arsenic trichloride and selenium oxychloride dissolve and decompose the diazo salt is not surprising.

*The Effect of Colloids.* In order to determine the effect of colloids upon the velocity of decomposition of diazo-benzene chloride in ethyl alcohol, a solution of du Pont's "Parlodion" in a mixture of ethyl alcohol and ether was added to

the reaction mixture. It was found that ether, in the absence of collodion, increased the velocity of the decomposition. The results are given in Table V.

TABLE V

The Effect of Collodion upon the Decomposition of Diazo-benzene Chloride in Ethyl Alcohol-Ether Solution at 30°.

| Mol % Ether | % Collodion | $K_a$ |
|---|---|---|
| none | none | 53.5 |
| 5.0% | 0.5% | 54.0 |
| 6.25% | none | 55.0 |
| 10.0% | 1.0% | 57.0 |
| 25.0% | none | 63.0 |
| 37.5% | none | 68.5 |

If the mol per cent of ether present is plotted against $K_a$, it will be found that the determinations in which collodion is present fall upon the straight line obtained when collodion is absent. The increase in velocity of the decomposition is therefore due to the presence of the ether, and the collodion is shown to be without effect.

## Discussion of Results

Any theory of the mechanism of the decomposition of the diazo compounds must explain:

(1) The fact that, although the substance undergoing decomposition is an electrolyte, the addition of an acid or of a common ion has no effect upon the velocity of the decomposition.

(2) The fact that diazo compounds derived from different amines decompose at different rates, while those derived from different acids decompose at the same rate.

(3) The unusual fact that no catalyst has been found that will either increase or decrease the velocity of the decomposition.

(4) Why the reaction with the various alcohols takes place at practically the same rate, and the reaction with acids is practically the same for the different acids.

In the light of present knowledge, it does not seem possible to advance any theory of the mechanism of the diazo decompositions that is in accord with all of the above observations.

In view of the data obtained in this study, the theory as proposed by Hantzsch becomes untenable. According to this theory, the decomposition velocity is determined by the rate of change of the addition compound into the syn-diazo body.

$$\begin{array}{l} Ar \\ | \\ N \\ \| \\ N \\ | \\ Cl \end{array} + \begin{array}{l} R \\ | \\ \cdot \\ | \\ H \end{array} \longrightarrow \begin{array}{l} Ar \\ | \\ N \\ \| \\ N \\ | \\ Cl \end{array} \begin{array}{l} R \\ | \\ \\ | \\ H \end{array} \longrightarrow \begin{array}{l} Ar \\ | \\ N \\ \| \\ N \\ | \\ H \end{array} \begin{array}{l} R \\ | \\ \\ | \\ \\ \end{array} \longrightarrow \begin{array}{l} Ar \\ | \\ N \\ \| \\ N \\ | \\ H \end{array} \begin{array}{l} R \\ | \\ \\ | \\ \\ \end{array} + HCl \longrightarrow Ar - R + N_2 + HCl$$

where Ar represents an aromatic residue and R represents an alkyl, acyl or hydroxyl group.

If the radical represented by Ar is changed, it is evident that the stability of the addition compound will undoubtedly be affected, with a consequent change in the velocity of the decomposition. This is in accord with the experimental facts. If, however, the radical R is changed, the stability of the addition compound will also be affected. This fact is well illustrated by the results of a study of the rate of saponification of esters derived from different acids and alcohols by sodium hydroxide, which show that the velocity of these reactions are dependent upon both the acid and the alcohol from which the esters are derived.[1] Thus, if R represents in one case the methyl group and in another case the ethyl group, the two compounds should be quite different in stability, and the decomposition should proceed at quite different rates. According to the data of the present paper, this is not the case. Further, since the presence of acid or of common ion (in this case chloride ion) has no effect upon the velocity of the decomposition, a very special case must be assumed; namely, that the diazonium ion is just as reactive as the undissociated diazonium salt. The theory of Hantzsch is thus improbable for two reasons.

If the series of reactions which Hantzsch proposes actually take place, we may assume that one of the other transformations is the one which is actually being measured. Thus either the formation of the addition compound, or the decomposition of the syn-diazo compound may be the measured reaction. But the former involves the rupture of the hydrogen-oxygen bond of the alcohol, and this rupture has been shown by Norris and Ashdown[2] using several different methods, to be about ten times as difficult in the case of iso-propyl alcohol as in the case of ethyl alcohol. The same relative order of reactivity of the hydroxyl hydrogen of alcohols has been observed by Menschutkin.[3]

Such a difference in reactivity is not observed in the decomposition of diazo-benzene chloride with the different alcohols, and consequently it is improbable that any reaction involving the hydroxyl hydrogen is the one which proceeds with measurable velocity in this decomposition. That the measured reaction is the decomposition of the syn-diazo compound is subject to the same objections as those which make it improbable that the measured reaction is the transformation of the addition compound into the syn-diazo compound; namely, that the reaction velocity is independent of the alkyl group introduced, and that the reaction velocity is independent of the concentration of either the undissociated diazonium salt or the diazonium ion. The Hantzsch theory, therefore, does not accord with the experimental results.

That the physical properties of the solvent used do not determine the rate at which the reaction proceeds may be seen from a study of the following table.

[1] Reicher: Ann., 128, 257 (1885).
[2] Norris and Ashdown: J. Am. Chem. Soc., 47, 837 (1925).
[3] Menschutkin: Z. physik. Chem., 1, 511 (1887).

TABLE VI

Some Physical Properties of Pure Liquids*

| Liquid | $K_s$ at 30° | Dielectric Constant | Viscosity | Surface Tension |
|---|---|---|---|---|
| Methyl Alcohol | 53.5 | 31.2 | 0.005564 | 23.02 |
| Ethyl " | 53.5 | 25.8 | 0.01114 | 20.20 |
| N-propyl " | 52.0 | 22.2 | 0.01962 | 23.82 |
| Iso-butyl " | 54.0 | 20.0 | 0.04034 | 22.72 |
| Amyl " | 46.3 | 16.0 | 0.03923 | 23.72 |
| Water | 24.5 | 81.1 | 0.00891 | 70.6 |

Millar and Braune[1] studied the decomposition of diazo-acetic ester, catalyzed by hydrogen ion, in alcohol-water mixtures, finding a minimum velocity at about 11% of water. The products of this reaction, as in the decomposition of diazo-benzene chloride, are different with alcohol than with water, both substances taking part in the reaction. The decomposition velocity of diazo-benzene chloride is a strictly additive function of the mol percent of water in the water-alcohol mixtures. Bohnson[2] found that the velocity of decomposition of hydrogen peroxide, catalyzed by iodide ion, in methyl, ethyl, and N-propyl alcohol-water mixtures does not conform to the mixture line.

In fact, the reactions which proceed in the presence of a catalyst and whose reaction velocities have been studied in mixed solvents, in general do deviate from the mixture line. That this reaction does not, may be taken as an indication that there is no substance present in the reaction mixture which functions as a catalyst in spite of the fact that it is a slow reaction.

## Summary

(1). The apparent order of the reaction of diazo-benzene chloride with methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, amyl, allyl, and benzyl alcohols, and with formic, acetic, propionic, butyric, and dichlor-acetic acids has been determined.

(2). The velocity constants for the reactions with the above alcohols and acids, and their temperature coefficients at temperatures between 30° and 50° have been measured.

(3). The kinetics of the decomposition of diazo-benzene chloride have been studied in methyl alcohol-water mixtures. The rate of reaction is a purely additive function of the mol percent of either the water or the alcohol in the mixture.

*Selected from Landolt-Börnstein

[1] Millar and Braune: Z. physik. Chem., **85**, 129, 170 (1913).
[2] Bohnson: J. Phys. Chem., **24**, 677 (1920).

(4). Diazo-benzene chloride has been shown to be insoluble in a large number of organic liquids with which this substance does not react.

(5). The colloid collodion has been shown to have no effect upon the velocity of the reaction of diazo-benzene chloride with ethyl alcohol.

(6). The theory of the mechanism of the diazo decomposition of Hantzsch has been shown to be inadequate to explain the results of these experiments.

(7). It has been pointed out that there is no simple relation between the physical properties of the solvent and the velocity of the decomposition.

*Madison,*
*Wisconsin.*

# THE CATALYTIC OXIDATION OF CARBON MONOXIDE IN CONTACT WITH QUARTZ GLASS*

BY ARTHUR F. BENTON AND THOMAS LEIGH WILLIAMS

## Introduction

The rate at which carbon monoxide and oxygen react to form carbon dioxide in contact with quartz glass as catalyst has been studied by Bodenstein and Ohlmer.[1] With excess carbon monoxide the reaction was relatively slow, and became continually slower as reaction proceeded toward completion. When oxygen was present in excess, however, the velocity increased as reaction progressed, in spite of the fact that the pressures of both reacting gases were steadily decreasing. Further study indicated that this abnormality was attributable to a retarding action of the carbon monoxide, which these authors expressed by the equation:

$$\text{Rate} = k\frac{m+(a-x)}{n+(b-x)},$$

where $x$ is the pressure decrease due to reaction, $a$ represents the initial pressure of oxygen, $b$ is half the initial pressure of the carbon monoxide, and $k$, $m$ and $n$ are constants. They regarded the equation as wholly empirical and did not attempt any explanation of the peculiarities observed.

Langmuir[2] proposed to account for Bodenstein and Ohlmer's results by assuming that the silica surface is almost completely covered by adsorbed carbon monoxide molecules which are incapable of reacting with impinging oxygen molecules unless the latter also become adsorbed on the surface. At higher pressures of carbon monoxide there would be fewer empty spaces available for oxygen and hence a slower reaction velocity. Thus the retarding effect of carbon monoxide would be qualitatively accounted for, although the constants m and n in the above equation would remain unexplained.

The striking results of Bodenstein and Ohlmer were first called to our attention some years ago by Professor H. S. Taylor, who pointed out the desirability of an experimental study of the adsorption by quartz glass of the gases in question. The results of such an investigation, the details of which are reported below, show that at the temperatures and pressures employed in the catalysis, the adsorption of carbon monoxide or oxygen is too small to be detected by the methods used. It may be stated with certainty that less than three per cent of the surface was covered with a unimolecular layer of either gas. There remained the possibility that the reaction is catalyzed only at a relatively small number of active spots on the surface of the silica, and that

* Contribution No. 31 from the Cobb Chemical Laboratory, University of Virginia.

[1] Bodenstein and Ohlmer: Z. physik. Chem., 53, 166 (1905).

[2] Langmuir: J. Am. Chem. Soc., 38, 2291 (1916).

carbon monoxide is preferentially adsorbed at these points. That only a small fraction of the surface would exhibit marked catalytic activity is rendered probable by the recent investigations of Pease[1] and Taylor.[2] However, the assumption of preferential carbon monoxide adsorption appears untenable in view of the fact that precipitated silica (which is also amorphous) adsorbs little more carbon monoxide, in relation to other gases, than would be expected from the relative boiling points.[3]

Another interesting question arises out of the fact that Bodenstein and Ohlmer, using only the walls of an empty quartz glass bulb as catalyst, obtained convenient reaction rates at about 300° or below. Thus, though less active than many other catalysts, silica would be highly efficient, and would provide a striking exception to the general rule[4] that active catalysts exhibit adsorption for at least one of the reacting substances.

In the light of these considerations it appeared desirable to attempt to check the results of Bodenstein and Ohlmer. Preliminary experiments with several different samples of quartz glass all showed so slow a reaction velocity even at 445° as to be scarcely measurable. Precipitated silica, with an enormously greater surface area, gave a similar result. The final experiments, reported in the second part of this paper, have definitely shown that quartz glass, when carefully freed from impurities, is a poor catalyst; furthermore, the retarding effect of carbon monoxide has not been confirmed.

## Adsorption Measurements

The apparatus for carrying out the adsorption experiments consisted of a soda-glass bulb containing the silica, connected by capillary tubing through a three-way cock to a Töpler pump and a compensated gas burette, fused glass joints being used exclusively. The details of the procedure have been described elsewhere.[5]

Perfectly clear quartz glass, for which we are indebted to Mr. F. W. Robinson of the Hanovia Chemical and Manufacturing Company, was broken up to pass between 30 and 100 mesh screens, boiled with concentrated nitric acid, carefully washed and dried. The sample taken weighed about 200 g., with an estimated surface area of approximately 2 sq. m. Before each measurement it was exhausted for several hours at 450°.

The volume of the free space in the bulb and connecting capillary was determined with nitrogen which was assumed not to be adsorbed in measurable quantities. In two experiments at 25°, 47.80 and 47.79 cc. of this gas, at N. T. P., were required to fill the bulb to a pressure of 760 mm. In two similar experiments with carbon monoxide 47.83 and 47.79 cc. were required. With the bulb at 0° the values were: nitrogen, 52.01 cc.; carbon monoxide,

[1] Pease: J. Am. Chem. Soc., 45, 2296 (1923); Pease and Stewart: 47, 1235 (1925).
[2] Taylor: Proc. Roy. Soc., 108A, 105 (1925).
[3] Benton: J. Am. Chem. Soc., 45, 887 (1923).
[4] Cf. Taylor, J. Franklin Inst., 194, 1 (1922).
[5] Benton: J. Am. Chem. Soc., 45, 889 (1923).

52.00 cc. It is evident from these results that under the conditions employed, carbon monoxide is not adsorbed in excess of 0.02 cc. Since a unimolecular layer of this gas covering the 2 sq. m. of surface would require[1] in the neighborhood of 0.50 cc., it follows that not more than four per cent of the surface is occupied by such a film. Even at $-79°$ no adsorption of the monoxide could be detected with certainty.

Another sample of quartz glass, ground to a fine powder and having an estimated surface of approximately 15 sq. m., was also investigated. By comparison with the volume of helium required to fill the free space, it was found that the adsorptions of carbon monoxide and oxygen at 25°, 218° and 300° were less than the experimental error (under 0.1 cc. in these cases); with carbon dioxide at 25°, 0.55 cc. were adsorbed. These results show that less than three per cent of the surface was covered by carbon monoxide or oxygen.

A further series of experiments was then made at low pressures, since it may be shown[2] that if the adsorption at low pressures is relatively strong, it may be measured with greater accuracy than at ordinary pressures. If the volume of the Töpler pump is known, and the fall tube is accurately calibrated, the pump may serve as a McLeod gage and also as a means of measuring small gas volumes accurately.[3] Thus, if a small quantity of gas, perhaps 1 cc., is introduced into the system, bulb plus pump, and allowed to come to equilibrium, a single stroke of the pump determines the pressure in the system and the amount of gas withdrawn. By adding together the amounts obtained by operating the pump repeatedly, the total quantity of gas originally present is found. The amount of gas occupying the free space can readily be calculated from the observed pressure and the previously measured volume of the system. The difference between this quantity and the total represents the amount of gas adsorbed. Measurements of this kind were made with nitrogen at 25° and with carbon monoxide at 25° and 400°, but in no case was any adsorption detected.

## Reaction Velocity Measurements

*Apparatus and Procedure.* The apparatus was similar to that used in the adsorption measurements, but with the addition of a mercury manometer for measuring pressure changes in the bulb. The latter was heated in a large electric furnace, and the temperature (usually 500°) was measured with a thermocouple and potentiometer set-up with a precision of about 2°. No special precautions were taken to prevent access to the bulb of the vapors of mercury or stop-cock grease ("Lubriseal").

Carbon monoxide was prepared by dropping formic acid on warm, concentrated sulphuric acid, and purified by successive passage through tubes filled with glass wool and cotton, soda-lime and phosphorus pentoxide. Oxy-

[1] Cf. Langmuir: J. Am. Chem. Soc., 40, 1391 (1918).
[2] Cf. Langmuir: J. Am. Chem. Soc., 40, 1365 (1918).
[3] Cude and Hulett: J. Am. Chem. Soc., 42, 392 (1920).

gen was generated by electrolysis of sodium hydroxide solution between nickel electrodes, and passed over calcium chloride, heated platinized asbestos and phosphorus pentoxide.

The desired gas mixture was made up in the burette, and thorough mixing insured by raising and lowering the leveling bulb at intervals for several hours. Meanwhile the reaction bulb was heated to 500° and evacuated. The gas mixture was then admitted up to approximately atmospheric pressure, and the bulb connected with the manometer. The reaction velocity was followed by observing the pressures at regular intervals, keeping the volume constant. The theoretical initial pressures could be calculated from the amount of gas introduced from the burette and the known volume of the free space in the bulb.

*Preliminary Results.* The first sample of quartz glass tested gave a measurable reaction rate at 218°; subsequently, after exhausting the bulb, both mercury and grease were found condensed in the capillary. The catalyst, which had previously been treated with concentrated hydrochloric acid and rinsed, was now boiled with concentrated nitric acid and carefully washed, finally with conductivity water. With the material thus treated, scarcely measurable rates of reaction were obtained below 445°. Further experiments on this sample after rewashing, as well as on two new samples of quartz glass, confirmed this result. On one occasion mercury was accidentally drawn over into the reaction bulb, doubtless carrying along with it some grease from the manometer stop-cock. The bulb was then exhausted for a long time at 500°, the mercury condensing in the upper parts of the line, after which the latter were replaced with new capillary. The next run (Run 25) was much faster than the previous ones. The catalyst was then thoroughly cleaned in the manner previously described, with the result that the reaction velocity in the next run (Run 26) was only one-seventh as great as in Run 25.

These observations show that substances such as grease or mercury, which act as powerful poisons toward active catalysts, may exert the opposite effect upon catalysts which are themselves less active. This would lead to the view that the quartz glass bulb used by Bodenstein and Ohlmer was probably not free from impurities, whether in or on the surface. These authors recorded the fact that mercury or petroleum occasionally entered their bulb from the manometer, producing disturbances in the reaction, but state that washing with nitric or chromic acid usually sufficed to remove the contamination. It is possible, however, that their bulb may have been difficult to rinse thoroughly.

*Determination of Reaction Kinetics.* The quartz glass used for the reaction velocity experiments was boiled for many hours with concentrated nitric acid and washed with the utmost care. The sample weighed 27.94 g. The particles averaged about 2mm. in diameter, giving a total surface of about 400 sq. cm. The free volume in the bulb and line amounted to about 16 cc., something over 1 cc. of which was accounted for by the connecting capillary. All the experiments with this material were carried out at 500° ±2°.

A series of seventeen runs with various carbon monoxide-oxygen mixtures was made in the ordinary way (Runs 28-44). It was usually found possible

to obtain good checks if two runs with the same mixture were made consecutively. If another concentration was used, however, and this then "bracketed" with a repetition of the first, the last run did not in general check the first. This behavior is illustrated by the curves for Runs 36-40, shown in Fig. 1. Runs 36, 37, 39 and 40 were made with a stoichiometric mixture; in Run 38 the mixture was 1:1. The curves for Runs 36 and 37 are almost identical, as are those for Runs 39 and 40, but the two pairs differ considerably. The circles in the figure represent the actual observations in a typical run (35).

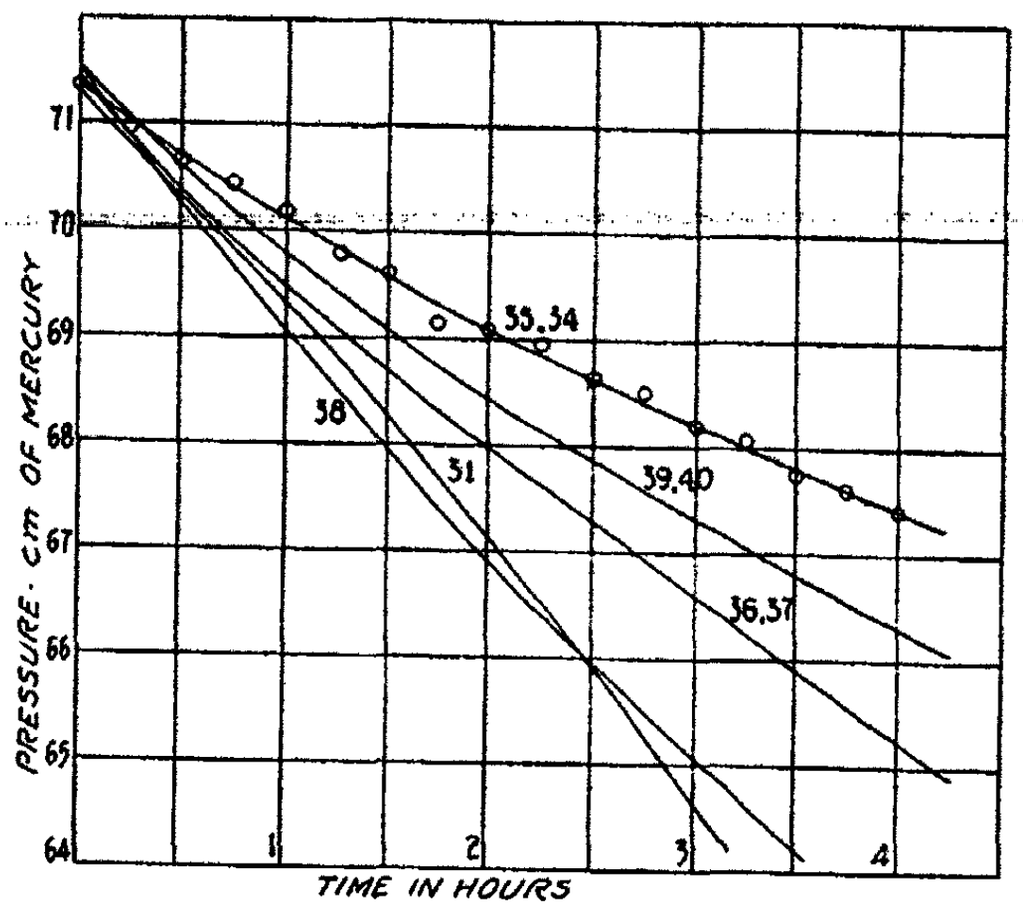



FIG. 1

Reaction velocity curves for various mixtures. The ratios of CO to $O_2$ were as follows: Runs 36, 37, 39 and 40, 2:1; Runs 34 and 35, 4:1; Run 31, 1:2; Run 38, 1:1.

In spite of the failure to obtain satisfactory checks, this series of runs furnishes qualitative information in regard to the kinetics of the reaction. Thus a 2:1 carbon monoxide-oxygen mixture gives a definitely slower rate than a 1:1, and hence the velocity equation is different from the stoichiometric equation. This is shown also by the much greater rate with a 1:1 mixture than with a 4:1 (Run 38 vs. Runs 34 and 35, Fig. 1), since these should be nearly equal if the velocity equation were stoichiometric. The probable kinetic equation will be considered more in detail below.

In an effort to obtain more reproducible results a series of runs was made in which the catalyst was heated in pure oxygen for at least an hour and then evacuated before the start of each run. Eight runs (45-52) were made under these conditions, all with a 2:1 mixture. The results are shown in Fig. 2. It is evident that the desired result was not attained; in fact, a new complication enters in the sudden breaks observed in some of these cases. It may be noted that the gas mixture used in Runs 45-48 came from the same mix, and the same is true of Runs 50-52. After Run 52 the catalyst was removed from

the bulb and thoroughly washed. The next five experiments (Runs 53-57) were all very slow in comparison with previous runs. Another washing of the catalyst was then resorted to, followed by two runs both of which showed relatively fast rates. These last experiments illustrate the great sensitivity of this catalyst to minute traces of impurities.

Owing to the fact that the reaction, in spite of the high temperature employed, was seldom more than 20% completed in the three hours duration of a run, the usual method of testing a velocity equation in the integrated

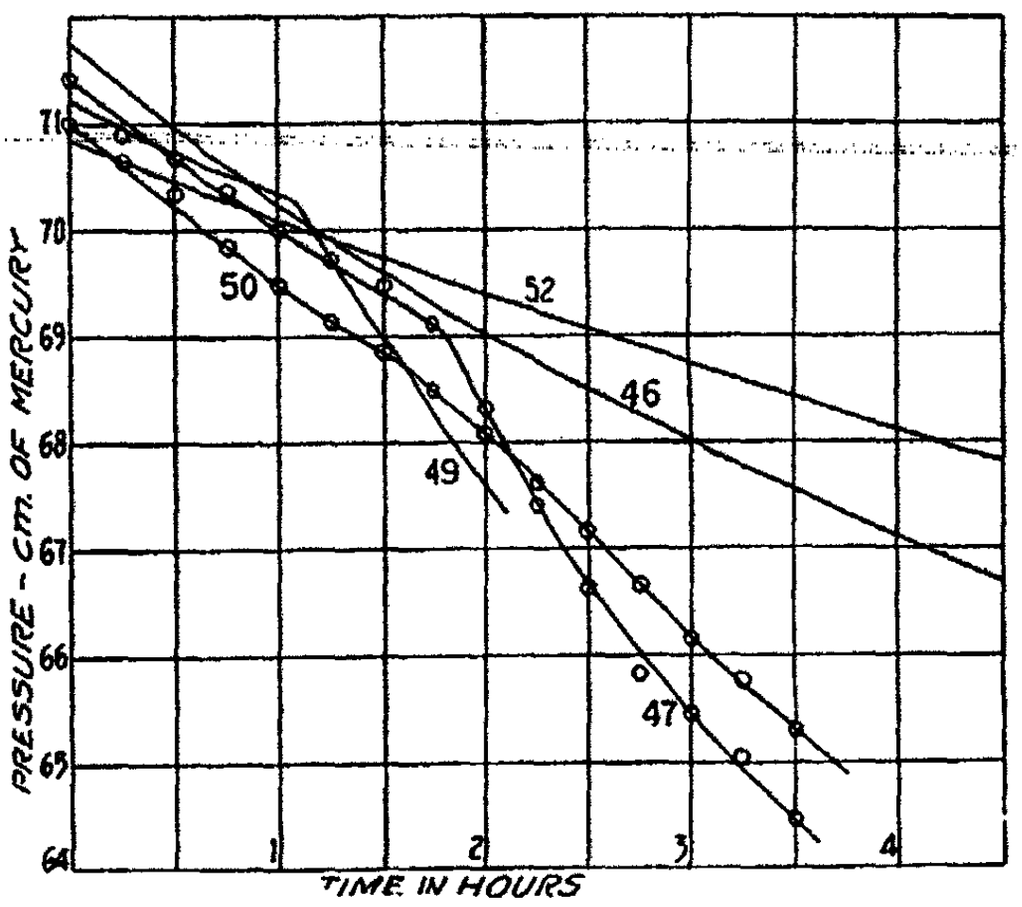



FIG. 2

Reaction velocity curves for a stoichiometric mixture. To avoid confusion the three other runs of this series are omitted. Of these the curve for Run 45 is similar to that for 46; 51 is similar to 52; 48 starts like 46 but later the rate decreases more rapidly.

form is hardly suitable. A more satisfactory procedure for the present purpose consists in comparing the relative initial rates for the several concentrations with those to be expected from the kinetic equation in question. To avoid any initial disturbances we have neglected the first half hour of each run, and have taken the total pressure decrease during the second half hour as a measure of the reaction velocity. This period is sufficiently short so that even in the fastest runs only a relatively slight change in the carbon monoxide-oxygen ratio occurred. That the effect of such changes was negligible for the present purpose is evident from the fact that the relative rates calculated below would be substantially unaltered if twice as long a time interval had been used. The reaction rates thus defined are tabulated in chronological order in the last column of Table I, which includes all the experiments made with this sample of quartz glass at 500°.

TABLE I

Reaction Velocity Experiments at 500°.

| Run | $CO:O_2$ Ratio in Mixture | Initial Pressure (cm. of Hg) | Initial Reaction Velocity (cm. per ½ hr.) |
|---|---|---|---|
| 27 | 2.02 | 71.96 | 0.72 |
| 28 | 1.00 | 71.87 | 0.96 |
| 29 | 1.00 | 71.38 | 0.62 |
| 30 | 2.03 | 71.44 | 0.50 |
| 31 | 0.49 | 71.64 | 1.02 |
| 32 | 2.02 | 71.08 | 0.54 |
| 33 | $O_2$ only | | |
| 34 | 4.03 | 71.30 | 0.68 |
| 35 | 4.03 | 71.44 | 0.56 |
| 36 | 1.95 | 71.38 | 0.92 |
| 37 | 1.93 | 71.71 | 0.94 |
| 38 | 0.98 | 71.55 | 1.20 |
| 39 | 1.98 | 71.39 | 0.82 |
| 40 | 1.98 | 71.08 | 0.80 |
| 41 | 0.99 | 48.05 | 0.46 |
| 42 | 1.00 | 47.04 | 0.54 |
| 43 | 2.01 | 70.93 | 0.60 |
| 44 | 2.01 | 71.68 | 0.60 |
| 45 | 2.01 | 71.18 | 0.68 |
| 46 | 2.01 | 71.33 | 0.72 |
| 47 | 2.01 | 71.43 | 0.68 |
| 48 | 2.01 | 70.94 | 0.70 |
| 49 | 2.00 | 71.25 | (0.34)[1] |
| 50 | 1.99 | 71.01 | 0.74 |
| 51 | 1.99 | 70.69 | 0.50 |
| 52 | 1.99 | 70.87 | 0.34 |
| 53 | 2.00 | 71.55 | 0.20[2] |
| 54 | 2.00 | 71.30 | 0.32 |
| 55 | 0.99 | 71.14 | 0.36 |
| 56 | 0.99 | 70.77 | 0.30 |
| 57 | 2.01 | 71.03 | 0.20 |
| 58 | 2.01 | 70.58 | (2.1)[1, 2] |
| 59 | 2.01 | 70.65 | 0.94 |

Owing to the variability previously mentioned, the best method of dealing with these results appears to lie in comparing the averages for each concentration. These averages for Runs 27-50, at one atmosphere initial pressure, are as follows:[3]

[1] Rate uncertain because of break in curve.

[2] Catalyst rewashed before Runs 53 and 58.

[3] Run 49 has not been included in the average because of its peculiar characteristics (cf. Fig. 2). Runs 51 and 52 have been left out of consideration because of the exceptionally low values obtained, but the average would not be affected greatly by their inclusion.

For $CO:O_2$ = 2:1, average rate = 0.71 ± 0.10
For $CO:O_2$ = 1:1, average rate = 0.93 ± 0.20
For $CO:O_2$ = 4:1, average rate = 0.62 ± 0.06
For $CO:O_2$ = 1:2, rate (1 run) = 1.02

At an initial pressure of ⅔ atmosphere, for $CO:O_2$ = 1:1, average rate = 0.50 ± 0.04.

Runs 53-57, after rewashing the catalyst, are considered as a separate series. The averages here are:

For $CO:O_2$ = 2:1, average rate = 0.24 ± 0.05
For $CO:O_2$ = 1:1, average rate = 0.33 ± 0.03.

The ratios of the average rates for each concentration to the average rate for a stoichiometric mixture are given in the second column of Table II, together with the corresponding ratios calculated from three assumed reaction equations. Because of the small number of runs involved, no great weight can be given to the values in the last two rows of the table. It is evident, nevertheless, that the facts are well represented by an equation in which the rate is made proportional to the oxygen pressure and to the square root of the pressure of the carbon monoxide. Other equations involving the square root or the square of the oxygen pressure give less satisfactory results. A direct test of the dependence of the velocity on the carbon monoxide pressure is made possible by the fact that in the two experiments at a total pressure of ⅔ atmosphere (Runs 41 and 42), the oxygen pressure was essentially the same as in a 2:1 mixture at one atmosphere. The average rate for runs 41 and 42 was 0.50; the average for the four stoichiometric mixtures bracketing these (Runs 39, 40, 43, 44) was 0.71 (the same as the average for all runs with this mixture). The ratio of these two values, 0.70, agrees well with that calculated from the above equation, 0.71.

TABLE II

Ratios of Rates for Different Concentrations

| Concentrations compared | Observed ratios | Calculated ratios $R=kp_{co}^{\frac{1}{2}}p_o$ | $R=kp_{co}.p_o$ | $R=kp_o$ |
|---|---|---|---|---|
| 1:1/2:1 (1 atm.) | 1.31 | 1.33 | 1.13 | 1.50 |
| 1:1/2:1 (⅔ atm.) | 1.37 | 1.33 | 1.13 | 1.50 |
| 4:1/2:1 | 0.87 | 0.66 | 0.72 | 0.60 |
| 1:2/2:1 | 1.44 | 1.45 | 1.00 | 2.00 |

It is assumed that the carbon dioxide formed in the reaction exerts no effect, retarding or otherwise, on the velocity. In view of the fact that the adsorption of this gas by quartz glass at 500° must be vanishingly small, such an effect would certainly not be expected, and Bodenstein and Ohlmer[1] showed that the reaction rates in their experiments were uninfluenced by a large excess of the dioxide.

[1] Bodenstein and Ohlmer: Z. physik. Chem., 53, 166 (1905).

*Discussion.* The kinetic equation which has been found to agree best with the initial reaction rates requires that for all concentrations the rate should decrease as reaction proceeds. This was the case in all but four experiments. Two of these were made with a 1:1 mixture (Runs 28 and 29), one with a 1:2 mixture (Run 31), and one with a 2:1 mixture (Run 27). The rare occurrence of this accelerating reaction, together with the fact that it occurred with a stoichiometric mixture as well as with an excess of oxygen, seems to point to some accidental influence which speeds up the reaction. Some such accidental effect is apparent in the very sharp breaks in several curves in Fig. 2. The same change which caused the sudden breaks in these curves could, by occurring more gradually, give the effect of a regularly increasing rate. These conditions seem to exist in Run 50 (Fig. 2), where the curve starts in the regular convex downward way but gradually changes to the opposite flexure. A possible explanation of this behavior seemed to lie in the formation of carbon dioxide and carbon from two molecules of the monoxide, but an experiment showed that the latter gas is perfectly stable in contact with quartz glass for at least six hours at 470°. It may be that the breaks, as well as the failure of runs to check when made under apparently identical conditions, are due to changes in the amount or the state of oxidation of accidental impurities. That mere traces of impurities might be capable of producing the observed irregularities may be shown by reference to some preliminary experiments with copper oxide as catalyst. This material at 50° gave about the same rate of reaction as quartz glass at 500°. Assuming an average temperature coefficient of 1.3 per 10° for the copper oxide, and taking its catalytic activity proportional to the quantity present, it may readily be calculated that less than 0.1 mg. of the oxide would give the same rate at 500° as the sample of quartz glass employed.

In view of the observed irregularities it may perhaps be questioned whether the kinetic equation obtained above represents reaction rates which are valid for an absolutely uncontaminated silica surface. In any case this equation suggests a reaction mechanism involving impacts of gaseous oxygen molecules on those few portions of the surface at which carbon monoxide is adsorbed, and further that this adsorption varies roughly as the square root of the pressure.

## Summary

The work of Bodenstein and Ohlmer on the catalytic oxidation of carbon monoxide in contact with quartz glass had indicated that excess of the monoxide exerts a retarding influence on the reaction. To account for this result Langmuir postulated that the quartz glass surface is largely covered with adsorbed carbon monoxide. In the present paper, however, it is shown that under the conditions of the catalysis the adsorption of all the gases involved in the reaction is immeasurably small. Certainly less than three per cent of the surface was occupied by any of them.

A redetermination of the kinetics of the reaction was then undertaken. Although the surface of our sample of catalyst was more extensive than theirs,

we have found much smaller rates of reaction at 500° than Bodenstein and Ohlmer obtained at about 300°. It seems probable that this difference is attributable to contamination of the catalyst in the latter case by small quantities of impurities, most of which would be more active catalysts than silica itself.

Our results do not confirm the retarding influence of carbon monoxide. In spite of considerable difficulty in securing quantitative checks, it has been shown that on the basis of the present experiments the reaction rate is proportional to the oxygen pressure and to the square root of the pressure of the carbon monoxide.

*University,*
*Virginia.*

3-195

# VAPOR PRESSURE OF NAPHTHALENE AT LOW TEMPERATURES

BY MARY R. ANDREWS

In an article[1] by the author on the carbonization of tungsten filaments by heating them to incandescence in naphthalene vapor it was stated that apparently not more than three-tenths of the molecules of naphthalene that struck the surface of the filament reacted. This fraction is called "E". The earlier calculation was based on vapor pressure values extrapolated from pressures determined at much higher temperatures by several other investigators.

It seemed possible that such extrapolation might be in considerable error at the lower extreme. Therefore, vapor pressure determinations of naphthalene at several low temperatures were made by two independent methods:

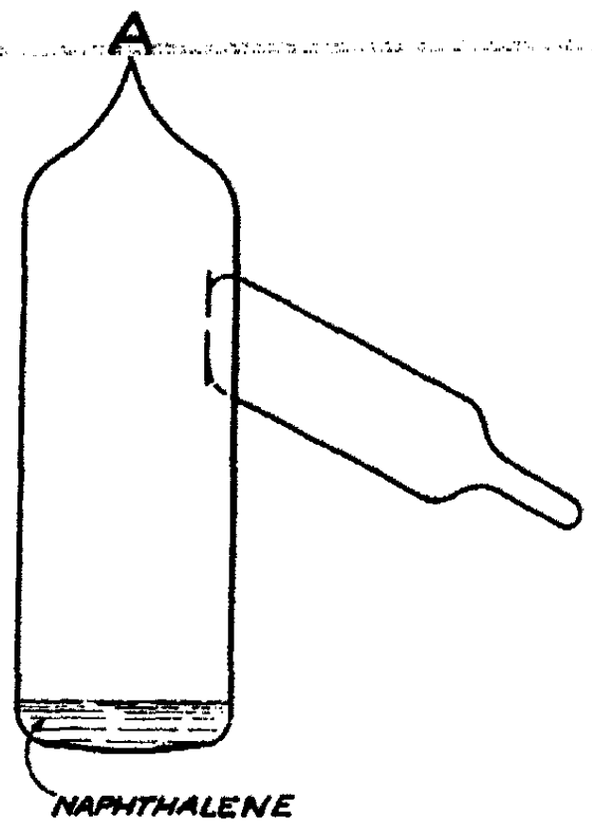



FIG. 1

The first was a modified Knudsen method. A bulb containing naphthalene was constructed with a side arm (see Fig. 1), the opening of which was covered with a platinum disk having a circular hole .508 cm. (200 mil) in diameter. This bulb was thoroughly exhausted and sealed off at the point A. The bulb was immersed in chilling solution at known temperature and the side-arm in liquid air until a convenient amount of naphthalene had distilled over. The side-arm was then cut off and the naphthalene distilled into the narrow tube at the end in which it could be weighed. Given weight, length of time for distillation, and resistance to flow of the apparatus the vapor pressure could be calculated. Resistance to flow was checked by calibration with mercury vapor using Knudsen's[2] values. Correction was made for the difference in temperature of the naphthalene in the lower part of the main bulb and of the platinum disk (which was at room temperature.)

Pressures as determined by this method are:

| | | |
|---|---|---|
| −30°C | .083, .084, .085 | × $10^{-3}$ mm. |
| −15°C | .35, .45 | " " |
| 0 | 2.4, 2.6 | " " |

The second method depended on the use of a vibration gauge in which the vibrating element instead of being a quartz fiber was a strip of four tenths

1497

[1] J. Phys. Chem., 27, 270 (1923).

[2] Ann. Physik, (4) 29, 179 (1909).

mil molybdenum about ten centimeters long by two millimeters wide. This was welded to a strip of ten mil nickel which was in turn welded to two leads in the stem of the bulb. Such a gauge (See Fig. 2), while its rate of vibration is much less than that of a quartz fiber, is very much more rugged, and difficulties due to precession are eliminated. The range of pressure over which it is useful, i. e., over which the decrement of vibration to ½ amplitude occurs in a reasonable time can be varied by varying the thickness of the strip.

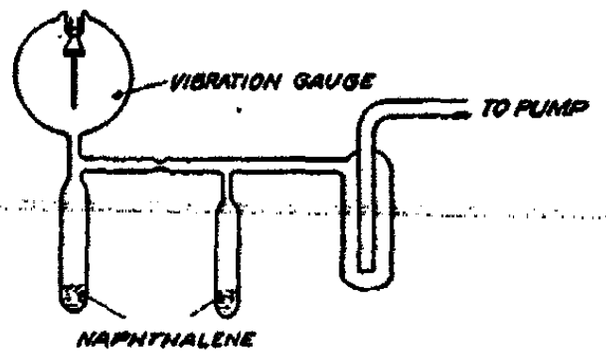


FIG. 2

Determinations with this gauge were made on a condensation pump exhaust system. A naphthalene reservoir which could be immersed in a bath at the desired temperature was connected to the lower end of the gauge. A second reservoir of naphthalene at the same temperature was connected to the tubing leading to the pump. This tubing was constricted between the two reservoirs. (See Fig. 2). A liquid-air trap near the pump caught the naphthalene as it distilled from the second reservoir. Calibration was made with water vapor using Scheel and Heuse's[1] data.

Vapor pressure determinations made by this method were as follows:

| *Temp.* | *Pressure* |
|---|---|
| −36°C | .034 × $10^{-3}$ mm |
| −30 | .045 |
| −21 | .24 |
| −14.5 | .79 |
| − 6 | 2.0 |
| + 3 | 5.6 |

The logarithms of the values obtained by these two methods as well as data published by Allen[2] and by Barker[3] and Miss Daly's data published in the paper on carbides of tungsten[4] have been plotted in Fig. 3 against the reciprocal of the absolute temperature. It will be observed that the results obtained by the two methods are in fair agreement and that the points lie closely along a straight line, which, if prolonged, coincides with Allen's data except for his two lowest points. Barker's three points and Miss Daly's data lie somewhat above this line. It is probable that Miss Daly's determinations, which were made with the ionization gauge, were high because of decomposition of the naphthalene by the hot filament of the gauge.

[1] Ann. Physik, **29**, 723 (1909).
[2] J. Chem. Soc., **77**, 410 (1900).
[3] Z. physik. Chem., **71**, 235 (1910).
[4] J. Phys. Chem., **27**, 270 (1923).

From the plot of the data obtained by the writer, and taking into account the possible errors in the various sets of observation, the most accurate values may be represented by a curve whose equation is

$$\log_{10} P = \frac{-4000}{T} + 12.275$$

where P is measured in millimeters. The following table gives values of the vapor pressure calculated from this equation.

*Vapor Pressure of Naphthalene*

| *Temperature Centigrade* | *Pressure in mm.* |
|---|---|
| −50 | $2.1 \times 10^{-6}$ mm. |
| −40 | $13 \times 10^{-6}$ |
| −30 | $65 \times 10^{-6}$ |
| −20 | $300 \times 10^{-6}$ |
| −10 | $1.15 \times 10^{-3}$ mm |
| 0 | 4.3 " " |
| +10 | 13 " " |
| 20 | 41 " " |
| 30 | 119 " " |
| 40 | 304 " " |
| 50 | 760 " " |
| 60 | 1.83 mm |
| 70 | 3.94 " |

The above formula gives a heat of evaporation of 18,280 calories per gram molecule.

Recalculation of "E" using the new vapor pressure curve gives values greater than unity, which is impossible. This is undoubtedly due to failure in the early experiments to maintain rigid cooling of the naphthalene reservoir. Stirring was intermittent and the upper layers of the chilling solution were probably considerably above the registered temperatures. A five degree error in the affective temperature would cover the discrepancies. It is, therefore, safe to assume that "E" is unity. Vapor pressure, on this basis, and without temperature correction, are shown in Fig. 3 under the caption "Assuming 'E' to be unity."

"E" is unity, however, only when the filament temperature is so high that all the carbon deposited on the surface diffuses into it immediately. Decomposition, as shown in the earlier article[1] takes place much less readily on a carbon surface.

[1] J. Phys. Chem., 27, 270 (1923).

In conclusion the author wishes to extend thanks to Dr. Saul Dushman and Dr. Irving Langmuir for their advice and helpful criticisms of this work.

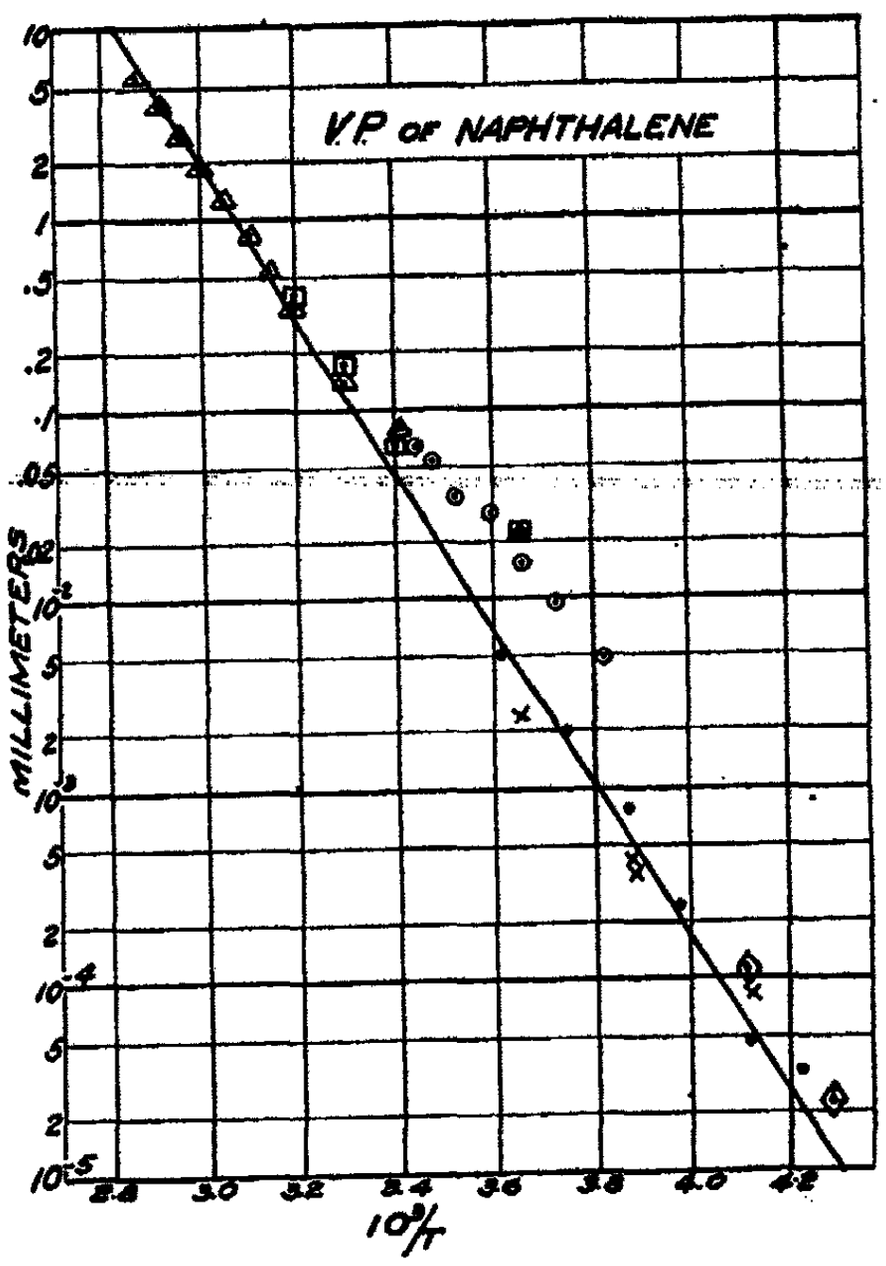



FIG. 3

△△ Determinations by Allen.
□□ Determinations by Barker.
○○ Determinations by Daly.
×× Using the modified Knudsen Method.
. . Using the modified vibration gauge.
◇◇ Assuming "E" to be unity.

## Summary

The vapor pressure curve of naphthalene from $+70°$ to $-50°$C is given. It is found that every molecule of naphthalene striking a surface of incandescent tungsten carbide is decomposed to carbon and hydrogen.

*Research Laboratory,*
*General Electric Company,*
*Schenectady, N. Y.*

# A STUDY OF THE ELECTROCAPILLARY CURVE NEAR ITS MAXIMUM

BY OSCAR KNEFLER RICE

## Introduction

All the investigators in the field of electrocapillarity have considered the charge in the mercury to be at the surface[1] (though Gouy[2] suggests, in considering some of his results, that this might not be the case), while they have generally supposed that there was a diffuse atmospheric layer of ions in the solution near the mercury. Such a supposition seems incapable of accounting for the facts. We propose to show that the idea of a diffuse layer in the mercury as well as in the solution offers a possibility of explaining the shape of the electrocapillary curve in the neighborhood of its maximum.

There is another possibility, however, which we will consider, and we shall find that it gives results too near to those of the theory above outlined to allow us to distinguish between them from the experiments. Suppose the mercury to act as a perfect conductor so that the charge is at the surface, B, of the mercury; but suppose that on account of their finite size the ions in the solution cannot come right up to the surface of the mercury, their closest effective approach being the surface A, which is some little distance from the surface B. There will then be a potential drop between B and A plus another potential drop due to the diffuse layer of ions in the solution back of A. B and A will act like the plates of a parallel condenser of constant capacity whose value is arbitrarily determined so as to best fit the data. This is a simple type of the cases considered by Stern[3].

## Two Diffuse Layers

Chapman[4] has worked out the theory of the diffuse layer for uniunivalent electrolytes, assuming perfect solution laws with equilibrium under osmotic and electric forces. These assumptions give the equations for the distribution

$$n_x = ne^{-\epsilon\phi_x/RT}$$

and

$$\bar{n}_x = ne^{+\epsilon\phi_x/RT}$$

where $n_x$ is the concentration of positive ions and $\bar{n}_x$ the concentration of negative ions at a distance x from the surface, $n$ the concentration of both in the solution at an infinite distance from the surface, $e$ the base of natural logarithms, $\epsilon$ the charge per unit mass of ions, $\phi_x$ the potential at $x$ above that in the solution, R the gas constant, and T the temperature.

---

[1] See, e.g., Herzfeld: Physik. Z., **21**, 38 (1920); Frumkin: Phil. Mag., (6) **40**, 384 (1920); Chapman: **25**, 475 (1913).

[2] Gouy: Ann. Phys. (9) **7**, 161 (1917).

[3] Stern: Z. Elektrochem., **30**, 508 (1924).

[4] Chapman: loc. cit.

With Poisson's equation these give for the charge per unit surface

$$Q = \sqrt{\frac{KnRT}{2\pi}}\left(e^{\frac{\epsilon\phi_{x_0}}{2RT}} - e^{\frac{\epsilon\phi_{x_0}}{2RT}}\right) \qquad (1)$$

where Q is the charge per unit surface, K the dielectric constant of the medium, and $\phi_x = \phi_{x_0}$ when $x = 0$.

The differential equation which gives the surface tension is $d\gamma = -Qd\phi$ where $\gamma$ is the surface tension, Q is the excess of positive charge in the mercury meniscus, per unit surface, and $\phi$ is the potential of the mercury meniscus above that of the solution. If the charge in the mercury is all at the surface then all the potential drop is in the solution (i.e. $\phi_{x_0} = \phi$), Q is given in terms of that potential drop by (1), and we can integrate immediately, getting

$$\gamma_0 - \gamma_1 = \frac{2RT}{\epsilon}\sqrt{\frac{KnRT}{2\pi}}\left(e^{\frac{\epsilon\phi_1}{4RT}} - e^{-\frac{\epsilon\phi_1}{4RT}}\right)^2 \qquad (2)$$

$\gamma_0$ being the surface tension at the maximum of the electrocapillary curve when $\phi$ is zero, and $\gamma_1$ being the surface tension when $\phi = \phi_1$. Such a theory of course only applies to capillary inactive substances in solution.

If there is a diffuse layer and consequent drop of potential in the mercury we can break the potential drop into two parts, putting $d\phi = d\phi' - d\phi''$, where $\phi'$ is the potential of the surface above that of the solution and $\phi''$ the potential of the surface above that of the mercury. We will also let Q' be the excess of positive charge in the mercury and Q'' the excess of positive charge in the solution. We will then have $Q' = Q = -Q''$, so that

$$d\gamma = -Qd\phi = -Q(d\phi' - d\phi'') = -Q'd\phi' - Q''d\phi''$$

We will let $\gamma_0' - \gamma'_1 = -\int_0^{\phi_1'} Q'd\phi'$ and $\gamma_0'' - \gamma_1' = -\int_0^{\phi_1''} Q''d\phi''$ where

$\phi' = \phi'_1$ and $\phi'' = \phi_1''$ when $\phi = \phi_1$.

Now the ions will be attracted to the mercury as they would to a surface whose charge per unit area was Q', so $\gamma_0' - \gamma'_1$ can be evaluated by integrating. Now if we assume that there is a diffuse layer in the mercury, and that it is caused by electrons and ions in thermal agitation, acting just as the ions in the solution, and if we assume that the positive mercury ions are singly charged (though, as suggested by Prof. G. N. Lewis, this might not be a good assumption, as singly charged mercury ions are not known in solution), $\gamma_0'' - \gamma''$ may also be readily evaluated by integration, in the same way that we obtained (2). Hence we have the equations, in which the primed quantities refer to the water layer and the doubly primed to the mercury:

$$\gamma_0 - \gamma_1 = \gamma_0' - \gamma'_1 + \gamma_0'' - \gamma_1''$$

$$\gamma_0' - \gamma_1' = \frac{2RT}{\epsilon}\sqrt{\frac{K'n'RT}{2\pi}}\left(e^{\frac{\epsilon\phi_1'}{4RT}} - e^{-\frac{\epsilon\phi_1'}{4RT}}\right)^2$$

$$\gamma_0'' - \gamma_1'' = \frac{2RT}{\epsilon}\sqrt{\frac{K''n''RT}{2\pi}}\left(e^{\frac{\epsilon\phi_1''}{4RT}} - e^{-\frac{\epsilon\phi_1''}{4RT}}\right)^2$$

$$\phi_1 = \phi_1' - \phi_1''$$

and, taking cognizance of the fact that $Q' = -Q''$,

$$\sqrt{\frac{K'n'RT}{\pi_2}}\left(e^{\frac{\epsilon\phi_1'}{2RT}} - e^{-\frac{\epsilon\phi_1'}{2RT}}\right) = -\sqrt{\frac{K''n''RT}{2\pi}}\left(e^{\frac{\epsilon\phi_1''}{2RT}} - e^{-\frac{\epsilon\phi''}{2RT}}\right)$$

In these five equations, aside from the known constants, the following quantities are measured experimentally, or are known: $\gamma_0 - \gamma_1$; $K'n'$; $T$; $\phi_1$. The following quantities are unknown: $\gamma_0' - \gamma_1'$; $\gamma_0'' - \gamma_1''$; $\phi_1'$; $\phi_1''$; $K''n''$. A word of explanation is perhaps still needed about $K''$ and $n''$. $n''$, the number of free electrons per unit volume in mercury, is not necessarily assumed to be equal to the number of atoms in mercury. $K''$ is the dielectric constant that mercury would have were there no free electrons in it; for this is the medium in which the ions and free electrons of mercury are immersed. $K''n''$ is constant throughout all the measurements, and may be determined so as to best fit them (as we are not now assuming the mercury to be a perfect conductor—if it were $K''n''$ would be infinite), giving us five equations from which to determine the other four unknowns and $\gamma_0 - \gamma_1$ which can then be compared with the experimental $\gamma_0 - \gamma_1$ values. This computation has been made by graphical means with the results given in Table I, and the results compared with data given by Frumkin[1], and with the results of other calculations in Table III. We have used, in order to do this, a value for $\sqrt{\frac{K''n''}{K'}}$ of .004. This value gives better results than .003 or .005. Some results calculated on the latter bases have also been tabulated, in order to show what kind of differences occur. We see that our calculations agree very much better with the data than those made on the assumption that the charge is at the surface of the mercury, with a diffuse layer only in the solution.

The method of making this calculation is as follows: We plot a curve from (1) of $Q/\sqrt{Kn}$ as ordinate against $\phi_{1_0}$ as abscissa. Now in order to find $\phi_1''$ and $\phi_1'$ we find on the above curve two points such that the ordinates are in the ratio $\sqrt{\frac{K'n'}{K''n''}}$, and the abscissae add to give $\phi_1$, they being then, respectively, $\phi_1''$ and $\phi'_1$. We now easily find $\gamma_0' - \gamma_1'$ and $\gamma_0'' - \gamma_1''$ corresponding to the $\phi_1'$ and $\phi_1''$ found, from equation (2), and hence we find their sum. (It may be readily verified from equation (1), knowing the con-

[1] Frumkin: Pil. Mag., (6) 40, 385 (1920).

centration of salt in the solution and the value of K″n″, that the values of $\phi_1'$ and $\phi_1''$ given in Table I are such as to give equal charges (disregarding signs) for the two sides of the boundary.)

TABLE I

Calculations of $\gamma_0 - \gamma$ for uniunivalent salts,

assuming two diffuse layers, at T = 18°, and taking $\sqrt{\frac{K'' n''}{K'}} = .004$

| $\phi_1$ Total (volts) | $n' \times 10^3$ (equiv. per cc) | $\phi_1''$ Mercury (volts) | $\phi_1'$ Water (volts) | $\gamma_0'' - \gamma_1''$ Mercury (dynes per cm) | $\gamma_0' - \gamma_1'$ Water (dynes per cm) | $\gamma_0 - \gamma_1$ Total (dynes per cm) |
|---|---|---|---|---|---|---|
| .05 | 1.0 | .043 | .007 | .286 | .047 | .33 |
| .05 | .1 | .035 | .016 | .188 | .075 | .26 |
| .05 | .01 | .022 | .028 | .070 | .093 | .16 |
| .05 | .001 | .011 | .039 | .016 | .057 | .07 |
| .1 | 1.0 | .084 | .016 | 1.31 | .28 | 1.59 |
| .1 | .1 | .067 | .033 | .76 | .42 | 1.18 |
| .1 | .01 | .046 | .054 | .34 | .38 | .72 |
| .15 | .01 | .070 | .080 | .84 | .92 | 1.76 |

### Diffuse Layer plus Condenser

We now proceed to make calculations for the surface tension of the mercury on the basis of the very different set, at least in principle, of assumptions which we have already outlined in the introduction. Our method of making the calculations, will not differ very greatly from that used above, however, for, as before, to get the total surface tension difference we may add the surface tension differences which would be contributed by each of the two layers. Instead of the equations connecting the charge and the surface tension with the potential, which we have written for the surface tension of the diffuse layer in the mercury, we have corresponding equations for a condenser of constant capacity. We find that the condenser which best fits the data is

TABLE II

Calculations of $\gamma_0 - \gamma$ for uniunivalent salts, assuming diffuse layer in water plus a condenser of constant capacity, at T = 18°C., the distance of the plates of the equivalent condenser in vacuo being $2.3 \times 10^{-9}$ cm.

| $\phi_1$ Total (volts) | $n' \times 10^3$ (equiv. per cc) | $\phi_1'$ Diffuse layer (volts) | $\phi_1'' *$ Condenser (volts) | $\gamma_0' - \gamma_1'$ Diffuse layer (dynes per cm) | $\gamma_0'' - \gamma_1''$ Condenser (dynes per cm) | $\gamma_0 - \gamma_1$ Total (dynes per cm) |
|---|---|---|---|---|---|---|
| .05 | 1.0 | .007 | .043 | .05 | .35 | .40 |
| .05 | .1 | .017 | .033 | .10 | .21 | .31 |
| .05 | .01 | .030 | .020 | .11 | .08 | .19 |
| .05 | .001 | .041 | .009 | .065 | .015 | .08 |
| .1 | 1.0 | .014 | .086 | .21 | 1.42 | 1.63 |
| .1 | .1 | .032 | .068 | .38 | .89 | 1.27 |
| .1 | .01 | .057 | .043 | .43 | .36 | .79 |
| .15 | .01 | .079 | .071 | .90 | .97 | 1.87 |

TABLE III

Comparison of observed and calculated $\gamma_o - \gamma_1$ at T = 18°C. (unless otherwise noted)

| $\phi_1$ (volts) | $n' \times 10^3$ (equiv. per cc) | $\gamma_o - \gamma_1$ (dynes per cm) Obs. KCl Frumkin | Obs.* KCl Smith | Obs. $KNO_3$ Frumkin | Calc. from Table I | Calc. from Table II | Calc.† $\sqrt{\frac{K''n''}{K'}} = .03$ | Calc.† $\sqrt{\frac{K''n''}{K'}} = .005$ | Calc.‡ one diffuse layer | Calc condenser only |
|---|---|---|---|---|---|---|---|---|---|---|
| .05 | 1.0 | | | .34 | .33 | .40 | .27 | | 2.67 | .26 |
| .05 | .1 | .43 | | .29 | .26 | .31 | .21 | | .96 | .26 |
| .05 | .01 | | | .25 | .16 | .19 | .14 | | .32 | .26 |
| .05 | .001 | .37 | | | .07 | .08 | .07 | .08 | .10 | .26 |
| .1 | 1.0 | | | 1.36 | 1.59 | 1.63 | 1.26 | 1.84 | 13.8 | 1.04 |
| .1 | .5 | | 2.0 | | | | | | | 1.04 |
| .1 | .1 | 1.38 | 1.8 | 1.20 | 1.18 | 1.27 | .85 | | 4.96 | 1.04 |
| .1 | .05 | | 1.0 | | | | | | | 1.04 |
| .1 | .01 | .85 | | .98 | .72 | .79 | .63 | | 1.67 | 1.04 |
| .15 | 1.0 | | 5. | | | | | | | 2.34 |
| .15 | .5 | | 4.2 | | | | | | | 2.34 |
| .15 | .01 | 2.2 | | 2.3 | 1.76 | 1.87 | 1.54 | | 5.57 | 2.34 |

* Temp. probably 16° or 17°C.

† As in Table I

‡ Calculated by Frumkin taking into account the degree of ionization of the salt. (In making our calculations we have assumed complete ionization. The difference is not great.)

equivalent to one in vacuo with a distance between the plates of $2.3 \times 10^{-9}$ cm., no allowance being made for possible differences when different ions are adsorbed. The calculations made on this basis are tabulated in Table II, and the results are also placed in Table III, for comparison. It will be seen that the values are very close to those calculated on the basis of two diffuse layers. The best calculations, assuming only a condenser of constant capacity with no diffuse layers, are also given in Table III, though this is an inherently improbable assumption.

TABLE IV

Observed values for methyl and ethyl alcohol solutions

A) .1N $NH_4NO_3$ in $CH_3OH$, T=8°C.

| $\phi_1$ (volts) | $\gamma_0 - \gamma_1$ (dynes per cm) |
|---|---|
| .05 | 0 |
| .10 | 1.2 |
| .15 | 1.9 |

B) 1.0N $NH_4NO_3$ in $CH_3OH$, T=8°C.

| $\phi_1$ (volts) | $\gamma_0 - \gamma_1$ (dynes per cm) |
|---|---|
| .05 | .4 |
| .10 | 1.1 |
| .15 | 2.4 |

C) .2N $NH_4NO_3$ in $C_2H_5OH$, T=10°C.

| $\phi_1$ (volts) | $\gamma_0 - \gamma_1$ (dynes per cm) |
|---|---|
| .05 | .09 |
| .10 | .77 |
| .15 | 1.5 |

D) 1.0 LiCl in $C_2H_6OH$, T=10°C.

| $\phi_1$ (volts) | $\gamma_0 - \gamma_1$ (dynes per cm) |
|---|---|
| .05 | .18 |
| .10 | 1.2 |
| .15 | 3.2 |

In Table III we have, in addition, estimated some values from data of S. W. J. Smith's[1]. It is seen that they do not check very well with Frumkin's values.

In Table IV we have made estimates from some data of Frumkin's[2] for solutions in methyl and ethyl alcohols. In comparing these with values in water solutions it should be remembered that their dielectric constants are, respectively, about 31 and 25, so in every case solutions should be compared with water solutions whose strengths are 31/81 and 25/81, respectively. These data were taken at a somewhat lower temperature, but the difference is not sufficient to have much effect.

### Other than Uniunivialent Salts

In order to generalize the calculations for other than uniunivalent salts one may readily derive, by a method similar to Chapman's, the more general formula

$$Q_1 = \sqrt{\frac{KnRT}{2\pi}\left\{\frac{1}{a}\left(e^{\frac{ae\phi_1}{RT}} - 1\right) + \frac{1}{b}\left(e^{-\frac{be\phi_1}{RT}} - 1\right)\right\}} \qquad (3)$$

where $a$ is the valence of the ion whose charge is opposite to that of the boundary, and $b$ the valence of the other, while $\phi_1$ is now the absolute magnitude of the difference in potential between solution and surface, and $n$ is con-

[1] Smith: Z. physik. Chem., 32, 433 (1900); Phil. Trans., 193A, 47 (1900).
[2] Frumkin: Z. physik. Chem., 103, 55 (1922).

centration in equivalents per cc. One can now proceed as before to make calculations for the double diffuse layer. This we have done in Table V, and compared with Frumkin's[1] values in Table VI.

TABLE V

Calculations for $\gamma_0 - \gamma_1$ for unibivalent salts, assuming two diffuse layers at T = 18°C., and taking $\sqrt{\frac{K''n''}{K'}} = .004$

| | $\phi_1$ Total (volts) | $n' \times 10^3$ (equiv. per cc.) | $\phi_1''$ Mercury (volts) | $\phi_1'$ Water (volts) | $\gamma_0'' - 2_1''$ Mercury (dynes per cm) | $\gamma_0' - \gamma_1'$ Water (dynes per cm) | $\gamma_0 - \gamma_1$ Total (dynes) per cm |
|---|---|---|---|---|---|---|---|
| | .05 | .1 | .038 | .012 | .220 | .075 | .29 |
| | .05 | .01 | .027 | .023 | .108 | .093 | .20 |
| a=2, b=1* | .1 | .1 | .074 | .026 | .96 | .38 | 1.34 |
| | .1 | .01 | .058 | .042 | .56 | .36 | .92 |
| | .15 | .01 | .091 | .059 | 1.60 | .88 | 2.48 |
| | .1 | .1 | .068 | .032 | .80 | .45 | 1.25 |
| a=1, b=2 | .1 | .01 | .046 | .054 | .33 | .41 | .74 |
| | .15 | .01 | .070 | .080 | .85 | .97 | 1.82 |

*a is the valence of the ion whose charge is opposite to that of the surface, b is the valence of the other one.

TABLE VI

Comparison of observed and calculated values of for unibivalent salts at T = 18°C.

| $\phi_1$ (volts) | $n' \times 10^3$ (equiv. per cc) | $\gamma_0 - 2_1$ (dynes per cm) Obs. $Na_2SO_4$ | Calc. from Table V a=2, b=1 | Calc. from Table V a=1, b=2 | Calc. from Table I (a=1, b=1) |
|---|---|---|---|---|---|
| .05 | .1 | .34 | .29 | | .26 |
| .05 | .01 | .34 | .20 | | .16 |
| .1 | .1 | 1.35 | 1.34 | 1.25 | 1.18 |
| .1 | .01 | 1.0 | .92 | .74 | .72 |
| .15 | .01 | 2.35 | 2.48 | 1.82 | 1.76 |

* It is not known whether the observed values are for a = 1 and b = 2, or vice versa, or whether they are an average of both.

## Discussion

At first sight it might seem that a combination of the two theories outlined above, i.e., a diffuse layer in the solution, plus a condenser of constant capacity, plus a diffuse layer in the mercury would be the final step in getting the theoretical results to agree better with the experimental. But this could not account for the high values of $\gamma_0 - \gamma_1$ which are observed in dilute solutions at low voltages. For, from (1) or (3), at low voltages $Q_1 = c\phi_1$, approximately, where $c$ is *a* constant depending on the concentration of the electrolyte in the solution, etc., but independent[2] of $\phi_1$.

[1] Frumkin: Phil. Mag., (6) 40, 385 (1920).

[2] This is not a very good approximation for $\phi_1 = .05$ volt, because in this case $\phi_1/2RT = 1.00$ at 18°C, but it will be sufficient for what we wish to do.

The expression for the surface tension becomes $\gamma_0 - \gamma_1 = c\phi/2$, where $c$ is the same constant as before. But equations of the same form hold for the condenser of constant capacity also. Writing primes for the diffuse layer in the solution, double primes for the mercury, and triple primes for the condenser, we have $Q_1' = Q_1'' = Q_1'''$ or $c'\phi_1' = c''\phi_1'' = c'''\phi_1'''$. And, as we may readily show, by a slight generalization, that we may still find our total surface tension by addition, it is given by

$$c'\phi'^2/2 + c''\phi_1''^2/2 + c'''\phi_1'''^2/2 = c'\phi'(\phi_1' + \phi_1' + \phi_1''')/2$$

But $\phi_1' + \phi_1'' + \phi_1'''$ is the total voltage drop, and in any experiment this is a fixed quantity. Also in a given experiment c' is fixed. c'' and c''' are the arbitrary quantities which are to be determined to fit the experiment. So, obviously, the maximum of the expression $c'\phi'(\phi_1' + \phi_1'' + \phi_1''')/2$ is to be found by setting $\phi_1''$ and $\phi_1'''$ equal to zero, so that $\phi_1'$ is the whole voltage drop. But this is just what is done when we consider only the diffuse layer in the solution. An examination of Table III will show that this does not help us appreciably. There is considerable possibility that the high values are due to experimental error.

It is interesting that if we take the value of $\sqrt{\frac{K''n''}{K'}}$ as being correctly given by the figure 0.004 it gives an upper limit for the number of free electrons in mercury. As K'' cannot possibly be less than 1, n'' cannot be greater than 0.0013 mols per cc. This means that no more than one in fifty of the mercury atoms is ionized into a positive ion and a free electron. Millikan and Eyring[1] have recently decided from other considerations that most of the electrons in a metal do not share in the thermal agitation. In view of these facts it would be of interest to study the maximum of the electrocapillary curves of various amalgams, and attempt to correlate the results with the thermoelectric power and the thermal and electrical conductivities. At the same time pains should be taken to find out if possible whether there is lack of symmetry in the electrocapillary curve in the case of unibivalent electrolytes, and even in the case of uniunivalent electrolytes, to see whether we are justified in assuming singly charged mercury ions to exist in mercury.

Before we leave the subject we must note a couple of obvious limitations to the theory. Stern[2] has pointed out that there is great piling up of the ions near the boundary required by Chapman's fundamental equation, which says that $n_x = ne^{-\epsilon\phi_x/RT}$ where $n_x$ is the concentration of ions at a distance $x$ from the surface, and $\phi_x$ is the potential at $x$ over that in the solution (this being written for positive ions—the piling up then occurs when $\phi_x$ is negative). Applying this formula to calculate the concentration of ions in the least favorable case with a uniunivalent electrolyte, that of the mercury side of the boundary in the 0.01N solution at 0.15 volts, we find the concentration of the attracted ions at the boundary to be 18.5 mols per liter, a high, but perhaps

[1] Millikan and Eyring: Phys. Rev., 27, 51 (1926).
[2] Stern: Z. Elektrochem., 30, 508 (1924).

not an excessively high figure for purposes of approximation, when it is remembered that the forces that Chapman considers increase at the same time as those he neglects. At much higher voltages, the diffuse layer theory obviously breaks down entirely, and this was one of the considerations that originally led Stern to the condenser theory.

That our assumption that there are only electrostatic forces acting on the ions is not strictly true is seen by the fact that the maximum value of the surface tension of the electrocapillary curve in solutions does not coincide exactly with the maximum value in water[1].

## Summary

Previous investigators in the field of electrocapillarity have considered the charge to reside on the surface of the mercury, as would occur if the mercury were a perfect conductor. Calculations made on this basis, and assuming a diffuse layer of ions in the solution near the mercury, do not agree with experimental results.

Two alternatives are suggested. (1) There may be a diffuse layer of positive particles and electrons in the mercury as well as the diffuse layer in the solution. (2) Due to the finite size of the ions it may be that they can only approach within a certain distance of the surface. Thus we might have a diffuse layer in the solution and a sort of condenser between the solution and the mercury. The difference in surface tension referred to the surface tension of the maximum of the electrocapillary curve may be considered to be equal to the sum of the differences which would be caused by the diffuse layer in the solution and the diffuse layer in the mercury (or the condenser) respectively, for any given potential drop across the respective layers. Also the distribution of the potential drop between the layers may be found. The surface tension is calculated in both the ways suggested above. The two methods give very similar results, which agree better with the experimental data than the calculations on the basis of the single diffuse layer.

In order to make the calculation on the assumption of two diffuse layers it is necessary to give such a value as will best fit the data to $K''n''$, where $K''$ is the dielectric constant which mercury would have were there no free electrons, and $n''$ is the concentration of free electrons in mercury. If the value thus found is correct we may set a maximum for $n''$, for $K''$ cannot be less than 1. From this we estimate that not more than 1 atom in 50 can be ionized into a positive ion and a free electron.

*Department of Chemistry,*
*University of California,*
*Berkeley, California.*

[1] See Gouy: Ann. Chim. Phys., (7) 29, 160 (1903).

SIL -918

# GERMANIUM XVII. FUSED GERMANIUM DIOXIDE AND SOME GERMANIUM GLASSES*

BY L. M. DENNIS AND A. W. LAUBENGAYER

## A[1]. Fused Germanium Dioxide.

Winkler, the discoverer of germanium, stated[2] that germanium dioxide appears to be highly refractory and that when heated to vivid incandescence it suffers no change or loss of weight.

Biltz[3] found that the dioxide when heated in nitrogen to 1025° did not appreciably lose in weight.

Nichols[4] heated the oxide with an oxy-hydrogen flame and observed that it fused at about 1400°.

Müller and Blank[5] state that when heated in a quartz tube the oxide fused and coalesced between 1090° and 1100°.

Fusion of germanium dioxide in such a manner as will yield a clear, transparent, homogeneous product, and will avoid reduction or contamination of the material, was found to be fraught with many difficulties. Fusion in crucibles over a flame such as that of a Meker blast-burner gave a black product because of the reducing action of the gases from the flame. After many trials, gas heating was abandoned and an Ajax-Northrup High Frequency Induction Furnace was used.

It was here found that the usual porcelain crucibles could not be employed as containers of the germanium dioxide because of the action of the latter upon the glaze of the crucible. Graphite crucibles were found to reduce the dioxide. When the sample was placed in an alundum crucible and this was inserted in a graphite tube which acted as a resistor, a clear, glass-like layer of fused germanium dioxide was found at the bottom of the crucible after the heating, but there was still some reduction of the substance which was doubtless caused by carbon monoxide resulting from the action of the oxygen of the air upon the graphite.

These results clearly showed that a reducing atmosphere must be avoided during the fusion. It was not feasible to cap the quartz tube of the furnace and heat the germanium dioxide in a vacuum, because production of a clear product free from striations can be accomplished only by stirring the fused mass to cause the escape of bubbles of air, which if retained in the melt would render the product milky and translucent.

---

*Contribution from the Department of Chemistry, Cornell University.

[1] The investigation upon which this part of this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Winkler: J. prakt. Chem., **142**, 177 (1886).

[3] Wilhelm Biltz: Z. anorg. Chem., **72**, 313 (1911).

[4] Nichols: Proc. Nat. Acad. Sci., **9**, 248 (1923).

[5] Müller and Blank: J. Am. Chem. Soc., **46**, 2358 (1924).

Since carbon could not be used as the resistor, there remained only high-melting metals. Tungsten, molybdenum and tantalum are not suitable because they are oxidized when heated to high temperatures in the presence of oxygen. Wrought iron pipe was found to withstand a temperature of 1400°, but this melted before the higher temperature necessary for the production of a homogeneous product was reached. Nickel gave a similar result.

A large platinum crucible was then used as the resistor. An unglazed porcelain crucible, packed tightly with germanium dioxide, was placed in the platinum crucible which itself was embedded in magnesia in the large quartz tube of the induction furnace. The platinum resistor being on the outside of the porcelain crucible had to be carried to a temperature considerably higher than is necessary to satisfactorily melt and fine the germanium dioxide. When the germanium dioxide reached a temperature of 1400°, as determined by an optical pyrometer, it was liquid and bubbles of air were steadily escaping, but the thin upper wall of the platinum crucible then over-heated and melted.

To avoid this difficulty the resistor was next made of heavy sheet platinum of uniform thickness, and this was placed on the inside of the crucible and was filled with the germanium dioxide. The arrangement of the apparatus is shown in Figure 1.

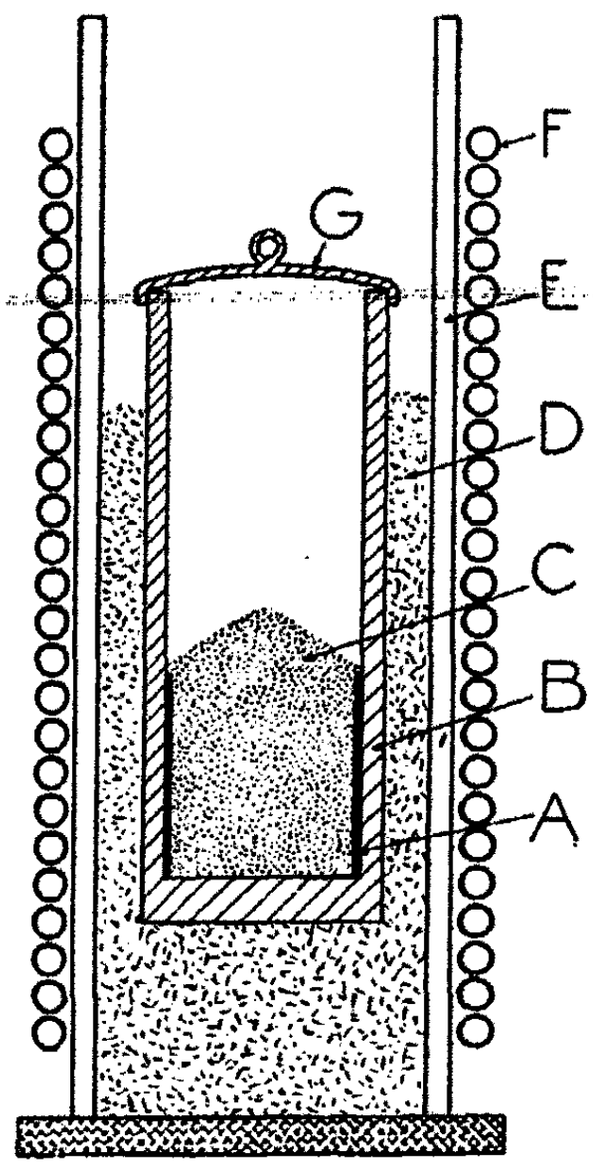


FIG. 1

*B* is a cylindrical alundum crucible. *A* is the platinum resistor made of sheet platinum about 0.4 mm. thick. The cylinder is 3 cm. high and 3 cm. in diameter. *D* is the insulating magnesia, *E* the quartz tube of the furnace, and *F* the induction coil. *G* is an alundum cover which can be removed when the melt is to be stirred. The platinum cylinder was placed in the crucible and was filled with 50 grams of germanium oxide, *C*. As the temperature rose, the oxide liquefied at about 1100°, but at that temperature was still quite viscous. At 1350° air bubles were seen to slowly escape, and the oxide began to volatilize. It was held at temperatures between 1400° and 1450° for about twenty minutes, and was frequently stirred with a platinum rod during this period. The temperature was then raised to about 1470° for about five minutes and the mass was then allowed to cool.

When fused in this manner, germanium dioxide was found to be colorless and transparent, free from air bubbles, and showing very few striae. It broke

with plane fractures, and the pieces were brilliant and sparkling. A spectrogram by Professor Papish of this Department showed that the material contained only slight traces of silicon, aluminum, iron and copper, the total amount of impurity being not more than 0.2 per cent. This product was used in all of the determinations described below. Selected pieces were ground and were then polished with rouge.

*Refractivity.*—Germanium dioxide, prepared from germanium tetrachloride by hydrolyzing the latter compound with water was found to have an index of refraction for sodium light of $n_D = 1.650$ when this was determined under the microscope by immersion in liquids of known refractive index. Fused germanium dioxide gave by this method $n_D = 1.610$. The fused dioxide tested with an Abbe refractometer gave $n_D = 1.6082$. To ascertain the refractivity for light of different wave-lengths, pieces of the fused dioxide were ground with two plane faces at right angles to each other, and these pieces were then examined with a Pulfrich refractometer. The results together with values for fused silicon dioxide[1] are in Table I.

TABLE I

| | Fused Germanium Dioxide | Fused Silicon Dioxide |
|---|---|---|
| $n_C$ | 1.60304 | 1.456415 |
| $n_D$ | 1.60696 | 1.458477 |
| $n_F$ | 1.61762 | 1.463165 |

These results show that the refractivity of fused germanium dioxide is considerably higher than that of fused silica. For sodium light the refractive index is ten per cent. above that of silica.

*Dispersion.*—Using the data for refractivity given in Table I, the values for the dispersion were calculated, Table II.

TABLE II

A = Fused Germanium Dioxide; B = Fused Silicon Dioxide

| | | Partial Dispersion | Mean Dispersion | Partial Dispersion Ratios | | Effective Refractivity |
|---|---|---|---|---|---|---|
| | $n_D$ | $n_D - n_C$ | $n_F - n_D$ | $n_F - n_C$ | $\frac{n_D - n_C}{n_F - n_C}$ | $\frac{n_F - n_D}{n_F - n_C}$ | $\nu = \frac{n_D - 1}{n_F - n_C}$ |
| A | 1.60696 | .00392 | .01066 | .01458 | .269 | .731 | 41.6 |
| B | 1.45848 | .002062 | .004688 | .006750 | .305 | .695 | 67.9 |

It will be seen that the dispersive power of the fused germanium dioxide is considerably higher than that of fused silica, the "mean dispersion" being 116 per cent. greater. The partial dispersion ratios for the two substances are practically identical. They therefore spread the spectrum in the same relative manner and could probably be used together in achromatic combinations. It will be noted that the "effective refractivity" of the germanium dioxide is 39 per cent. lower than that of fused silica.

*Transmission.*—Fused germanium dioxide is colorless and hence shows little absorption in the visible part of the spectrum. Mr. C. V. Shapiro of the

[1] Gifford: Proc. Roy. Soc., **70**, 329 (1902); **84**, 193 (1910).

Department of Physics kindly determined the transmission for us and found a piece 2.5 mm. thick transmitted about 76 per cent. of the visible part of the spectrum, and gave no noticable absorption bands. The loss of the 24 per cent. is probably to be ascribed to reflection and dispersion due to imperfectly polished surfaces and to striae in the sample. The transmission of the piece was 90 per cent. that of a clear piece of quartz.

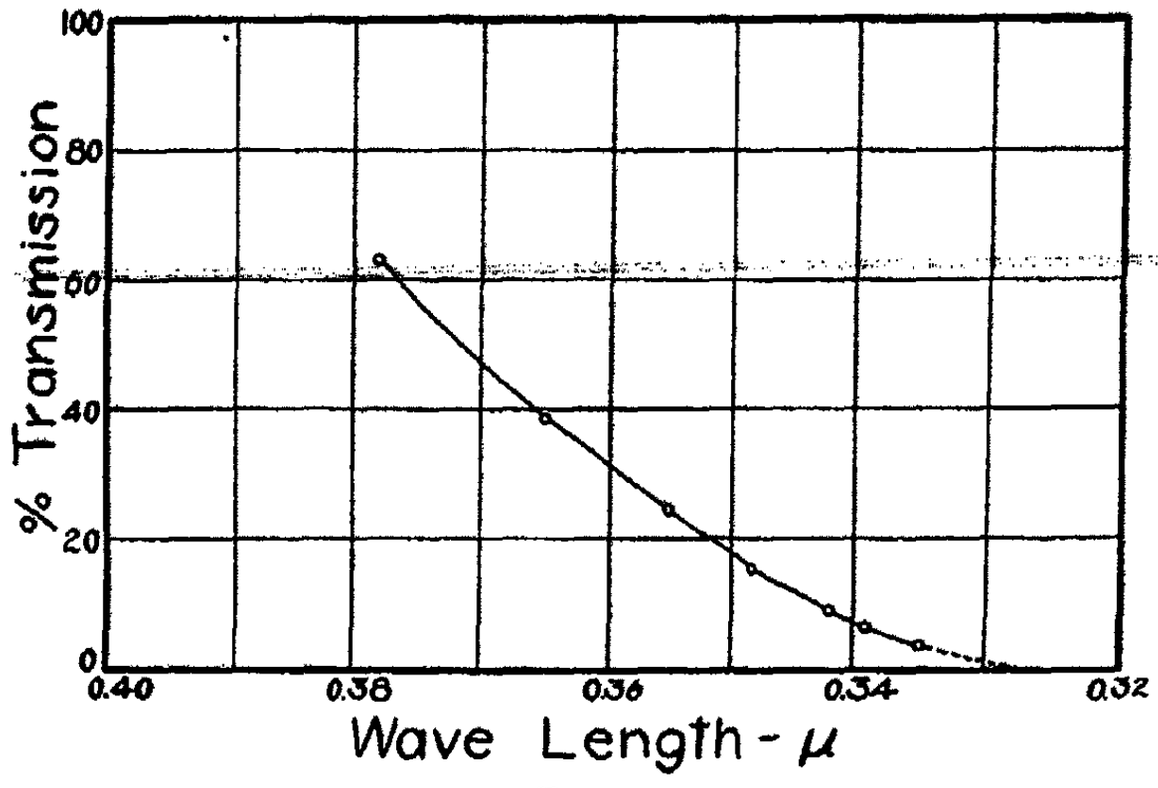



FIG. 2

Determinations of the transmission in the ultraviolet gave the results shown in Table III.

TABLE III

| Wave Length in $\mu$ | Per Cent. Transmission |
|---|---|
| 0.3780 | 63.0 |
| 9.3650 | 39.8 |
| 0.3550 | 25.1 |
| 0.3480 | 15.9 |
| 0.3420 | 10.0 |
| 0.3390 | 6.3 |
| 0.3350 | 4.0 |

If these results are plotted (Fig. 2) extrapolation shows that fused germanium dioxide is opaque to light of wave-lengths less than 0.3250$\mu$.

We are indebted to Professor J. R. Collins of the Department of Physics for measurement of the transmission of fused germanium dioxide in the infrared. The substance showed no adsorption bands between 0.8$\mu$ and 1.7 $\mu$. The transmission in this region was about 82 per cent., the loss probably being due to slight striations and to slight imperfections in the surface.

Fused germanium dioxide is, therefore, not as transparent as is quartz in the ultraviolet, but transmits quite as well as the latter substance throughout the remainder of the field that was investigated.

*Density.*—This was determined with a pycnometer using toluene as the immersion liquid because of the solubility of germanium dioxide in water. Two determinations at 20° gave 3.6388 and 3.6366, Aver., 3.6377. This value is nearly 65 per cent. above that for fused silicon dioxide which has a density of 2.213.[1]

*Hardness.*—Professor A. C. Gill determined the hardness of fused germanium dioxide, which he found to be slightly under five, somewhat softer than apatite. Fused silica has a hardness of seven.

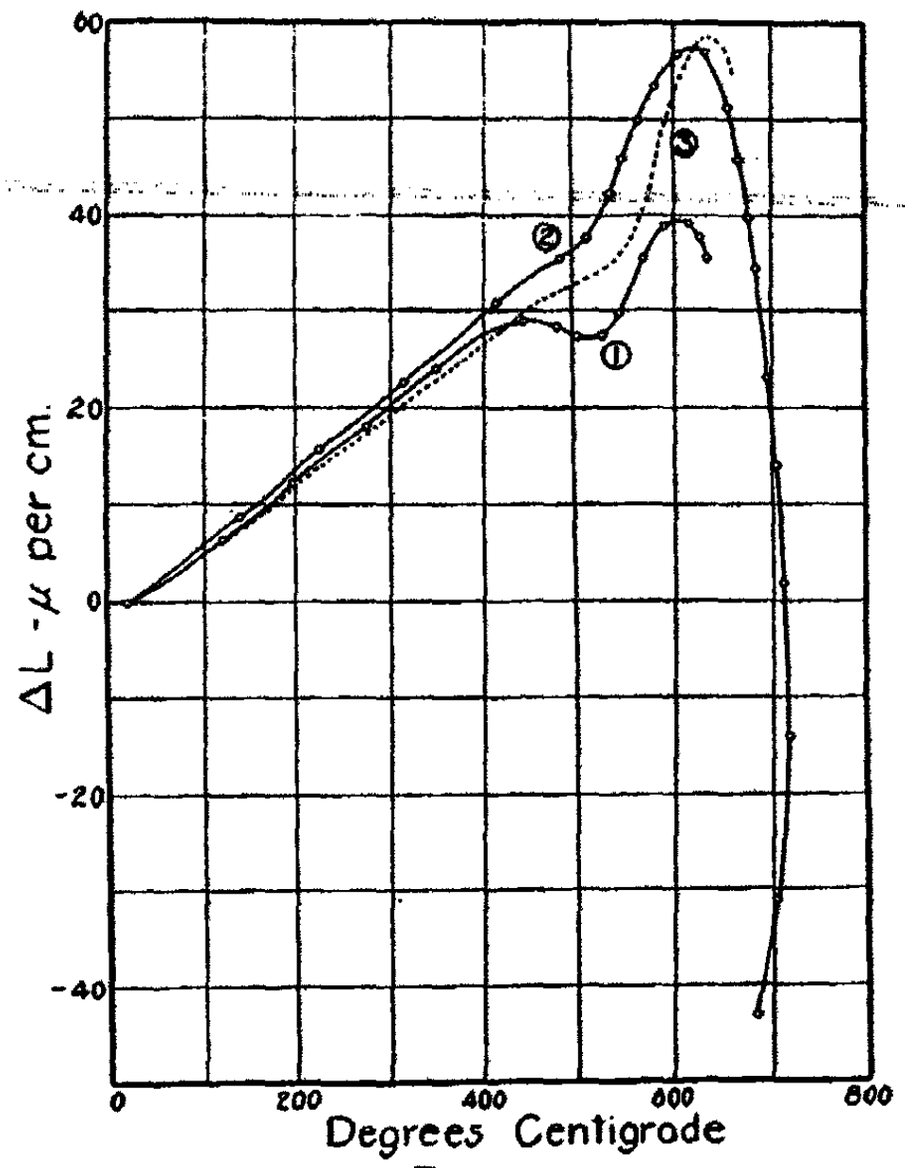



FIG. 3

*Expansivity.*—The Bureau of Standards at Washington obligingly measured the expansivity of samples of fused germanium dioxide, and the report of the Director, Mr. George K. Burgess, is, in part, as follows:

"On first view of the samples, we were impressed by their similarity in general appearance to fragments of glass and we found that this similarity persisted on further examination. Their reaction to the abrasives used in reducing them to size is very similar to that of the usual glass sample.

"The similarity of expansivity of fused germania and certain glasses is even more marked. During the first run (Fig. 3, curve 1) the sample expanded uniformly from 20° to about 425°C. Between 450° and 510°C, it contracted and then expanded rapidly from 510° to 610°C. Above 610°C, the

[1] Day and Shepherd: Am. J. Sci., (4), 22, 265 (1906).

sample softened sufficiently so that the weight of the cover plate and the tendency to spheroid caused a decrease in length. In the second run the sample expanded at a slightly higher rate from 20° to 510°C than in the first run, and at a much higher rate from 510° to 615°C and showed the effect of softening above 615°C.

"All the glasses we have investigated show this increased expansivity between the beginning of the annealing range and the softening point. A glass can be annealed in time at any temperature in this rapid expansion region, but to leave it in equilibrium at the lower temperatures, it must be cooled very slowly, especially through the lower part of the annealing range. If the glass is cooled rapidly through that region, as your fused germania was, then it will not be in equilibrium until heated to some temperature above the lower limit of the annealing range. When this chilled glass is heated, as in the first run, the molecules tend to assume an arrangement compatible with equilibrium at the existing temperature of the glass. This rearrangement in the case of the germania produces a permanent change in density and volume which causes the decrease in expansivity or contraction between 450° and 510°C. After the sample had been heated to 640° in the first run, it was allowed to cool in the furnace at a rate of about 5° per minute. This treatment removed most of the effects of the previous treatment but that it was not sufficient to leave the sample in perfect equilibrium at the lower temperature, is shown by the decrease in the expansivity in the second run between 450° and 410°C.

"The second curve ( curve 2) lies above the first. In the upper part of the curves, this is due to the tendency to shrink during the first run. In the lower part of the curves, below 300° perhaps, the divergence is an actual difference in expansivity. Our past work has shown that for each equilibrium temperature, there is a corresponding expansivity at room temperature. On this second run, the temperature of the sample was carried to 720° to make sure that the decrease in length was the result of the softening of the material. Devitrification nuclei could be seen in the samples after cooling to room temperature. There was no apparent crystallization after the first run.

"As this tendency toward devitrification is not very different from that found in many of the simpler glasses, it is probable that this glass could be annealed at 510°C for very long periods of time without becoming devitrified. From the shape of the curve, it would seem that the most advantageous temperature at which the annealing could be done would be about 525°C. It could probably be held for some time at temperatures just short of 565°C safely, while our results show that a brief heating to 640° C did not injure it perceptibly.

"For comparison, we have plotted curve 3, the curve for a glass of the following composition:

| $SiO_2$ | $Na_2O$ | MgO | ZnO | $Al_2O_3$ | $B_2O_3$ |
|---|---|---|---|---|---|
| 73 | 11 | 4 | 5 | 1 | 4 |

By increasing the sodium at the expense of the boron, a still closer agreement would result.

"The average coefficient of expansion for any temperature interval $\Delta t$ is

$$C = \frac{\Delta L}{\Delta t \times 10{,}000}$$

"The average coefficient of expansion of the fused germanium dioxide can be calculated from the second run and is about 7.7 $10^{-6}$ for the first 400° C."

| 1st Run | | 2nd Run | |
|---|---|---|---|
| Temperature in Degrees Centigrade | L in $\mu$ per cm | Temperature in Degrees Centigrade | L in $\mu$ per cm. |
| 22 | 0 | 20 | 0 |
| 119 | 6.26 | 135 | 8.41 |
| 196 | 12.18 | 226 | 15.52 |
| 272 | 18.01 | 313 | 22.51 |
| 348 | 23.78 | 414 | 30.59 |
| 445 | 28.99 | 482 | 35.19 |
| 479 | 28.48 | 510 | 37.48 |
| 501 | 27.39 | 534 | 42.01 |
| 526 | 27.42 | 546 | 45.39 |
| 541 | 29.68 | 564 | 49.91 |
| 567 | 35.30 | 583 | 53.32 |
| 594 | 38.68 | 608 | 56.72 |
| 619 | 38.70 | 638 | 56.75 |
| 631 | 37.50 | 660 | 51.14 |
| 637 | 35.37 | 670 | 45.52 |
| | | 679 | 39.91 |
| | | 686 | 34.30 |
| | | 698 | 23.05 |
| | | 706 | 14.05 |
| | | 714 | 2.81 |
| | | 718 | −14 |
| | | 702 | −31 |
| | | 686 | −43 |

*Devitrification.*—Early in our own study of the fused germanium dioxide, it was found that the substance devitrified readily at temperatures between 750° and its melting point. The Bureau of Standards, as stated in their report, observed devitrification nuclei in samples that had been heated only to 720°.

*Durability.*—Pieces of fused germanium dioxide which were kept in card board boxes in the laboratory still showed untarnished surfaces after six months. In the presence of moisture, however, the luster soon disappears. Placed in water the substance would, of course, slowly dissolve. It is readily soluble in hydrochloric acid, and alkaline solutions rapidly attack it.

*Summary.*—Clear, transparent, colorless, fused germanium dioxide was produced by holding the substance at a temperature between 1450° and 1500° for thirty minutes, and stirring it frequently during that interval.

As compared with fused silicon dioxide, the fused germanium dioxide was found to possess a higher refractivity, about twice as great dispersion, the same dispersion ratios, a lower effective refractivity, about the same transmission except in the ultraviolet where it is inferior, much higher density, and about ten times the thermal expansion. It is not so hard or so resistant to water or acid as is quartz, but it can be fused and freed from bubbles at lower temperatures than can quartz. At high temperatures carbon, organic compounds of carbon, and carbon monoxide rapidly reduce it.

## B[1]. Some Germanium Glasses

Dating from the extended study by Schott and Abbe in 1881 of the substances which might be used in the manufacture of glass and of the manner in which the properties of the products were affected by differences in their composition, there has gradually been developed a large number of glasses possessing peculiar and valuable characteristics. An extension of the list is possible only through the employment of new mixtures of already familiar ingredients, or by variations in the treatment of the glasses, or through the introduction of new substances. Up to the present time only three acid oxides have been employed as primary constituents in glasses, namely, silicic acid, phosphoric acid and boric acid.

Germanium is an analogue of silicon, lying immediately below it in the fourth group of the Periodic Table of the Elements. For this reason it seemed reasonable to expect that silicon dioxide in glasses might be replaced wholly or in part by germanium dioxide. A preliminary experiment in 1924 demonstrated that a brilliant and transparent "flint" glass, in which germanium dioxide was used in place of silica, could easily be prepared. The systematic study of some germanium glasses was then taken up.

*Material.*—The germanium dioxide which was used was extracted from germanium-bearing zinc oxide by the method of Dennis and Johnson[2]. Spectroscopic examination showed that the material was pure except for the presence of a slight trace of silica. All other materials were of the highest grade of purity purchasable on the market.

*Apparatus.*—Because of the rarity of germanium dioxide the amount of each glass that was made was necessarily small, at most not over fifty grams. There was consequently relatively large area of contact between the walls of the crucible and the melt, and advoidance of contamination from this source was carefully studied.

It was found that platinum crucibles could not be used because on prolonged heating the metal was attacked. This was probably due to the re-

[1] This part of this article is based upon the thesis presented to the Faculty of the Graduate School at Cornell University by A. W. Laubengayer in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Dennis and Johnson: J. Am. Chem. Soc., 45, 1380 (1923).

duction of some of the germanium dioxide by the furnace gases and the resultant formation of an alloy of germanium with the platinum. Moreover the fusion could not be allowed to cool in the platinum crucibles, because the more rapid contraction of the platinum fractured the walls. Pouring the small melts into heated graphite molds resulted in the formation of striae. Alundum crucibles were attacked by the melt and spectroscopic examination showed that the resulting glass was contaminated with alumina, both in solution and as large particles in suspension. The glasses also were colored, probably because of the presence of iron in the alundum. Quartz crucibles always broke upon cooling and were therefore not used because of their high cost. The glaze of the usual porcelain crucibles softened and mixed with the melt.

Mr. Adolf Coors of the Coors Porcelain Company of Golden, Colorado, then kindly undertook to make for us dense, unglazed porcelain crucibles of assorted sizes, and these were found to be very satisfactory indeed. The molten glass did not penetrate the porcelain to any appreciable extent, nor was there any marked attack of the glass upon the porcelain wall. Unglazed crucible covers were used in all the fusions.

The fusions were made in small regenerator gas furnaces constructed in the laboratory upon the principle of the small furnaces designed by W. Hempel.[1] The furnace was heated with a blast Meker burner by means of which a temperature of 1400° could easily be maintained. The crucible temperatures were measured with an optical pyrometer by sighting it through the opening in the bottom of the furnace by means of a mirror. The top of the furnace was removable which permitted easy addition of the fused mixture and stirring of the melt from time to time with a platinum rod. The glasses were annealed in an electric muffle furnace which was fitted with a recording pyrometer which gave continuous temperature records over long periods. The rate of cooling could easily be regulated by means of a rheostat.

The samples were ground and polished for optical examination with a small machine of special design in which the rotating spindle was fitted with interchangeable brass laps that could be covered with any desired abrasive or polishing cloth.

*Procedure.*—The ingredients of each glass were mixed in carefully measured proportions, were thoroughly ground together in an agate mortar, and the mixture was heated in the furnace in the unglazed porcelain crucibles to a temperature from 1200° to 1400°. This temperature was maintained from two to three hours, and during the last hour the melt was frequently stirred with a platinum rod. The crucible and its contents were next rapidly cooled in air to about 800°, and the crucible was then placed in the annealing oven.

The procedure followed in the annealing was patterned after that of Adams and Williamson,[2] in which the glass is first rapidly cooled to the annealing temperature, is held there for some time and then is cooled at an increasingly

[1] Z. anal. Chem., 16, 454 (1877).

[2] Adams and Williamson: J. Franklin Institute, 190, 835 (1920).

rapid rate. The glass was usually found to have cracked into several pieces when it reached room temperature, but in each case fragments sufficiently large for satisfactory optical examination were obtained.

*Properties.*—Following the early experiments described in our preliminary note,[1] four different typical optical glasses were made, a light flint, a crown, a barium-crown, and a boro-crown glass. In each of these the silica of the usual glasses of this type was replaced by an equi-molecular amount of germanium dioxide. Table III gives the percentage composition of the glasses as calculated from the batch formulas[2].

Germanium flint glass, Melt No. 28, was fined for three hours at 1300° and was annealed for twenty-two hours at 450°.

Germanium crown glass, Melt No. 29, was more difficultly fusible than No. 28, but at 1400° it was sufficiently mobile to permit of its being cleared of air bubbles by stirring. It was annealed at 450° for twenty hours.

The germanium barium crown glass, Melt No. 27, was fined at 1300° and was annealed at 440° for twenty-two hours.

The germanium boro-crown glass, Melt No. 26, was fined at 1200° and was annealed for twenty hours at 450°.

Pieces of these glasses were ground and polished with two plane parallel faces, and a third plane face at right angles.

*Refractivity.*—This was determined with a Pulfrich refractometer. The test pieces showed some striae and consequently no claim for high accuracy can be made for the absolute values. The indices of refraction are given in Table IV, together with indices of the corresponding silicate glasses furnished to us by Bausch and Lomb.

It will be seen from the table that the substitution of silica by an equi-molecular amount of germanium dioxide increases in each case the refractive index for sodium light by about ten per cent. This is about the same difference as was found for fused germanium dioxide and fused silica. (See page 1512).

*Dispersion.*—The dispersion relations of the glasses, Table V, were calculated from the refractive data given in Table IV. The data shows that substitution of silica by germanium dioxide in the several glasses increases the mean dispersion by from 65 per cent. to 87 per cent, and lowers the effective refractivity by from 24 per cent. to 31 per cent. The partial dispersion ratio. of each of the germanium glasses vary but slightly from those of the correspons ding silicate glasses, and spread the spectrum in about the same proportion. Consequently the two kinds of glasses could probably advantageously be used together in achromatic combinations. The partial dispersion ratios for $(n_{G'} - n_F)/(n_F - n_C)$ for the corresponding silicate glasses were not available but the values in the parentheses are those given by Wright[3] for very similar

[1] J. Am. Soc., 47, 1945 (1925).

[2] We are indebted to Messrs. Kurtz and Montgomery of the firm of Bausch and Lomb for the batch formulas and optical constants of the corresponding silicate glasses which are given in the tables.

[3] F. E. Wright, Manufacture of Optical Glass and of Optical Systems, Ord. Dept. Doc. No. 2037, Gov. Printing Office, Washington, 1921, p. 59.

TABLE III

| | Light Flint | | Crown | | Barium Crown | | Boro-Crown | |
|---|---|---|---|---|---|---|---|---|
| | Ge. No.28 | Si. o-2460 | Ge. No.29 | Si. o-3442 | Ge. No.27 | Si. o-968 | Ge. No.26 | Si. o-2756 |
| | % | % | % | % | % | % | % | % |
| $GeO_2$ | 60.432 | | 81.476 | | 61.80 | | 78.499 | |
| $SiO_2$ | | 46.879 | | 71.77 | | 48.323 | | 67.850 |
| $K_2O$ | 4.846 | 6.503 | | | 6.15 | 8.326 | 5.738 | 8.580 |
| BaO | 0.271 | 0.364 | | | 22.20 | 30.039 | 2.115 | 3.163 |
| PbO | 34.117 | 45.785 | | | | | | |
| $As_2O_3$ | .349 | 0.469 | .33 | 0.50 | .358 | 0.483 | 0.136 | 0.204 |
| $Na_2O$ | | | 10.11 | 15.41 | | | 5.573 | 8.333 |
| CaO | | | 6.59 | 10.05 | | | | |
| $B_2O_3$ | | | .17 | 0.26 | 2.338 | 3.163 | 7 .938 | 11.869 |
| $Sb_2O_3$ | | | 1.32 | 2.01 | | | | |
| Zno | | | | | 7.14 | 9.665 | | |

TABLE IV

| Glass | | Indices of Refraction $n_C$ | $n_D$ | $n_F$ | $n_{G'}$ |
|---|---|---|---|---|---|
| Germanium Flint | No. 28 | 1.77210 | 1.78001 | 1.79979 | 1.82932 |
| Silicate Flint | 0-2460 | 1.61237 | 1.6171 | 1.62918 | |
| Germanium Crown | No. 29 | 1.67771 | 1.68252 | 1.69455 | 1.70474 |
| Silicate Crown | 0-3442 | 1.52068 | 1.5234 | 1.52971 | |
| Germanium Barium Crown | No. 27 | 1.68643 | 1.69077 | 1.70321 | 1.71300 |
| Silicate Barium Crown | 0-968 | 1.56965 | 1.5726 | 1.57973 | |
| Germanium Boro-Crown | No. 26 | 1.63861 | 1.64267 | 1.65289 | 1.66120 |
| Silicate Boro-Crown | 0-2756 | 1.51486 | 1.5172 | 1.52280 | |

TABLE V

| Glass | $n_D$ | Partial Dispersions $n_D - n_C$ | $n_F - n_D$ | $n_{G'} - n_F$ | Mean dispersion $n_F - n_C$ | Partial Dispersion Ratios $\frac{n_D - n_C}{n_F - n_C}$ | $\frac{n_F - n_D}{n_F - n_C}$ | $\frac{n_{G'} - n_F}{n_F - n_C}$ | Effective refractivity $\nu = \frac{n_D - 1}{n_F - n_C}$ |
|---|---|---|---|---|---|---|---|---|---|
| Ge Flint No. 28 | 1.78001 | .00791 | .01978 | .02953 | .02769 | .284 | .716 | 1.066 | 28.02 |
| Si Flint o-2460 | 1.6171 | .00473 | .01208 | | .01681 | .289 | .720 | | 36.7 |
| Ge Crown No. 29 | 1.68252 | .00481 | .01203 | .01019 | .01684 | .283 | .717 | .606 | 40.53 |
| Si Crown o-3442 | 1.5234 | .00272 | .00631 | | .00903 | .300 | .700 | | 58.0 |
| Ge Barium Crown No. 27 | 1.69077 | .00434 | .01244 | .00979 | .01678 | .259 | .741 | .583 | 41.2 |
| Si Barium Crown o-968 | 1.5726 | .00295 | .00713 | | .01008 | .293 | .707 | (.592) | 56.8 |
| Ge Boro-Crown No. 26 | 1.64267 | .00406 | .01022 | .00831 | .01428 | .283 | .717 | .582 | 45.0 |
| Si Boro-Crown o-2756 | 1.5172 | .00234 | .00560 | | .00794 | .293 | .707 | (.556) | 65.1 |

silicate barium crown and boro-crown glasses. The differences between these results and those for the corresponding germanium glasses are probably due to the difficulty of securing accurate readings for light of $G^1$.

*Transmission.*—Mr. C. V. Shapiro of the Department of Physics kindly determined for us the transmission of the flint and boro-crown glasses in the ultraviolet. The results are doubtless not exact because of the presence of some striae in the samples. Table VI gives the wave lengths at which the glasses cease to transmit light.

Table VI

| Glass | Wave length in $\mu$ |
|---|---|
| Germanium boro-crown No. 26 | .322 |
| Silicate boro-crown 0-2756 | .320 |
| Germanium flint No. 28 | .365 |
| Silicate flint 0-2460 | .347 |

The germanium glasses are not as transparent to light of short wave lengths as the corresponding silicate glasses, which is to be expected because fused germanium dioxide is much less transparent than fused silica in this region.

All four of the germanium glasses were colorless and they exhibited no absorption bands in the visible portion of the spectrum. No measurements were made in the infra-red, but since fused germanium dioxide is transparent to light of wave length of at least 1.7 $\mu$, the glasses made of this substance should show no absorption in that region.

*Density.*—The determinations were made with a pycnometer with water as the immersion liquid. In the determination of the density of fused germanium dioxide by this method, water could not be used because of its solvent action on the substance. The germanium glasses, however, are but very slowly attacked by cold water.

It will be seen that the germanium glasses have much higher density than the corresponding silicate glasses, as is to be expected from the relative densities of the two fused dioxides.

TABLE VII

| Glass | | Density 20°/20° 1st Run | 2nd Run | Average |
|---|---|---|---|---|
| Germanium Flint | No. 28. | 4.768 | 4.758 | 4.763 |
| Silicate Flint | 0-2460 | 3.607 | 3.608 | 3.607 |
| Germanium Crown | No. 29 | 3.889 | 3.891 | 3.890 |
| Silicate Crown | 0-3442 | 2.522 | 2.524 | 2.523 |
| Germanium Barium Crown | No. 27 | 4.178 | 4.169 | 4.173 |
| Silicate Barium Crown | 0-968 | 3.203 | 3.193 | 3.198 |
| Germanium Boro-Crown | No. 26 | 3.716 | 3.713 | 3.714 |
| Silicate Boro-Crown | 0-2756 | 2.5355 | 2.536 | 2.536 |

*Hardness.*—The hardness of the germanium glasses as determined by the abrasive method is about the same as that of the corresponding silicate glasses.

*Expansivity.*—The thermal expansion of the germanium glasses was determined by comparing them with standard samples of silicate glasses which were kindly furnished to us by Dr. W. C. Taylor of the Corning Glass Works. The comparison is made by holding the two pieces, one of the standards and the test piece, together and heating them until they fuse. They are then quickly drawn out at the junction into a long thread, one side of which is the germanium glass and the other the silicate glass. The thread is held taut until cool, and is then released, whereupon it bends toward the glass of the greater coefficient of expansion. This is repeated with others of the standards of known expansivity until the thread does not bend on cooling. Its coefficient of expansion is then regarded as identical with that of this particular standard.

Table VIII gives the result for the four germanium glasses and the corresponding silicate glasses.

TABLE VIII

| Glass | | Coefficient of Linear Expansion |
|---|---|---|
| Germanium Flint | No. 28 | .0000087 |
| Silicate Flint | 0-2460 | .0000067 |
| Germanium Crown | No. 29 | Devitrified so rapidly that it could not be tested. |
| Silicate Crown | 0-3442 | .0000085 |
| Germanium Barium Crown | No. 27 | .0000085 Slight devitrification |
| Silicate Barium Crown | 0-968 | .0000082 |
| Germanium Boro-Crown | No. 26 | .0000090 |
| Silicate Boro-Crown | 0-2756 | .0000079 |

It was observed that in all cases the germanium glasses softened much more readily than the silicate standards. The samples of silicate glasses furnished by Bausch and Lomb, however, softened at about the same temperature as the standard glasses from Dr. Taylor. The germanium flint glass and the germanium boro-crown glass with which good tests were secured, showed much higher linear expansion than the corresponding silicate glasses.

*Softening Point.*—The germanium glasses can usually be melted in an unglazed porcelain crucible by heating with the flame of a Bunsen burner, whereas the silicate glasses need much higher temperatures.

Furthermore, the fused germanium glasses yield very mobile melts and fining takes place quite rapidly. This property would be of importance in the manufacture of germanium glasses, because they could be prepared at temperatures so low as to greatly diminish the danger of attack on the crucible or pot.

The relative softening points of the germanium and silicate boro-crown glass were determined by placing sharp fragments side by side in a porcelain boat in a quartz tube which was then heated in an electric furnace. The temperature inside the tube was measured with a platinum-rhodium thermocouple. The germanium flint glass began to soften at 570°, the silica flint glass at 800°. The germanium boro-crown glass softens at 680°, the silicate boro-crown glass at 850°.

*Devitrification.*—The germanium glasses in general show greater tendency to devitrify than the corresponding silicate glasses, and this is particularly true of the germanium crown glass, Melt No. 29. In the preparation of the samples, devitrification can usually be avoided by rapidly cooling the molten glass to a temperature below that at which it devitrifies.

*Durability.*—The relative durability and resistance to weathering of germanium glasses and the corresponding silicate glasses were determined by the method proposed by Peddle.[1] The sample is powdered to pass through a 160 mesh sieve, and five grams of the powder is digested with 100 cc of water at 80° for one hour. The residue is collected in a Gooch crucible and weighed. The filtrate is then titrated with sulphuric acid. Peddle states that the amount of acid required to neutralize the dissolved material is a reliable gauge of the durability of the glass.

The results of these tests are given in Table IX.

All of the germanium glasses show greater solubility, that is, less durability, than the corresponding silicate glasses, but with the exception of the germanium boro-crown glass, the solubility is not high enough to prevent the use of these glasses for optical purposes.

The polished surfaces of all of these four germanium glasses were still brilliant after they had been kept in cardboard boxes in the laboratory for three months or more.

TABLE IX

| Glass | | | Milligrams dissolved | Milligrams $H_2SO_4$ required |
|---|---|---|---|---|
| Ge | Flint | No. 28 | 8.4 | 2.6 |
| Si | Flint | 0-2460 | 7.1 | 1.7 |
| Ge | Crown | No. 29 | 195.7 | 73.2 |
| Si | Crown | 0-3442 | 34.6 | 19.1 |
| Ge | Barium Crown | No. 27 | 60.5 | 13.4 |
| Si | Barium Crown | 0-968 | 50.3 | 3.0 |
| Ge | Boro-Crown | No. 26 | 969.0 | 154.0 |
| Si | Boro-Crown | 0-2756 | 28.3 | 6.5 |

[1] Peddle: J. Soc. Glass Tech., 4, 36, (1920).

Experiments which have just been concluded show that satisfactory glasses can be made by replacing any part of the silica in the ordinary glass by germanium dioxide. In this manner products with properties intermediate between those of the two types may be secured.

*Summary.*—Germanium light flint, crown, barium crown, and boro-crown glasses were prepared by substituting equi-molecular amounts of germanium dioxide for silicon dioxide in the corresponding silicate glasses. As compared with the silicate glasses, these germanium glasses were found to have higher refractivity and dispersion, approximately the same transmission in the visible and infra-red regions, and lower transmission in the ultraviolet. The partial dispersion ratios of the germanium and silicate glasses are practically the same. The germanium glasses show greater density and expansivity, about the same hardness, and lower softening temperatures. They devitrify somewhat more readily, but they are more easily fined. Their durability and probable resistance to weathering is somewhat lower than with the silicate glasses, but not markedly so.

The optical properties of the germanium glasses differ so greatly from those of the corresponding silicate glasses as to render it probable that they can advantageously be employed in the construction of optical systems.

*Ithaca,*
*New York.*

# THE ANTAGONISTIC ACTIONS OF IONS IN THE NEUTRALIZATION OF SOLS. II

BY HARRY B. WEISER

In the first paper which appeared under the above title[1] it was pointed out that the precipitation value for sols of mixtures of two electrolytes may be additive, may be greater than the additive values, or may be less than the additive values. The factors which determine the precipitation concentration of mixtures are: (1), the effect of each precipitating ion on the adsorption of the other; (2), the stabilizing action of ions having the same charge as the sol; and (3), the relatively greater adsorbability of ions at lower concentrations. The effect of the first two of these factors will be to raise the precipitation concentrations for mixtures above the additive value while the effect of the third will be to lower them below the additive value. The precipitation values will be additive for mixtures of salts having similar precipitating power. All of these cases have been realized experimentally.

In a number of recent papers Dhar, Ghosh, and their collaborators[2] have attributed the variation from an additive relationship with salt pairs, exclusively to the stabilizing actions of ions having the same charge as the sol and have discredited the influence of any antagonism between ions of the same charge. Thus for arsenious sulfide sol the increased precipitation concentration of barium chloride in the presence of alkali chloride was attributed to the stabilizing effect of adsorbed chloride ion although the bulk of the evidence seemed to support the view that cationic antagonism between the barium and alkali ions was the more important in this case.

That the stabilizing action of adsorbed chloride is probably not the most important factor is further emphasized by the agglomerating action on arsenious sulfide sol of relatively low concentrations of alkali chloride. An arsenious sulfide sol containing 0.7 grams $As_2S_3$ per liter was prepared according to the method of Freundlich and Nathanson.[3] This sol when viewed in the ultramicroscope, gives a light-cone but is practically free from ultramicrons. The addition of small amounts of NaCl causes some agglomeration of the particles as evidenced by the appearance of ultramicrons on standing. This phenomenon was investigated carefully in the following way: A quantity of the sol was prepared and filtered through an ultrafilter which removed any ultramicrons that might be present. The preparation gave a clear uniform light cone. Ten cubic-centimeter samples of the sol were taken and diluted to 20 cc with ultrafiltered water to which was added 0, 0.2, 0.5, and 0.7 cubic centimeters, respectively, of ultrafiltered N sodium chloride. Special care

[1] J. Phys. Chem., **30**, 20 (1926).

[2] J. Phys. Chem., **28**, 313, 457, 1029 (1924); **29**, 435, 517, 659 (1925); Kolloid-Z., **34**, 262 (1924); **36**, 129 (1925); Z. anorg. Chem., **142**, 345 (1925). See also Mukherjee and Ghosh: Quart. J. Indian Chem. Soc., 1, 213 (1924).

[3] Kolloid-Z., **28**, 258 (1921).

was taken in the cleaning of all apparatus with ultrafiltered water and in protecting the samples from dust. After standing for two hours, the samples were placed in the Biltz cell of a Zeiss slit ultramicroscope supplied with a camera, and the light cone photographed. The time of exposure was two minutes. A comparison of the photographs obtained indicates agglomeration of particles in the presence of relatively small amounts of NaCl as evidenced by the gradually increasing intensity of the light cone in going from sample 1 containing no sodium chloride to sample 4 containing 0.7 cc of N salt.

For the sake of comparison, the precipitation value curve of mixtures of $BaCl_2$ and NaCl for the sol is given in Table I and shown graphically in Figure 1. The precipitation values were determined as described elsewhere,[1]

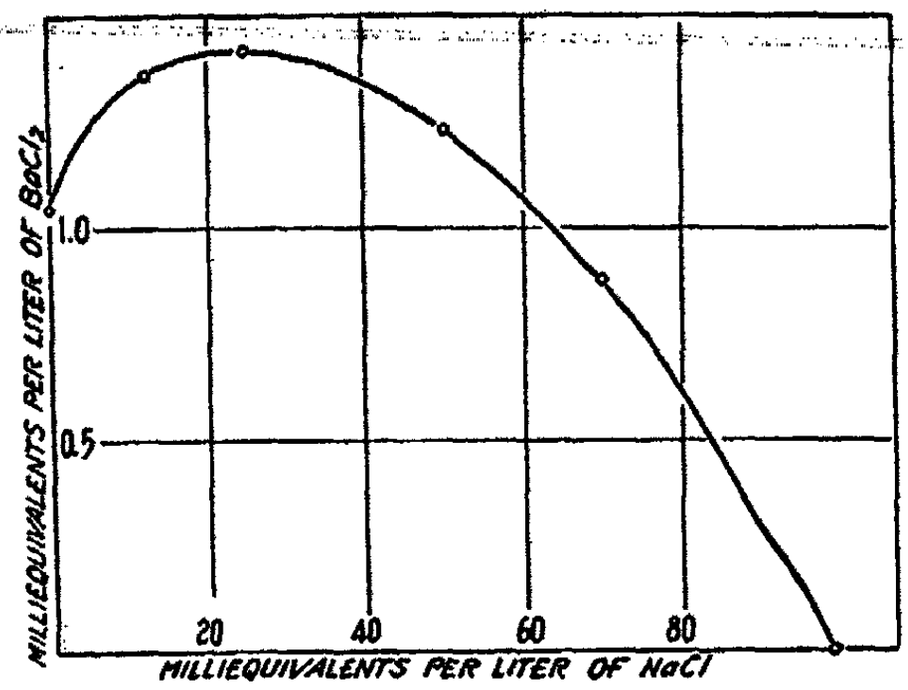



FIG. 1
Precipitation of Arsenious Sulfide Sol with Mixtures of $BaCl_2$ and NaCl.

TABLE I

Precipitation of Arsenious Sulfide Sol with Mixtures of $BaCl_2$ and KCl

| KCl Millieq. per liter | $BaCl_2$ Millieq. per liter |
|---|---|
| 0.0 | 1.05 |
| 12.5 | 1.36 |
| 25.0 | 1.42 |
| 50.0 | 1.22 |
| 70.0 | 0.88 |
| 99.0 | 0.00 |

observations for complete precipitation being made after two hours. The ultramicroscopic observations referred to above were made on the pure sol and on samples containing 10, 25, and 35 milliequivalents of NaCl per liter, respectively. In this region the precipitation value of $BaCl_2$ is increased appreciably by the presence of sodium chloride although the agglomeration

[1] J. Phys. Chem., **28**, 238 (1924).

of the particles by the latter is clearly indicative of a decrease in the stability of the sol. It would seem, therefore, that in this case, cationic antagonism rather than the stabilizing action of the anion is the most important factor in bringing about the variation from an additive relationship.

Ionic antagonism such as that between alkali and alkaline earth cations in the precipitation of arsenious sulfide sol has been recognized recently by other investigators. Thus Mann[1] finds that $NH_4Cl$, $MgCl_2$, and $AlCl_3$ cut down the adsorption of methylene blue and neutral red by discs of mangold root, the magnitude of the reduction being a function of the valency and concentration of the cation. The adsorption of both dye and salt attains equilibrium at a lower point than would be reached by either in the absence of the other, indicating mutual hindrance. And Dhar and his collaborators who have in several papers ignored or opposed the concept of antagonism between ions of the same charge, have finally embraced this view.[2] "As is known, crystal violet and strychnine hydrochloride cations are more strongly adsorbed by arsenious sulfide than barium and aluminum ions. On this account, the presence of the dye cations cuts down the adsorption of $K^{\cdot}$,$Ba^{\cdot\cdot}$, and $Al^{\cdot\cdot\cdot}$ ions and therefore more than the calculated amount of KCl, $BaCl_2$, and $Al(NO_3)_3$ is required for the precipitation of the sol. On the other hand, in precipitating arsenious sulfide sol with mixtures of strychnine chloride and crystal violet, the values are practically additive since the cations of both substances are about equally adsorbed and, at the precipitation concentration, there is no antagonistic effect on the adsorption."

Although in certain cases the antagonistic action between precipitating ions may be the most important factor in determining the precipitation values of salt pairs, in other instances the effect of stabilizing ions may predominate. Thus Sen, working with copper ferrocyanide sol, observed an increase in precipitation value of potassium chloride and of barium chloride in the presence of potassium ferrocyanide. With mixtures of potassium chloride and potassium ferrocyanide it is quite obvious that cationic antagonism can not come in since both precipitating cations are the same. Mukherjee and Ghosh[3] observed a similar behavior with mixtures of sodium benzoate and sodium chloride on arsenious sulfide sol; and the same is true with mixtures of potassium ferrocyanide and potassium chloride.[4] The determining factor in the latter cases is the stabilizing action of the relatively strongly adsorbed benzoate and ferrocyanide, respectively.

Consider the case of Graham's ferric oxide sol which owes its stability to preferential adsorption of hydrogen ion derived from hydrolysis of ferric chloride. It is too well known to need comment, that the stability of the sol falls off as the hydrogen ion concentration is decreased by dialysis and if the dialysis is continued long enough, all of the sol will precipitate. Conversely, if we add hydrochloride acid to a highly purified sol, the stability toward all

[1] Ann. Bot., 38, 753 (1924).
[2] Ghosh, Bhallacharya, and Dhar: Kolloid-Z., 38, 145 (1926).
[3] J. Indian Chem. Soc., 1, 213 (1924).
[4] Weiser: J. Phys. Chem., 30, 82 (1926).

electrolytes will increase. Similar stabilization would be expected on adding ferric chloride, aluminum chloride, or lanthanum nitrate, as Freundlich and Wosnessensky[1] have shown. With the relatively insoluble Péan de St. Gilles sol, a maximum in the stability is reached on adding hydrochloric acid; and at a suitable concentration, the adsorption of the precipitating chloride ion neutralizes the adsorption of hydrogen ion and precipitation takes place.[2] Similarly, colloidal copper ferrocyanide and Prussian blue are stabilized by preferential adsorption of ferrocyanide ion. The lower the concentration of the ferrocyanide ion the less the stability. On adding potassium ferrocyanide to a highly purified ferrocyanide sol, the stability toward all electrolytes should be increased until the concentration is high enough for the adsorption of the precipitating potassium ion to decrease the stability of the sol below the critical value. This is exactly what Sen[3] observed with two electrolytes of widely varying precipitating power. The precipitation value of both potassium chloride and barium chloride is increased to a maximum that lies above the value for either electrolyte alone.

A survey of the data obtained by Sen indicates that the form of the precipitation value curve of salt pairs for negative colloidal copper ferrocyanide sol depends on whether cationic antagonism may come in or whether it is eliminated by using salt pairs with a common cation. Thus when precipitation concentration of potassium ferrocyanide as abscissa is plotted against that of potassium chloride as ordinate, the curve rises sharply to a maximum, bends sharply, and then follows an almost straight course to the precipitation value of pure potassium ferrocyanide. On the other hand, with concentrations of barium chloride as ordinate the curve rises gradually to a broad maximum, dropping sharply when near the precipitation value of pure potassium ferrocyanide. The difference between these curves obtained with copper ferrocyanide sol, and between either of them and curves obtained with arsenious sulfide sol, called for further investigation. Furthermore, certain discrepancies exist in the data. Thus Sen finds the precipitation values of KCl and $K_4Fe(CN)_6$ to be 40 and 140, respectively, for one copper ferrocyanide sol and for another similar sol, the values to be 35.6 and 260, respectively. Moreover, difficulty was encountered in determining the exact precipitation values because of reported slowness in settling of the ferrocyanide sol.

Colloidal copper ferrocyanide was prepared by precipitating dilute solutions of cupric chloride with a very slight excess of copper ferrocyanide. The precipitate was washed thoroughly by means of the centrifuge until it was carried into colloidal solution from which it could not be thrown down by centrifuging for ten minutes in a No. 1 International centrifuge making 3000 r.p.m. The sol thus formed was subjected to dialysis for three weeks, changing the water continuously in a Neidle dialyzer. Prepared in this way, the sol is quite pure as evidenced by the relatively low precipitation value of salts.

---

[1] Kolloid-Z., 33, 222 (1923).

[2] Weiser: J. Phys. Chem., 25, 665 (1921).

[3] J. Phys. Chem., 29, 517, 539 (1925); Sen and Mehrotra: Z. anorg., Chem., 142, 345 (1925).

Since the finely divided precipitate obtained with univalent precipitating ions does not settle readily, the following procedure was used to obtain accurate precipitation values: Ten cubic centimeters of sol were mixed with a definite amount of electrolyte diluted to 10 cc. The mixture was allowed to stand two hours, after which 10 cc of the supernatant liquid in the region of the precipitation value was withdrawn and centrifuged for 10 minutes at 3000 r.p.m. The supernatant liquid after centrifuging was transferred to a Nessler tube and examined for completeness of precipitation. With the exception of being rather time-consuming, the procedure was entirely satisfactory. After getting the approximate precipitation values in a given series of experiments, the final, accurate values were obtained within 48 hours. The results with mixtures of potassium ferrocyanide and both potassium chloride and barium chloride are given in Table II and shown graphically in Fig. 2.

TABLE II

Precipitation of Colloidal $Cu_2Fe(CN)_6$ by Mixtures (a)

(Precipitation values in milliequivalents per liter)

| $K_4Fe(CN)_6$ + | $BaCl_2$ | $K_4Fe(CN)_6$ + | KCl |
|---|---|---|---|
| 0.0 | 1.58 | 0.0 | 23.8 |
| 12.5 | 1.90 | 12.5 | 157.5 |
| 25.0 | 2.00 | 25.0 | 155.0 |
| 50.0 | 2.10 | 50.0 | 140.0 |
| 100.0 | 2.00 | 100.0 | 112.5 |
| 150.0 | 1.60 | 150.0 | 82.5 |
| 262.5 | 0.0 | 262.5 | 0.0 |

It will be seen that the addition of potassium ferrocyanide causes the precipitation value of potassium chloride to mount sharply to a value more than six times that of pure chloride. This indicates that the purity of the original sol with respect to ferrocyanide ion is much greater than that of Sen's sol. After the maximum is reached, the curve bends sharply and then follows an almost linear course as Sen also observed. This means that if one takes an impure copper ferrocyanide sol the precipitation values of mixtures of potassium ferrocyanide and chloride will be approximately additive on account of the absence of cationic antagonism. A similar type of curve should result with mixtures of barium ferrocyanide and barium chloride. This was found to be true so far as the linear part of the curve is concerned; but the sharp maximum could not be detected with certainty since the precipitation concentrations of the chloride and ferrocyanide of barium were so close together.

On turning to the potassium ferrocyanide—barium chloride curve, contrary to Sen's observations, one is impressed with the very great similarity to the curves obtained with alkali-alkaline earth salt pairs on arsenious sulfide sol. Since in the latter case, both cationic antagonism and the stabilizing action of the anion play a rôle, it is possible that the difference between the potassium ferrocyanide—barium chloride curve and the potassium ferrocy-

anide—potassium chloride curve with copper ferrocyanide sol, is due to the absence of cationic antagonism in the first instance and its presence in the second.

It should be emphasized however that the initial increase in precipitation value of $BaCl_2$ in the presence of potassium ferrocyanide is due primarily to the effect of ferrocyanide ion. Thus from the results recorded in Table III and shown graphically in Fig. 3 it will be seen that the precipitation values of mixtures of KCl and $BaCl_2$ fall slightly below the additive value at the lower

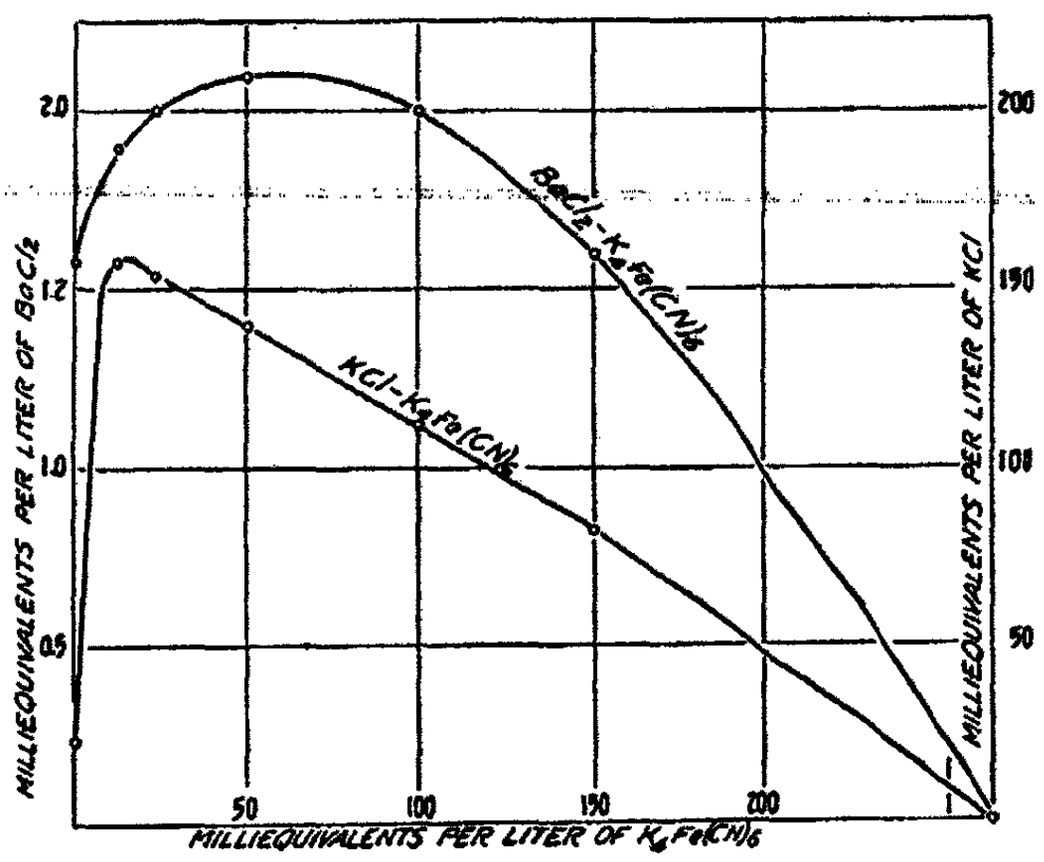



FIG. 2
Precipitation of Copper Ferrocyanide with Mixtures of Electrolytes (a).

TABLE III

Precipitation of Colloidal $Cu_2Fe(CN)_6$ by Mixtures (b)
(Precipitation values in milliequivalents per liter)

| KCl | + | $BaCl_2$ | KCl | + | $CuCl_2$ |
|---|---|---|---|---|---|
| 0.0 | | 1.58 | 0.0 | | 0.350 |
| 2.5 | | 1.38 | 2.5 | | 0.275 |
| 5.0 | | 1.26 | 5.0 | | 0.265 |
| 10.0 | | 0.97 | 7.5 | | 0.245 |
| 12.5 | | 0.83 | 11.8 | | 0.180 |
| 13.8 | | 0.75 | 16.8 | | 0.100 |
| 20.0 | | 0.25 | 23.8 | | 0.000 |
| 23.8 | | 0.0 | | | |

concentrations of KCl; but at higher concentrations of KCl the values are slightly greater than additive. The same is true for mixtures of KCl and $CuCl_2$ and of KCl and $CuSO_4$.[1] For arsenious sulfide sol the cationic antagon-

[1] Cf., however, Gurchot: J. Phys. Chem., **30**, 98 (1926).

ism between potassium and barium ion is greater in ferrocyanide than in chloride solution.[1] No experiments have been carried out to determine whether a similar condition exists with copper ferrocyanide sol.

Since the addition of alkali chloride to arsenious sulfide sol and of alkali ferrocyanide to copper ferrocyanide sol increases the precipitation value of $BaCl_2$, the question arises whether the sols coagulated by $BaCl_2$ alone will be repeptized by the addition of alkali salt. The answer is, that it will be provided the alkali salt exerts an appreciable peptizing action. When a sol like

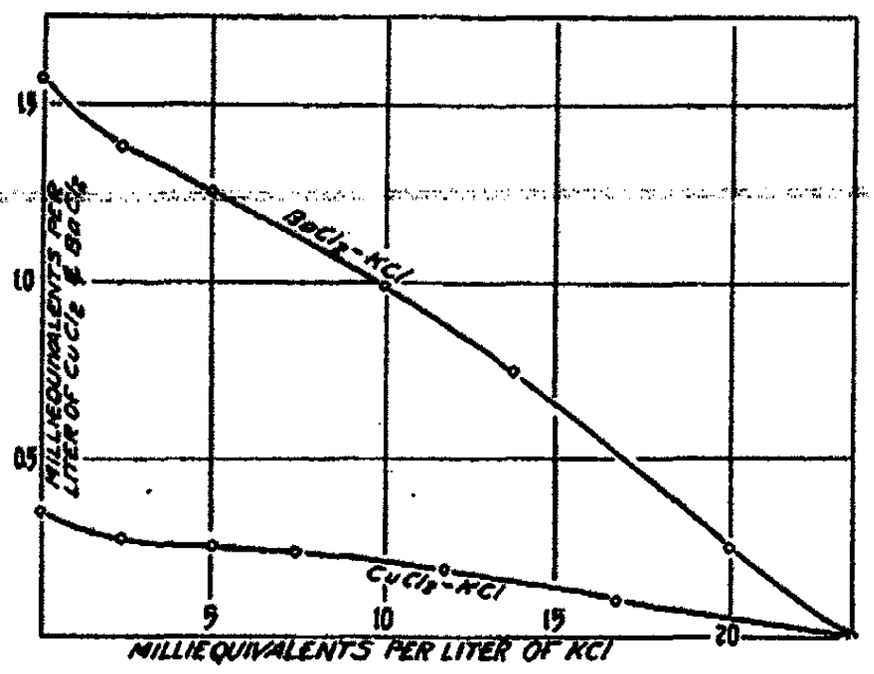



FIG. 3
Precipitation of Copper Ferrocyanide with Mixtures of Electrolyte (b).

Freundlich and Nathanson's arsenious sulfide is treated with barium chloride, the very minute, primary colloidal particles coalesce into larger, primary ultramicrons which finally agglomerate into secondary particles and these in turn, into clumps. If potassium chloride is added to such a coagulum a sol is not reformed on account of the relatively low peptizing action of chloride ion. On the other hand, the addition of potassium ferrocyanide to a copper ferrocyanide coagulum reverses the coagulation on account of the marked peptizing power of the anion for copper ferrocyanide.

Attention should be called, in passing, to an interesting property of arsenious sulfide. It has been observed repeatedly that the critical concentration of electrolytes does not cause agglomeration of the neutralized particles into a clump, unless the mixture is shaken. What apparently happens is, that the charge on the particles is neutralized; but instead of agglomerating into a clump, the individual particles with their film of adsorbed water coalesce to a loose jelly structure that is broken up by shaking. If a concentration of electrolyte close to the critical value is used and the sol is allowed to stand quietly for a day or two, the surface of the precipitate as it settles, appears to be a fairly strong, translucent, mobile film strikingly similar in appearance to that of a copper ferrocyanide membrane.

[1] Weiser: J. Phys. Chem., 30, 29 (1926).

## Ionic Antagonism in Biological Systems.

The behavior of colloidal solutions of such substances as arsenious sulfide and copper ferrocyanide in the presence of salt pairs is of importance owing to the existence of what appear to be analogous phenomena in biological systems.

Forty-five years ago, Ringer[1] attempted to use a sodium chloride solution isotonic with the blood, for the continuous perfusion of the heart of a frog. This solution was unsatisfactory as the beats diminished gradually and ceased entirely after a few minutes. It was discovered that traces of the chlorides of calcium and potassium added to the salt solution gave a perfusion liquid capable of maintaining the heartbeat at a satisfactory height for a considerable time. The so-called "Ringer's solution" contains 0.13M NaCl, 0.0011 M $CaCl_2$, and about 0.0002 M KCl.[2] Similarly, Jacques Loeb[3] found that certain marine organisms are killed quickly when transferred to a solution of sodium chloride having the same concentration as sea water; but the destructive action of the sodium chloride is neutralized by adding $CaCl_2$ in the ratio of one or two mols of the latter to one hundred of the former. It is a striking fact that the optimum ratio of NaCl to $CaCl_2$ is approximately the same as it is in nature, in sea-water, and in the blood of animals. A similar relationship obtains with certain plants. Thus Osterhout[4] demonstrated that wheat grown in a solution containing 0.12 M NaCl and 0.0012 M $CaCl_2$ develops extensive rootlets and shows other signs of healthy growth whereas in solutions of either 0.12 M NaCl or 0.0012 M $CaCl_2$ alone no growth occurs. Moreover, zoöspores of Vaucheria grow rapidly in a solution of 0.01 M NaCl and 0.0001 M $CaCl_2$ or even in pure water; but show no signs of growth in either 0.01 M NaCl or 0.0001 M $CaCl_2$. Observations of a similar character have been made repeatedly by a number of other biologists[5] so that the antagonistic action of salts on living organisms can be considered as one of the commonplaces of biological science.

The influence of salts on living cells appears to be closely related to their permeability. Osterhout[6] studied the effect of various electrolytes on the conductivity of certain sea weeds such as Laminaria. Immediately after removal from sea water he found the tissues to exhibit a practically constant resistance to the passage of the current; but on exposure to a comparable NaCl solution the resistance decreased and to a comparable $CaCl_2$ solution the resistance increased; while exposure to properly balanced mixtures containing 100 mols NaCl to 1 to 2 mols $CaCl_2$ caused no appreciable variation from the normal. If Laminaria is first immersed in a 2.5 per cent solution of pure sodium

[1] J. Physiol., 3, 380 (1880-82); 4, 29, 222 (1882-83); 7, 291 (1886).

[2] Bayliss: "Principles of General Physiology," 207 (1920).

[3] Pflüger's Arch., 97, 394 (1903); Loeb and Wasteneys: Biochem. Z., 32, 308 (1911); J. Biol. Chem., 21, 223 (1915).

[4] Plant World, 16, 129 (1913); J. Biol. Chem., 19, 335 (1914).

[5] Cf. Lillie: Am. J. Physiol., 29, 372 (1912); Netter: Höber's "Physik. Chem. der Zelle u. Gewebe," Part II, 662, 658; Spiro: Schweiz. med. Wochschn, 51, 457 (1922); Utin: Chem. Zentr., 3, 887 (1922).

[6] Science, (2) 35, 112; 36, 350 (1912).

chloride the electrical conductivity is increased; on adding a little calcium chloride to the solution, the sea weed returns to normal conductivity without showing signs of permanent damage.[1] It appears therefore, that the protoplasmic membrane is a physical system capable of undergoing reversible variations in permeability as a result of exposure to solutions containing varying amounts of sodium and calcium salts. From such observations, Osterhout[2] divides substances into two groups (1) those which cause an increase in permeability and (2) those which can produce a decrease in permeability. From this point of view, substances belonging to the first class will antagonize those belonging to the second and vice versa. "The soundness of this point of view is indicated not only by the fact that we are able to predict both qualitatively and (to a considerable extent) quantitatively the effect of combinations of salts but also by the very significant fact that we are able to extend this conception to organic compounds and to show that non-electrolytes which decrease permeability can also antagonize such substances as NaCl. These facts indicate that the hypothesis may be applied in a general manner so as to include both electrolytes and non-electrolytes."

This hypothesis does not account for the change in permeability but Clowes[3] has sought to explain it by comparing the cell membrane to an oil-water emulsion in which soaps concentrate at the interface between oil and water lowering the surface of one or the other depending on whether the soap is oil-soluble or water-soluble.[4] Thus we should expect an emulsion of oil in water in the presence of sodium salts and of water in oil in the presence of calcium salts. "Salts of calcium promote and alkalies and salts of sodium inhibit the transformation of a system consisting of a non-aqueous phase dispersed in water into the reverse type of system, consisting of water more or less perfectly dispersed in a non-aqueous phase. If the analog of islands surrounded by water and lakes surrounded by land is considered, it will be obvious that a transformation has been effected from a system which is freely permeable to water to one which is impermeable, if the transformation is complete. Since the transformation in one direction is effected by salts of calcium and in the reverse direction by salts of sodium, any intermediate degree of permeability might well be obtainable by simply varying the proportions of the salts of sodium and calcium introduced into the systems." From this point of view, it would follow that the critical ratio of sodium and calcium salts is one which produces a balance between the two types of emulsion that is most favorable for life and growth. In support of his hypothesis Clowes, working with oil, water, and soap, showed that the ratio of sodium and calcium salts necessary to produce a balancing between these two types of emulsions was about the same as that found in sea water. Although quite suggestive, Clowes' view that a cell membrane is a labile emulsion is inadequate to account

[1] Osterhout: Science, (2) 34, 187 (1911).
[2] Science, (2) 41, 265 (1915).
[3] J. Phys. Che., 20, 407 (1916).
[4] Bancroft: "Applied Colloid Chemistry," 261 (1921).

for the marked osmotic pressure which a cell manifests. It seems better, at least for the present, to consider the cell membrane as a more or less rigid, semi-permeable pellicle comparable in certain respects to a copper ferrocyanide membrane.

From what we know of the structure of jellies and gelatinous precipitates,[1] it seems probable that a copper ferrocyanide membrane consists of myriads of minute particles which adsorb water strongly. As a result of investigations carried out in Bancroft's laboratory Gurchot[2] considers a copper ferrocyanide film to be a negative colloidal film analogous to a colloidal sol. It is therefore a granular membrane the space between the particles of which is more or less completely filled with adsorbed water. The film is therefore a dynamic system capable of reversible coagulation.

This concept of the nature of a copper ferrocyanide membrane enables one to account for a number of facts. To illustrate, it is known that below a certain concentration of salts the latter will pass through a copper ferrocyanide membrane and sugar will not; while at higher salt concentrations, both will pass through. This is explained by assuming that no coagulation of the membrane takes place below a certain critical concentration of salt. The salts being soluble in water dissolve in the water layer and so pass through the membrane. Sugar molecules can not go through in this way because of strong negative adsorption. When the salt concentration reaches the critical coagulation value, there results agglomeration of the particles which carry with them their film of adsorbed water leaving cracks through which the sugar can pass. Reversing the coagulation by adding a peptizing agent reforms the semi-permeable film and the sugar will no longer pass through. Gurchot apparently succeeded in accomplishing this reversal in permeability to sugar after coagulation with alcohol and salts, by means of $CuSO_4$. For some reason Gurchot did not try potassium ferrocyanide which would doubtless have produced the desired results in low concentrations. The difficulty of testing for sugar in the presence of ferrocyanide does not seem to be sufficient reason for not trying the latter reagent.

If the membrane of a living cell is a colloidal film similar to a colloidal sol that can undergo reversible coagulation, there would appear to be a close analogy between the action of salt pairs in the precipitation of such sols as copper ferrocyanide and arsenious sulfide and the antagonistic action of salt pairs on the permeability and hence on the life and growth of living cells. From this point of view, all of the factors influencing the precipitating action of salt pairs as it effects the stability of sols, which I have outlined above, will be concerned in the antagonistic action of salt pairs as it affects the permeability of protoplasm.

## Summary

1. The addition of a small fraction of the precipitation concentration of of alkali chloride to an arsenious sulfide sol results in agglomeration of the particles with a consequent decrease in the stability of the sol.

[1] Cf. Weiser: Bogue's "Colloidal Behavior," 1, 377 (1924).
[2] J. Phys. Chem., 30, 83 (1926).

2. With arsenious sulfide sol, the higher precipitation value of barium chloride in the presence of alkali chloride is due for the most part to cationic antagonism rather than to the stabilizing influence of chloride ion.

3. The addition of potassium ferrocyanide to copper ferrocyanide sol increases the stability of the sol toward all electrolytes, owing to strong adsorption of ferrocyanide ion. Cationic antagonism plays a minor rôle in the precipitation with mixtures of barium chloride and potassium ferrocyanide.

4. The antagonistic action of salt pairs on protoplasm is determined by their effect on the permeability of the cell membrane.

5. The membrane of a living cell may be a colloidal film similar to a colloidal sol that can undergo reversible coagulation. If so, there would appear to be a close analogy between the action of salt pairs toward such sols as copper ferrocyanide and arsenious sulfide and the antagonistic action of salt pairs on the permeability and hence on the life and growth of living cells.

*The Rice Institute,*
*Houston, Texas.*

# HEAT OF ADSORPTION OF CARBON MONOXIDE ON COPPER CATALYST

BY RALPH ALONZO BEEBE

In an earlier communication, the writer in collaboration with H. S. Taylor[1] described a method for the direct measurement of heats of adsorption. Both the integral and differential values of Q, the heat of adsorption per mol of adsorbed gas, were given for hydrogen on a nickel adsorbent. The thermal

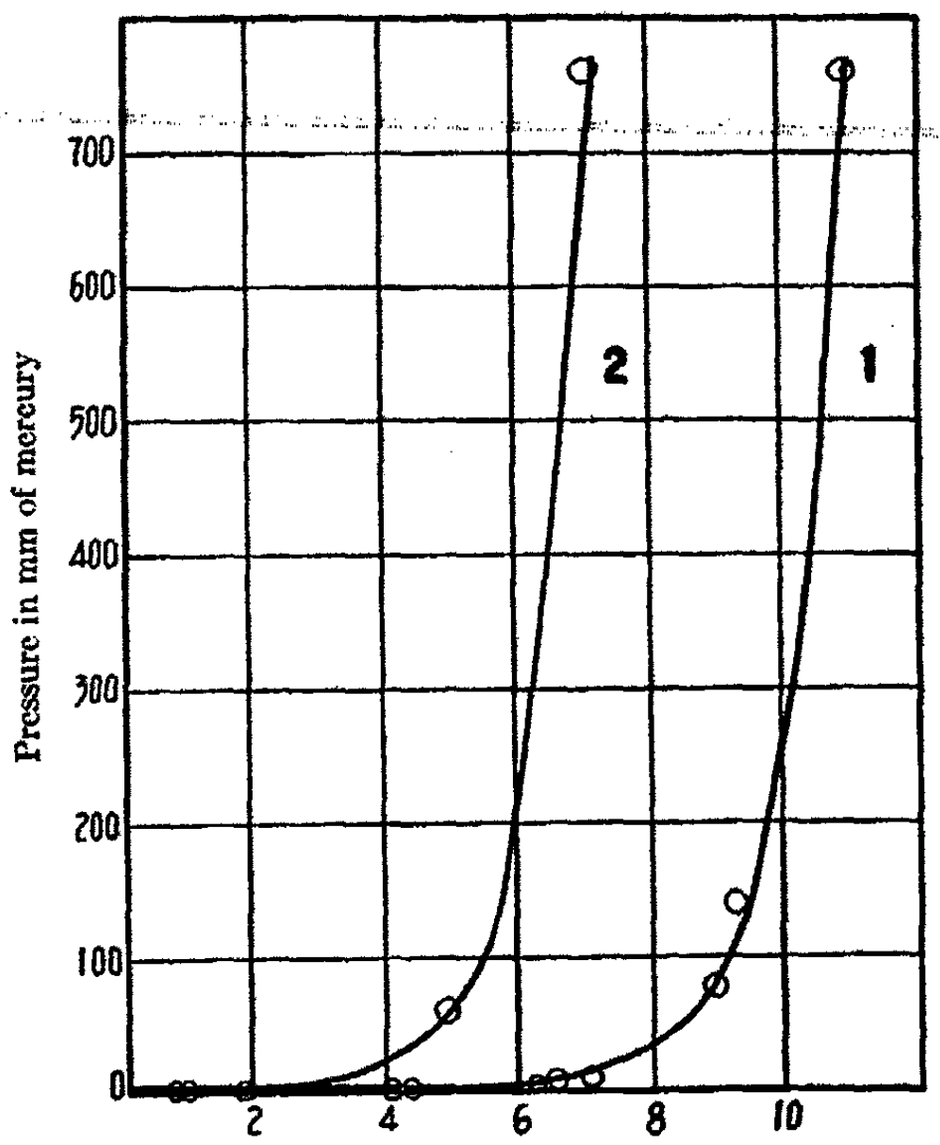



FIG. 1

Cc adsorbed

effect was found to vary in a surprising manner according to the past history of the catayst. A recent paper by B. Foresti[2] made this point a particularly important one. The following measurements of Q for a totally different gas-metal combination should, therefore, be presented at this time.

Preparation of the Catalyst.—The adsorbent sample was prepared by reduction of copper oxide granules in a stream of pure, dry hydrogen at 170°-180° C, reoxidation in a stream of oxygen at the same temperature and subsequent reduction by hydrogen at a temperature that was kept at all times

[1] Beebe and Taylor: J. Am. Chem. Soc., 46, 43 (1924).

[2] B. Foresti: Gazz., 45, 185 (1925).

below 135° C. The 57g sample thus prepared adsorbed 11.5 cc of carbon monoxide and 6.0 cc. of hydrogen at 0°C and 760 mm. pressure. After measurements of Q had been completed for the catalyst in this state, which will be called the "active" sample, due to some mischance, the catalyst became poisoned so that its adsorptive capacity for carbon monoxide was cut down to approximately 7.0 cc. at 0°C and 760 mm. The catalyst in this reduced adsorptive capacity will be designated as the "poisoned" sample. Unfortunately, the writer is unable to state the cause of the poisoning. A comparison of the isotherms I and II in Fig. 1 for adsorption of CO by the catalyst in the "active" and "poisoned" states with the similar pair of curves obtained by Pease[1] for a copper catalyst before and after poisoning by mercury, would lead one to attribute the poisoning in the present instance to a similar cause. The observations recorded in this paper were completed in June 1925. The author hoped at that time to repeat the measurements for a catalyst poisoned under controlled conditions. Unforeseen interruptions have made this impossible during the past year. The striking and apparently anomalous nature of the data obtained, however, make it advisable to present them without further delay.

Discussion of Experimental Method.—The method described in the earlier paper was employed in this research. The temperature of evacuation was 140° to 150°C. As was pointed out therein for the case of hydrogen and copper, there was practically no drift in the adsorption of carbon monoxide by the copper. This made for very reliable values, since all the heat was liberated almost instantaneously. In the measurement of the differential values it was found possible to obtain the thermal data for much smaller increments of x, the volume adsorbed, than had previously been considered practicable. As stated in the discussion of the method it was necessary to make a correction for the thermal effect accruing from (a) compression of the gas in entering the calorimeter, (b) cooling of the gas from room temperature to 0°C. In determination of integral values, when the final pressure of gas over the catalyst is 760 mm, this correction is an important one. To cite an actual case, in Determination 1, Table I, the true temperature rise was 0°.520C, the correction for effects (a) and (b) was 0.°075, hence the rise due to the adsorption was 0.°445. There was, therefore, a 17 % correction. Note that in this case effects (a) and (b) for the 42.53 cc CO occupying the free space above the catalyst had to be considered as well as for the 11.04 cc adsorbed. The correction became of minor importance, however, in obtaining the differential values, since as is evident from Curve I, Fig. 1, the pressure of CO in the gas phase in equilibrium with as much as 7.0, of the total 11.0 cc which is adsorbed at 760 mm, is only 6.0 mm, i. e. there is practically no correction for gas to fill the free space of the chamber. In Det. 4 C the true temp. rise was 0.°145, the correction was 0°.007, and hence the temp. rise due to adsorption was 0.°138. Here the correction is only a 5% one. It has been found possible to obtain consistent results for increments as small as 1.0 cc, for the

[1] Pease: J. Am. Chem. Soc., 45, 2300 (1923).

first 7.0 cc of the total 11.0 cc adsorbed, i. e. while equilibrium pressure is still low. As the isotherm shows, the equilibrium pressure increases rapidly for amounts adsorbed beyond 7.0 cc, and the correction again becomes important. The differential values of Q are, therefore, less reliable for these last portions.

*Results.*

TABLE I

Integral Values for Heat of Adsorption of CO on Copper

| Sample | Determination | a $C_c$ (0-760) adsorbed by sample | $(T-T_o)$ True rise in Temp. | Q Heat of adsorption in calories per mol |
|---|---|---|---|---|
| | 1 | 11.04 | 0.445 | 12,200 |
| "Active" Copper | 2 | 10.92 | 0.405 | 11,200 |
| | 3 | 11.07 | 0.423 | 11,700 |
| "Poisoned" Copper | 1 | 7.10 | 0.358 | 15,300 |

TABLE II

Differential Values for CO on Copper (Q at Partial Pressures)

| Sample | Determination | Initial P in mm Hg | Final P in mm Hg | Region covered (11.0 cc Total) | X | $(T-T_o)$ | Q |
|---|---|---|---|---|---|---|---|
| | 1 A | 0 | 6 | 0–6.26 | 6.26 | 0.255 | 12,500 |
| | 1 B | 6 | 74.9 | 6.26–1.54 | 5.28 | 0.166 | 9,500 |
| | 2 A | 0 | 2.2 | 0–4.42 | 4.42 | 0.217 | 17,000 |
| | 2 B | 2.2 | 78.1 | 4.42–9.62 | 5.20 | 0.168 | 9,800 |
| "Active" Copper | 3 A | 0 | 0.7 | 0–2.09 | 2.09 | 0.166 | 24,200 |
| | 3 B | 0.7 | 1.9 | 2.09–3.96 | 1.87 | 0.084 | 13,300 |
| | 3 C | 1.9 | 5.7 | 3.96–6.58 | 2.62 | 0.092 | 10,700 |
| | 3 D | 5.7 | 75.6 | 6.58–8.93 | 2.35 | 0.069 | 8,900 |
| | 4 A | 0 | 0.8 | 0–0.90 | 0.90 | 0.093 | 31,000 |
| | 4 B | 0.8 | 1.8 | 0.90–2.70 | 1.80 | 0.103 | 17,400 |
| | 4 C | 1.8 | 8.8 | 2.70–7.10 | 4.40 | 0.138 | 9,700 |
| | 4 D | 8.8 | 140.8 | 7.10–9.31 | 2.21 | 0.065 | 8,900 |
| | 5 A | >.0 | <1.0 | 0.20–1.13 | 0.93 | 0.100 | 32,800 |
| | 6 A | > 0 | <1.0 | 0.59–1.51 | 0.92 | 0.068 | 21,700 |
| "Poisoned" Copper | 1 A | 0 | 0.4 | 0–0.89 | 0.89 | 0.093 | 31,900 |
| | 2 A | 0 | 0.8 | 0–0.95 | 0.95 | 0.096 | 30,800 |
| | 2 B | 0.8 | 1.8 | 0.95–1.91 | 0.96 | 0.042 | 13,900 |
| | 2 C | 1.8 | 61.8 | 1.91–4.88 | 3.38 | 0.110 | 11,300 |

The data recorded in the tables are self explanatory with the possible exceptions of 5 A and 6 A in Table II. It had been found possible to cut down the increment in volume to 0.90 cc. Following a statement by Pease and Stewart,[1] that less than 0.05 cc of carbon monoxide reduced the rate of

[1] Pease and Stewart: J. Am. Chem. Soc., 47, 1235 (1925).

reaction for hydrogen ethylene catalysis to about 10 % of its initial value, in presence of 100 g. of copper catalyst which adsorbed 12 cc of CO at 0° and 760 mm, the writer attempted to find whether the value of Q for very small initial increments was excessively higher than the 31,000 calories found for the first 0. 90 cc. Since the experimental method did not warrant measurements for volumes less than about 1.0 cc, an indirect method was used. After evacuation, 0.2 cc of CO were admitted to the catalyst chamber without measuring the thermal effect. Q was, however, determined for the next 0.93 cc and found to be 32,800 calories. The author admits that the percentage

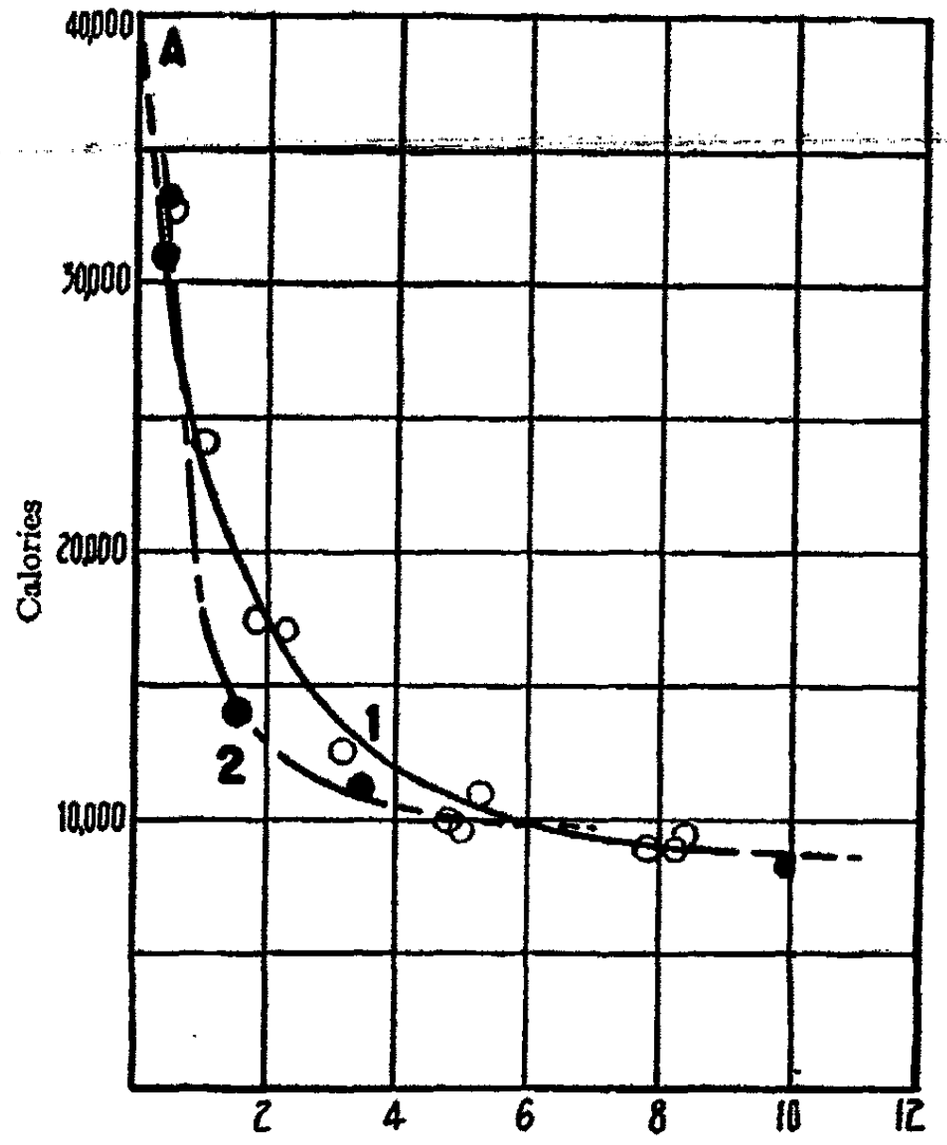



FIG. 2

error for these small increments is probably rather high. The above value of Q for the interval between 0.20 cc and 1.13 cc when compared with the value of 31,000 cal. for the interval between 0.00 cc and 0.90 cc, would indicate that the first 0.20 cc portion had no enormously greater value than had the following 0.93 cc. Det. 6 A does indicate that there was a falling off in Q soon after 0.59 cc had been adsorbed. The author feels that experiment 5 A was inconclusive. All that may be said is that the value obtained is unfavorable to a value of Q for the first 0.2 cc much in excess of 32,800 calories. It would be worth while for some one to develop an experimental method sufficiently delicate to determine what the upper limit of Q is for the smallest possible initial increments of adsorbed gas.

The data in Table II are graphically represented in the cumulative curves of Fig. 2 plotting successive volumes adsorbed which correspond to percentage available surface covered, against the corresponding molar heats of adsorption. If these curves were to represent the exact truth it would be necessary to have the thermal data for infinitesimally small increments in available surface covered. To illustrate, the point 4 C is determined as follows: Q = 9,700 cal. and the portion of the surface covered is that between 2.70 cc and 7.10 cc. The average volume between these two is 4.90 cc. Hence 4 C has the ordinate 28,000 and the abscissa 4.90 which is $\frac{4.90}{11.0} = 44.9\%$ of the available surface covered. This method of plotting is not rigorous, while the increments have a finite value, especially for the first portions added where the curve is steep, but it does give a good approximation to the truth.

As a check on the integral and differential values of Q determined for the "active" and "poisoned" samples, the integral values were calculated from the average of the differential values. The area under Curve I, if we assume that it crosses the y axis approximately at point A as Det. 5 A indicates, is 135,000. The average value of Q is therefore 135,000 ÷ 11.0 = 12,300 cal. The integral value found by direct measurement was 11,700 cal. From curve II the average value of Q is 14,800 cal. The integral value as measured was 15,300.

Discussion of results.—(a) Relatively high value of Q for first portions. A study of the data in Table II or of curves I and II reveals that the first portions of carbon monoxide to be adsorbed give rise to a much higher thermal effect than do the latter portions. Compare the 31,000 cal per mol for 4 A to the 9,700 cal per mol for interval 4 C. In Det. 4, after the first 2.7 cc or 24.5% has been adsorbed, Q for the remaining 75% has reached an almost constant value at 9,000 to 10,000 cal. It would seem then that the catalyst surface contains copper atoms at various energy levels and that those of highest level are the first to adsorb the incoming gas molecules. After these have been saturated the gas is adsorbed on atoms of lower energy level and, for the catalyst in question (Curve I) the atoms in the last 75% of available surface were approximately the same level.

(b) The differential value of Q is never less than 8,000 cal. Since Q is never less than the above value even for the last portions measured, the possibility is precluded of a polymolecular layer of adsorbed gas, since the heat of condensation of CO is only 1,430 cal. per mol.

(c) High value of Q for "poisoned" catalyst. The integral value of Q for the "poisoned" catalyst was some 20% higher than for the "active" sample before poisoning. The author is confident that this is not due to any experimental error. Moreover for the "poisoned" catalyst the first 0.93 cc portion gives a Q of 32,000 cal. This indicates that in the process of poisoning, the points on the copper surface that were robbed of their adsorptive capacity were not those of high energy level.

In the adsorption of CO on copper catalyst, then, we have a case similar to the case of hydrogen and nickel observed by Beebe and Taylor. In one instance the integral value of Q for an active sample adsorbing 16.0 cc being 14,200 cal. per mol and for the same sample 21,000 cal. after the adsorptive capacity had been reduced to about 8.0 cc by heating for 21 hours at 450° C. The writer welcomes new data, using different metals and gas, which are similar to those obtained by Beebe and Taylor for hydrogen and nickel, because B. Foresti has repeated their work, obtaining quite different results. Foresti finds no increase in heat of adsorption with decreasing adsorptive capacity. The writer notes that Foresti used nickel samples of very much higher adsorptive capacity as compared with those of Beebe and Taylor. In Table III are recorded adsorptive capacities in cc of hydrogen per cc. of nickel. It will be

TABLE III

| | Foresti | | Beebe and Taylor | |
|---|---|---|---|---|
| | Before Heating | After Heating | Before Heating | After Heating |
| Sample I | 57.8 | 26.8 | 5.1 | 2.6 |
| Sample II | 45.0 | 23.0 | 11.0 | 5.2 |

seen in Table II of Beebe and Taylor's paper that the change in Q for Sample I was 14,000 to 21,000 cal., and for Sample II 13,500 to 15,500 cal. In other words the increase was much less marked for the catalyst of higher adsorptive capacity. Foresti's samples adsorbed roughly five times as much as the most active ones of Beebe and Taylor. It seems quite possible that using Foresti's nickel we might expect little or none of the increase in Q on heating. The above disagreement in observations shows that it is not safe to generalize about metal adsorbents until we have some way of assuring ourselves that their surfaces are in the same condition—a difficult task, indeed.

Another generalization which, insofar as the writer is aware, has been tacitly accepted in most of the writings on contact catalysis is that the points of greatest catalytic activity are those of highest energy level. Following Taylor's theory of catalytic surface, these points would be the metal atoms which are least saturated by neighboring metal atoms and show the highest heat of adsorption for gases. Now we may conceive of catalysis at a surface as a three-stage process: (1) adsorption of one or more reactants, (2) interaction to form result antmolecules adsorbed on the surface, (3) desorption of resultant molecules. May it not be that certain points of high energy level on the catalyst surface have such affinity as to prevent the ready desorption of the resultants of a given reaction, that other points of low energy level either fail to adsorb or fail to distort the electronic configuration of the reactants sufficiently to bring about their combination, and finally that there are certain atoms or surface points which strike such a happy medium that adsorption and desorption both occur at rates which are advantageous to the reaction at hand? It seems unnecessary, for the sake of consistency, to assume that the points of highest degree of unsaturation on the metal surface are the seat of catalytic power.

## Summary and Conclusions

1. The integral and differential values for the heat of adsorption of carbon monoxide on copper catalyst have been determined.

2. The differential values were much higher for the initial portions of CO adsorbed than for later portions.

3. After accidental poisoning, resulting in decreased adsorptive capacity, the integral heat of adsorption was found to have increased markedly. This result is similar to a previous observation for hydrogen on nickel.

4. The following question is raised: Are the points of highest energy level, or highest degree of unsaturation for a metal surface, always the most active catalytically for every reaction?

*Amherst College,*
*Amherst, Massachusetts.*

# THE EQUILIBRIA UNDERLYING THE SOAP-BOILING PROCESSES. THE SYSTEM POTASSIUM LAURATE-POTASSIUM CHLORIDE-WATER

BY JAMES WILLIAM McBAIN AND MALCOLM CLIFFORD FIELD

The study of soap solutions has shown that they exist in a number of forms, each with very striking characteristics.[1] In pursuing the systematic study of the constitution of these liquids, jellies, liquid crystals and curds it is essential that the conditions under which each form exists should be exactly delimited. Further the processes of soap boiling depend upon the existence of this series of well-defined equilibria.

All soaps, pure, mixed commercial, whether potassium or sodium, are essentially of the same type. The differences are in degree and not in kind and the equilibria are so similar in the various cases that by means of numerical factors the effect of any electrolyte or mixture of electrolytes can be fairly closely predicted.[2] Finally, to a large extent, the behaviour of a mixture of soaps can be inferred from that of its pure constituents taken separately. It is found also that the results from such small scale laboratory experiments as are described in the present paper are in numerical agreement with similar results obtained on a full commercial scale.

Two preliminary contributions from this laboratory[3] dealt with sodium laurate and sodium palmitate in which the chief results were to find the various kinds of soap systems which exist and to indicate some of the limits for the existence of ordinary isotropic soap solutions at various temperatures with and without the presence of salt. McBain and Elford[4] describe a more thorough study of systems derived from potassium oleate which like potassium laurate possesses the advantage of being so soluble that all the possible forms can be observed at room temperature. Reference should be made to the papers cited for justification of the applicability of the phase rule to the external equilibria of reversible colloids and for a description of the special methods of investigation which have been developed in this study.

The present installment dealing with potassium laurate, includes the first successful delimitation of the field of existence of the important anisotropic liquid (liquid crystal, liquide à conique) middle soap[5] and also the first information obtained as to the upper limits of existence of that other aniso-

[1] The state of knowledge of this subject was summarised by one of us in 1922 (Fourth Colloid Report of Brit. Assocn. for the Advancement of Science, 244), now under revision and a more recent account revised up to date has been contributed as chapter V in Vol. 1, (pp. 137-164) of Jerome Alexander's "Colloid Chemistry" (1926).

[2] McBain and Pitter: J. Chem. Soc., 129, 893-898 (1926).

[3] McBain and Burnett: J. Chem. Soc., 121, 1320 (1910); McBain and Langdon: 127, 852 (1925).

[4] J. Chem. Soc., 129, 421 (1926).

[5] Discovered by McBain and Langdon.

tropic liquid the soap boiler's neat soap. Potassium laurate is so soluble that solutions less than $2N_w$ cannot be salted out at room temperature by potassium chloride as the latter cannot reach a high enough concentration. Concentrations of potassium laurate higher than $2N_w$ at room temperature and all solutions at temperatures above 60° can be salted out.

All these phases exist equally well in the absence of salt and the simplest procedure is to begin with the two-component system laurate and water, in which most of the typical equilibria appear. Accordingly, this will be discussed first, together with observations made upon individual phases, followed by the data obtained with systems in which potassium chloride is added as a third component.

## Materials

Throughout this work one sample of potassium laurate was used, specially prepared by Kahlbaum. It had been carefully freed from alcohol, its purity and neutrality checked and found to be satisfactory, data from two further samples being found to agree within the experimental error. The potassium chloride used was also from Kahlbaum and was dried by careful warming in a silica dish.

The soap, as a dry powder, was weighed into a thick-walled duro glass tube 6 to 9 inches long and ½ to ⅝ inches in diameter, sealed at one end in the form of an ordinary testtube. Potassium chloride (if any) was next added as required and the tube reweighed. Finally 1 to 3 grams of water (conductivity) were introduced by means of a 1 cc pipette according to the concentration of soap required, and the tube again weighed and sealed.

After preparation of the experiment, the tube was heated and shaken until the contents were transformed into a single homogeneous liquid. For this purpose a water bath was sometimes sufficient, but when higher temperatures were required either a glycerine bath (up to 200°) or an electric oven was employed. The latter was made by winding a resistance coil round a hollow cylinder of sheet asbestos (length 8 to 9 inches, diameter 3 to 4 inches) containing two mica windows through which the system could be examined. The temperature was read by a thermometer, the bulb of which was kept in contact with the soap tube. Stirring was effected by slowly shaking the furnace as a whole.

## Methods of Observation

In every system, as in the case of all other soaps studied, it was possible to observe a temperature $T_i$ on heating to which a clear, transparent, homogeneous, isotropic liquid was formed. On allowing this liquid to cool slowly, the critical temperature for the separation of a second phase (in the more concentrated soap systems) or for the formation of two liquid layers (in the more dilute soap systems with salt) could be determined. Thus, for any concentration of soap above approximately $2.3N_w$, with or without potassium chloride, on cooling a point was reached where the clear system became turbid, slight heating destroyed the turbidity, but re-cooling caused it to reappear at the

same temperature. For concentrations of soap below $2.3N_w$ a similar point was reached on cooling, provided the concentration of potassium chloride present was at least $5.0N_w$. In this latter case the cloudiness was more apparent, and on further cooling, the tube contained globules of two liquid phases, which gradually separated into two layers, the relative volumes of which depended on the temperature. Determination of this turbidity temperature delimits the boundary between homogeneous isotropic solutions and other phases which exist. In all cases the turbidity temperature can be approached either on cooling or heating, provided the latter is carried out sufficiently slowly, showing (as has been observed by previous workers) that the system is in true equilibrium, and that no supersaturation occurs on cooling. The two methods of observation were employed which are described in McBain and Elford's paper (loc. cit.); namely, the direct visual observation of $T_i$ and the microscopic method of examining a sample of soap solution in a small flattened glass bulb between crossed Nicols, the system being heated by a small electric furnace on the state of the microscope.

The determination of $T_h$, the temperature to which a wholly anisotropic solution has to be heated in order that an isotropic phase begins to separate from it, may be approximately determined by noting the fall in rigidity that accompanies formation of the isotropic liquid. The microscopic method is more accurate but even here difficulty is experienced in obtaining a thin enough sample. A combination of the two methods however gives a very good indication of the temperature $T_h$.

*Equilibria in the two-component system potassium laurate-water.*

It will be seen from a comparison of Fig. 1 with that of Fig. 1 of the paper by McBain and Elford (loc. cit.) or pp. 142, 143 Alexander (loc. cit.) that exactly the same phases occur in both soap systems; namely, hydrated crystals, neat soap, middle soap and isotropic homogeneous solutions. Only the limiting concentrations which mark off these fields differ for the various soaps thus making a difference in the size of the corresponding fields. Thus for potassium laurate solutions below about $2.3N_w$ are composed of a single homogeneous isotropic phase for all temperatures down to room temperature; solutions between $2.3N_w$ and $5.4N_w$ are composed of two phases at room temperature, one optically anisotropic, the other isotropic. On heating these solutions a homogeneous isotropic solution is readily obtained. Similarly if the system is wholly anisotropic (middle soap) at room temperature, it becomes heterogeneous on heating to a definite temperature $T_h$, while at a slightly higher temperature $T_i$ it finally becomes homogeneous and isotropic. These transformations are reversible and may be represented thus:

$$\text{Anisotropic phase} \overset{T_h}{\rightleftharpoons} \text{Heterogeneous (anisotropic and isotropic phase)} \overset{T_i}{\rightleftharpoons} \text{Isotropic phase}$$

For soap concentrations above $7.0N_w$, cooling to room temperature leads either to the partial, or total separation of lamellar crystals of hydrated

potassium laurate. Thus, 9.0$N_w$ potassium laurate at room temperature, exists in the tube as an upper portion of anisotropic liquid (about 50%) and a lower portion of solid white hydrated crystals which exhibit a distinct sheen when interlocked together. McBain and Elford[1] described the hydrated crystals of potassium oleate as being wax-like; the hydrated crystals of potassium laurate are on the contrary much more solid.

Vorländer[2] tabulated the melting points of many fatty acids and soaps but omitted that of potassium laurate. Pure potassium laurate in its white powdery condition was introduced into a fine melting point tube and attached to the bulb of a thermometer, which was placed in the electric furnace. At 264° the soap lost its white powdery appearance and formed a transparent gelatinous solid; this would be termed by Vorländer the first melting point of the soap, but it is really the transition point to the conic anisotropic liquid, neat soap. At 376° the true melting point to an isotropic liquid was observed, this being the lowest temperature at which a meniscus existed. Care was taken to observe the soap at the bottom of the melting point tube because contact with air at this temperature decomposes it.

The so-called first melting point represents the highest temperature at which hydrated potassium laurate crystal can exist and is therefore a point on the boundary of the neat soap field. The upper neat soap boundary has been completely determined in this two component system, by observing the temperature when the last trace of hydrated crystal dissolves and forms the homogeneous neat soap phase ($T_o$). The systems were heated in the electric oven until they formed a homogeneous isotropic liquid, they were then allowed to cool slowly until the first trace of hydrated crystal separated (considerable supersaturation always occurred, the crystal separating many degrees below the temperature at which it dissolved). The system containing a trace of hydrated crystal in neat soap was reheated and the temperature observed when the last trace of solid matter disappeared. If complete separation of hydrated crystal took place, i. e. the system was allowed to cool down to room temperature, a mass of bubbles was formed interspersed with crystals, and on reheating this completely obscured the point at which the crystals finally disappeared.

Calculations have shown that the degree of hydration of the crystal cannot exceed one molecule of water per molecule of potassium laurate; thus the homogeneous hydrated crystal boundary is exceedingly narrow. The highest soap concentration as yet examined (approx. 43$N_w$ or 92% soap) still contained a trace of anisotropic liquid together with hydrated crystal. Examination under the microscope has shown that two types of crystal exist (1) hexagonal lamellae which are apparently hydrated potassium laurate crystal; when the system is crystalline it consists almost entirely of this type, but traces of (2) small needles or rods have been noticed, and are probably acid soap produced by hydrolysis. No method of exact delimitation of the lower neat soap

[1] Loc. cit. or Alexander: "Colloid Chemistry," pp. 142, 143 (1926).
[2] Ber., 43, 3120 (1910).

boundary has yet been practicable in the case of potassium laurate and thus the shape of this one particular line in the diagram can only be taken as approximate. The position of one end was determined in the two-component system. For concentrations of soap below $7.5N_w$ hydrated crystal separates if the system is cooled in melting ice.

Table I includes all the data obtained for the aqueous potassium laurate systems. $T_h$ was determined by the viscosity method, and checked by the microscope method. $T_i$ was determined by direct observation of the turbidity

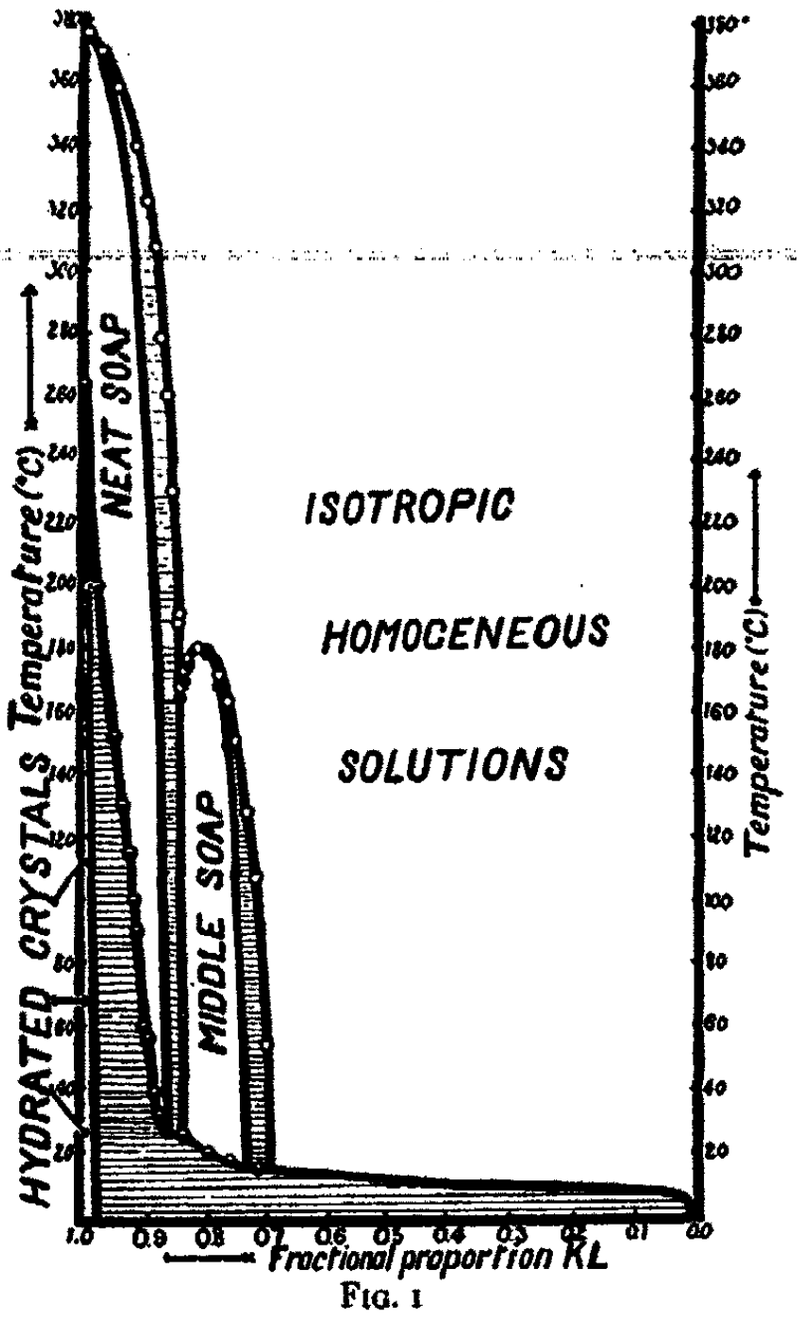



FIG. 1

Equilibrium diagram for the two-component system water-potassium laurate, showing the stable, homogeneous phases that occur at various temperatures.

temperature and again checked in many cases by the microscopic method. $T_c$ was determined as described above.

The results of Table I are represented diagrammatically in Fig. 1 where fractional proportions of potassium laurate are plotted.

Before turning to the study of the equilibria in the three-component system potassium laurate-potassium chloride-water, mention must be made of a phenomenon for which no explanation has yet been put forward. In aqueous potassium laurate systems between the limits 6.0 and $7.5N_w$, at temperatures ranging from 155° for the former, to 60° for the latter concentration, the

TABLE I

Appearance of aqueous potassium laurate at room temperature and phases present together with temperatures $T_l$, $T_h$ and $T_c$[1]

| System | Fractional proportion of K laurate | Description of material at room temperature | $T_l$ | $T_h$ | $T_c$ |
|---|---|---|---|---|---|
| 2.156 | 0.6831 | Isotropic liquid. | | | |
| 2.356 | 0.7070 | Isotropic liquid.[2] | 54° | | |
| 2.508 | 0.7150 | 2 phases, aniso. and iso. flows readily. | 107 | | 15° |
| 2.735 | 0.7323 | " | 127.5 | | |
| 3.0 | 0.750 | Homo. firm aniso. M soap | 150.5 | 108.0° | |
| 3.222 | 0.7632 | " | 162.6 | 149.0 | 17.5 |
| 3.500 | 0.7777 | " | 171.3 | 168.0 | |
| 4.004 | 0.8002 | " | 179.0 | 178.7 | 20.0 |
| 4.455 | 0.8168 | " | 179.8 | 179.5 | |
| 5.006 | 0.8335 | " | 176.0 | 173.5 | |
| 5.136 | 0.8370 | " | 172.8 | 169.3 | |
| 5.373 | 0.8431 | " | 168.0 | 164.0 | 25.5 |
| 5.496 | 0.8463 | Firm aniso. liquid, plastic | 167.2 | | |
| 5.550 | 0.8474 | " | 191.0 | | |
| 5.653 | 0.8498 | " | 187.8 | | 26.0 |
| 6.112 | 0.8594 | " | 230.0 | | |
| 6.643 | 0.8692 | " | 261.0 | | |
| 7.226 | 0.8784 | Traces of lamellar cryst. in cloudy firm aniso. liq. | 279.5 | | 32.0 |
| 8.004 | 0.8890 | White cryst. in cloudy firm aniso. liquid. | 308.0 | | 39.0 |
| 8.878 | 0.8986 | "[3] | 323.0 | | 56.0 |
| 9.694 | 0.9061 | "[3] | | | 60.0 |
| 10.98 | 0.9164 | "[3] | | | 90.0 |
| 11.52 | 0.9198 | "[3] | 340.0 | | 100 |
| 12.96 | 0.9283 | "[3] | | | 100 |
| 16.14 | 0.9414 | "[3] | | | 130 |
| 19.36 | 0.9513 | "[3] | 358.5 | | 152 |
| 43.32 | 0.9774 | Almost totally white, hydrated crystal. | 370.0 | | 200 |

*Homo.* = *homogeneous.* aniso. = anisotropic. iso. = isotropic. M. soap = middle soap.

[1] $T_l$ = temperature above which the system consists of a single isotropic phase.
$T_h$ = temperature below which the system consists of a single anisotropic liquid phase.
$T_c$ = temperature above which soap is completely in solution, crystals having completely disappeared.

[2] This system appears isotropic at room temperature owing to the system lying on a very steep portion of the curve, and the slight trace of water vapour condensing at room temperature is sufficient to lower the concentration into the region of homogeneous isotropic solutions.

[3] The volume occupied by the solid crystalline phase gradually increases in each succeeding system marked thus.

cloudy anisotropic phases (middle soap and neat soap as heterogeneous mixtures) were observed to become clear. This clearing appeared according to the microscopic method to be due to the formation of an isotropic phase; furthermore, when true equilibrium is attained in a tube the whole system can be obtained isotropic. This isotropic region lay between very narrow temperature limits (above and below which the anisotropic phases exist), and could be approached either by heating or cooling the system, provided that it is carried out in sufficiently small temperature increments. It is not like the usual homogeneous isotropic soap solutions, in that it is highly viscous and will not flow. A study of the phase rule diagram already plotted for this system seems to offer no apparent explanation for its existence. The suggestion that the conic anisotropic particles arrange themselves on the surface of the glass in such a manner as to appear isotropic cannot well be the explanation of the whole system becoming clear in the tube. The possibility that the phenomenon is due to an unstable isotropic state representing a continuation of the isotropic "arm" (see Fig. 1.) is supported by the fact that the temperature at which the isotropic region exists never exceeds 155°, which is approximately the minimum temperature reached by the true isotropic "arm." But again, the fact of formation of this isotropic phase both on heating and cooling the system does not suggest an unstable phase.

*Equilibria in the system water-potassium laurate-potassium chloride.*

Each of the four phases met with in the aqueous potassium laurate systems exist equally well when the third component, potassium chloride, has been added. The first stage in this study was to delimit the boundary of homogeneous isotropic soap solutions containing salt. This was carried out by the "turbidity temperature" method already described. Concentrations of soap up to approximately $2.0N_w$ with added potassium chloride of $5.0N_w$ or more became turbid on cooling, and further slight cooling caused the separation of two isotropic liquid layers, these being the well known "nigre" and "lye". By increasing the concentration of salt for any one concentration of soap, the turbidity temperature ($T_i$) or upper critical temperature for separation of liquid phases was gradually raised. If the concentration of potassium chloride was less than approximately $5.0N_w$ for soap concentrations up to $2.0N_w$, no turbidity temperature was observed, i.e. the system remained clear down to room temperature or until potassium chloride separated. However, for potassium laurate concentrations above $2.3N_w$ approximately, with decreasing concentrations of potassium chloride down to zero, a turbidity temperature was observed, but the plastic phase that separated was so rigid that the heterogeneous mixture of the latter with isotropic soap solution scarcely ever separated into layers. This conic anisotropic plastic phase is the middle soap met with in the two-component system.

*Experimental.*

The method employed was to fix the concentration of the soap for a series of determinations and vary the concentration of the salt. This enabled a rectangular cross sectional graph to be drawn for any one concentration of

soap showing the variation of turbidity temperature with weight normality of potassium chloride. In some cases it was found more convenient to fix the concentration of potassium chloride and vary the concentration of soap. From the results obtained, a series of curves were plotted from which it was possible to obtain an isotherm of any required temperature for plotting in the three-component system.

All normalities are weight normalities, that is, they refer to gram mols of salt or soap associated with 1 kilogram of water. Fractional concentrations are used for plotting on the triangular diagrammatic method of representation of this three component system. They are obtained thus:—

$$\text{Fractional proportion of potassium laurate} = \frac{\text{weight normality of potassium laurate}}{N_w \text{ potassium laurate} + N_w \text{ KCl}} + 1$$

Table II contains the observations of the turbidity temperatures together with notes describing the appearance of each system at room temperature.

TABLE II

Effect of addition of potassium chloride to $0.15N_w$ potassium laurate; appearance and phases present at room temperature, and $T_i$ the temperature on heating to which the system becomes a clear homogeneous liquid

| Conc. of KCl ($N_w$) | Description of material at room temperature | $T_i$ (visual) |
|---|---|---|
| | Isotropic, homogeneous liquid | Iso. to room temp. |
| 4.865 | Trace acid soap and KCl crystals in iso. liquid | 127.5° |
| 5.012 | " " " " " " " " | 145.7 |
| 5.781 | Few acid soap and KCl " " " " | 180.5 |
| 6.466 | " " " " " " " " | 203.0 |

Effect of addition to $0.25N_w$ solutions of potassium laurate.

| | | |
|---|---|---|
| | Isotropic, homogeneous liquid | Iso. to room temp. |
| 4.528 | Trace acid soap and KCl crystals in iso. liquid | " |
| 4.643 | KCl in an isotropic liquid | " |
| 4.732 | " " " " " | 102.0 |
| 4.995 | Acid soap and KCl crystals in iso. liquid | 163.2 |
| 5.885 | Trace acid soap and KCl crystals in iso. liquid | 182.0 |
| 6.555 | Acid soap and KCl crystals in iso. liquid | 209.0 |
| 6.992 | " " " " " " " | 224.0 |

Effect of addition to $0.50N_w$ solutions of potassium laurate.

| | | |
|---|---|---|
| | Isotropic. homogeneous liquid | Iso. to room temp. |
| 4.465 | Acid soap and KCl crystals in iso. liquid | " " |
| 4.740 | KCl crystals in isotropic liquid | " " |
| 4.915 | KCl and trace of acid soap crystals in iso. liq. | 114.5 |
| 4.990 | " " " " " " " " | 143.5 |
| 5.503 | Acid soap and KCl crystals in iso. liquid | 165.2 |
| 6.080 | " " " " " " " " | 191.7 |
| 6.076 | " " " " " " " " | 226.7 |
| 7.489 | " " " " " " " " | 240.5 |

TABLE II continued

| Conc. of KCl ($N_w$) | Description of material at room temperature | $T_i$ (visual) |
|---|---|---|
| | **Effect of addition to $0.75N_w$ solutions of potassium laurate.** | |
| | Isotropic, homogeneous solution. | Iso. to room temp. |
| 5.063 | KCl crystals in iso. liquid. | 109.0 |
| 5.253 | " " " " " | 144.5 |
| 5.424 | Acid soap and KCl crystals in iso. liquid | 155.7° |
| 5.766 | " " " " " " " " | 177.0 |
| 6.572 | " " " " " " " " | 210.0 |
| 7.231 | " " " " " " " " | 240.5 |
| | **Effect of addition to $1.0N_w$ solutions of potassium laurate.** | |
| | Few acid soap crystals in isotropic liquid. | Iso. to room temp. |
| 4.516 | Acid soap and KCl crystals in " " | " |
| 5.066 | KCl crystals in isotropic liquid | " |
| 5.077 | " " " " " | " |
| 5.223 | Acid soap and KCl crystals in isotropic liquid | 118.5 |
| 5.392 | " " " " " " " " | 148.0 |
| 5.547 | " " " " " " " " | 153.0 |
| 5.914 | " " " " " " " " | 191.5 |
| 6.294 | " " " " " " " " | 198.3 |
| 6.699 | " " " " " " " " | 214.5 |
| | **Effect of addition to $1.5N_w$ solutions of potassium laurate.** | |
| | A few acid soap crystals in iso. liquid. | Iso. to room temp. |
| 4.990 | KCl crystals in isotropic liquid | " |
| 5.655 | " " " " " | 82.2 |
| 5.720 | Acid soap and KCl crystals in iso. liquid | 92.0 |
| 6.013 | KCl crystals in isotropic liquid | 167.7 |
| 6.261 | " " " " " | 189.7 |
| 6.573 | Acid soap and crystals in iso. liquid | 205.5 |
| 7.028 | " " " " " " | 225.5 |
| | **Effect of addition to $2.0N_w$ solutions of potassium laurate.** | |
| | Acid soap crystals in isotropic liquid. | Iso. to room temp. |
| 4.235 | KCl crystals in isotropic liquid | " |
| 4.580 | Acid soap and KCl crystals in iso. liquid. | 64.0 |
| 4.777 | KCl crystals in isotropic liquid | 74.0 |
| 5.242 | Acid soap and KCl crystals in iso. liquid | 91.2 |
| 5.898 | " " " " " " " " | 128.2 |
| 5.954 | KCl crystals in isotropic liquid | 132.2 |
| 6.497 | Acid soap and KCl crystals in iso. liquid. | 166.0 |
| 7.318 | " " " " " " " " | 227.5 |

TABLE II Continued

| Conc. of KCl ($N_w$) | Description of material at room temperature | $T_1$ (visual) |
|---|---|---|
| | Effect of addition to $2.5N_w$[1] potassium solutions of potassium laurate. | |
| | M. soap and iso. liquid, moderate plasticity | 107 |
| 0.2845 | " " " " " " " | 98.7 |
| 0.5034 | " " " " " " " | 92.5 |
| 0.9499 | " " " " " " " | 78.0 |
| 1.563 | " " " " " " " | 66.5 |
| 1.763 | " " " " " " " | 59.0 |
| 2.890 | " " " " " " " | 25.0 |
| | Effect of addition to $3.0N_w$ solutions of potassium laurate. | |
| | Homo. aniso. clear, firm, M soap. | 150.5 |
| 0.2079 | " " " " " " | 148.2 |
| 0.4783 | " " " " " " | 141.7 |
| 0.8443 | Hetero., clear, firm (M. soap traces iso. liq.) | 131.2 |
| 0.9961 | Hetero. clear, fairly firm (M. soap, iso. liq.) | 128.5 |
| 1.252 | " " " " " " " " | 114.5 |
| 1.731 | " " " " " but flows slightly | 76.5 |
| 2.092 | " " " " " " " " | 64.5 |
| 2.253 | Hetero., M. soap and iso. liquid, flows readily | 56.7 |
| 3.229 | Hydrated soap crystal in viscous iso. liquid | 13.5 |
| 3.599 | Ditto and traces of KCl crystals | 84.5 |
| 4.216 | Hydrated soap and KCl crystals in iso. liquid | 115.2 |
| 4.932 | " " " " " " | 146 |
| 5.846 | " " " " " " | 177.0 |
| 6.966 | Ditto and a few needle crystals. | 215.7 |
| | Homo., aniso. clear, firm, M. soap | 179.0 |
| 0.2736 | " " " " " | 174.2 |
| 0.5106 | " " " " " " | 168.0 |
| 0.8102 | " " " " " " | 158.2 |
| 0.9800 | Hetero. clear, firm M. soap, traces iso. liquid | 152.0 |
| 1.520 | Hetero., M soap and iso. liquid, fairly firm | 118.0 |
| 1.980 | Ditto but flows slightly | 67.2 |
| 2.482 | Hydrated soap crystal in iso. liquid | 27.7 |
| 3.497 | " " " " " " | 159.3 |
| 4.937 | Ditto and KCl crystals | 194.7 |
| 5.962 | Hydrated soap and KCl crystals in iso. liquid | 216.5 |

[1] Only half of the $2.5N_w$ potassium laurate system was plotted, increasing the concentration of potassium chloride would again find the turbidity temperature rising.

TABLE II Continued

| Conc. of KCl ($N_w$) | Description of material at room temperature | $T_i$ (visual) |
|---|---|---|
| **Effect of addition to 5.0$N_w$ solutions of potassium laurate.** | | |
| | Homo. aniso. clear firm M. soap | 176.0 |
| 0.3344 | " " " " " | 167.8 |
| 0.4990 | " " " " " | 160.7 |
| 0.6170 | " " " " " | 155.7 |
| 0.8849 | " " " " " | 140.0 |
| 1.035 | Hetero. M. soap and iso. liquid, clear and fairly firm | 128.5 |
| 2.065 | Hydrated soap crystal in an aniso. and iso liquid | 195.5 |
| 3.571 | Hydrated soap crystal in iso. liq. traces KCl crys. | 216.5 |
| **Effect of addition to 0.5$N_w$ solutions of potassium chloride.** | | |
| 2.241 | Isotropic liquid | Iso. to room temp. |
| 2.488 | Hetero., M. soap and iso. liquid, flows slightly | 92.5 |
| 2.988 | Homo. aniso. clear firm M. soap | 141.7 |
| 4.009 | " " " " " " | 168.0 |
| 4.957 | " " " " " " | 160.7 |
| 6.006 | Cloudy aniso. plastic liquid, M. soap | 244.0 |
| **Effect of addition to 1.0$N_w$ solutions of potassium chloride.** | | |
| 2.238 | Hetero. aniso. M. soap and iso liquid, flows readily | 42.5 |
| 2.500 | Ditto but fairly firm. | 80.0 |
| 2.976 | " " " " | 128.2 |
| 3.993 | Much firmer. | 152.0 |
| 4.977 | Hetero., clear aniso. M. soap and trace iso. liq. | 128.5 |
| 6.010 | Hydrated soap crystal and platsic aniso. liquid | 245.0 |
| **Effect of addition to 2.0$N_w$ solutions of potassium chloride.**[1] | | |
| 2.5 | | 49.0 |
| 3.0 | | 70.0 |
| 4.0 | | 65.0 |
| 5.0 | | 192.5 |

[1] The data in this section were obtained graphically from sections 9 to 12 thus giving a further series of points on the isotherms.

Figs. 2 and 3 are deduced from the data in Tables I and II and each isotherm thereon represents the boundary of the isotropic liquid solution at that temperature. The high solubility of potassium laurate is reflected in the large portion of the diagram which represents these isotropic solutions even at room temperature. No explanation has been suggested for the extraordinary shape of the boundary which runs out in a very narrow tongue almost surrounding the portion of the diagram where middle soap occurs at temperatures below 180°.

*Determination of the middle soap boundary.*

The delimitation of the middle soap boundary in the presence of salt has been carried out at room temperature only; but the data thereby obtained are sufficient to give a good approximate idea of the position of the boundary at all other temperatures up to 180°.

The method employed was to examine the systems, between a microscope slide and cover glass, with polarised light. The middle soap phase, being doubly refracting, lights up the field, whereas any isotropic phase present appears dark and remains so on rotation of the microscope stage. Thus by

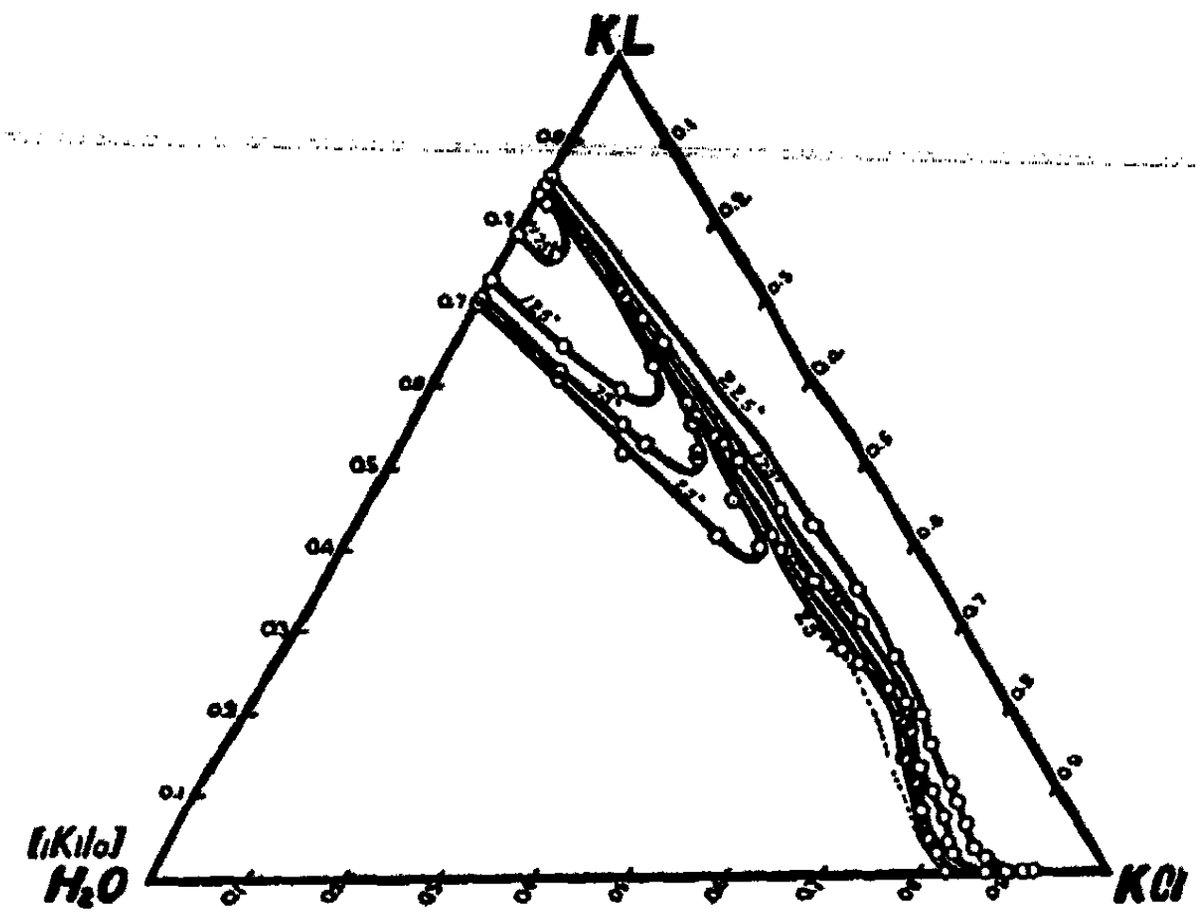



FIG. 2

Solubility curves for potassium chloride and potassium laurate at 25°, 75°, 125°, 175° and 225° showing the extreme limits of the field of homogeneous isotropic solutions capable of existing at these temperatures.

taking a fixed concentration of potassium laurate (say 3.0$N_w$), and progressively decreasing the concentration of salt and examining these systems under polarised light, a concentration of salt is reached when no more isotropic liquid can be detected; that is, the whole system is homogeneous middle soap, this therefore represents a point on the middle soap boundary. Results obtained in this manner are given in Table II, sections 9 to 14. Any isotropic liquid present in these systems was most readily detected when the cover glass was pressed firmly on the specimen, thus obtaining as thin a layer as possible. Any isotropic liquid was generally squeezed out and found at the edge of the field.

Figs. 4 and 5 show that the homogeneous middle soap phase extends about one-third of the way into the region bounded by the isotropic phase, the other two-thirds of this region comprising a heterogeneous mixture of middle soap and isotropic solution. The tie lines in this heterogeneous region must

radiate as shown, for, any other method of drawing them would mean, that a region exists where equilibrium is between two isotropic phases (cf. nigre-lye two layer systems); whereas it has been shown by microscopic examination that one of the phases in this region is always the anistropic middle soap. Actual analysis is impossible due to an insufficient separation of the two phases. The middle soap field decreases in size as the temperature rises until at 180° it is represented by a point only in the aqueous potassium laurate system. Above this temperature middle soap never exists.

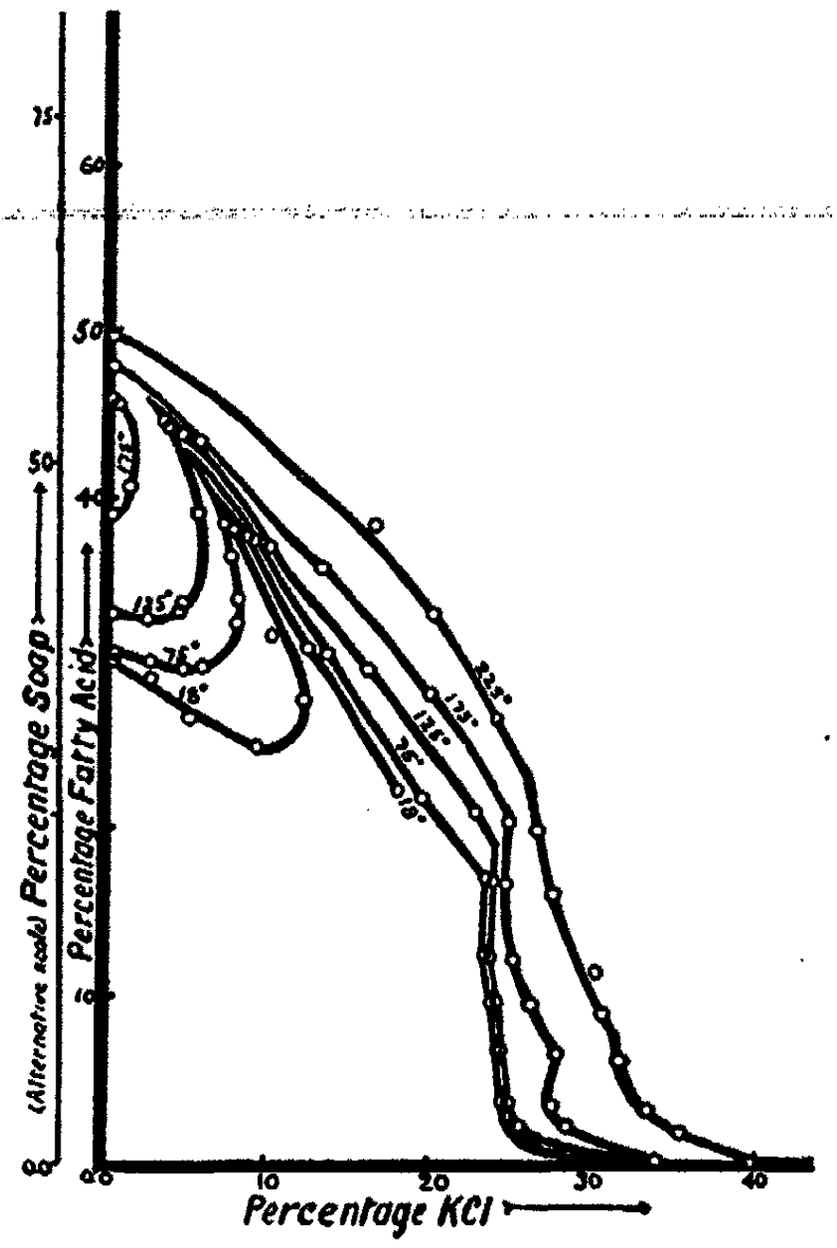



FIG. 3

Limits of existence, in technical units, of homogeneous isotropic solutions containing potassium chloride and potassium laurate at 18°, 75°, 125°, 175°, and 225° .

*Determination of the neat soap boundary.*

The delimitation of the region of existence of neat soap in the presence of potassium chloride is a very much more difficult matter than the delimitation of that of middle soap. Analytical methods for this have not been used, but these possibilities will be discussed later.

The method employed to obtain the upper part of the boundary in the triangular diagrams was to study the temperature at which hydrated soap crystals just completely dissolve. Referring to Fig. 6, which represents

equilibria in the three-component system at 90°, one sees that equilibria exist between homogeneous neat soap and hydrated soap crystal; thus the crystal should dissolve when the neat soap boundary extends to the point given by the composition of the system; or in other words, the temperature when the last trace of crystal disappears gives a point on the neat soap boundary at that temperature. Systems were made up therefore fixing the concentration of potassium chloride, and varying the concentration of potassium laurate from 6.0$N_w$ upwards. They were heated until they formed an homogeneous

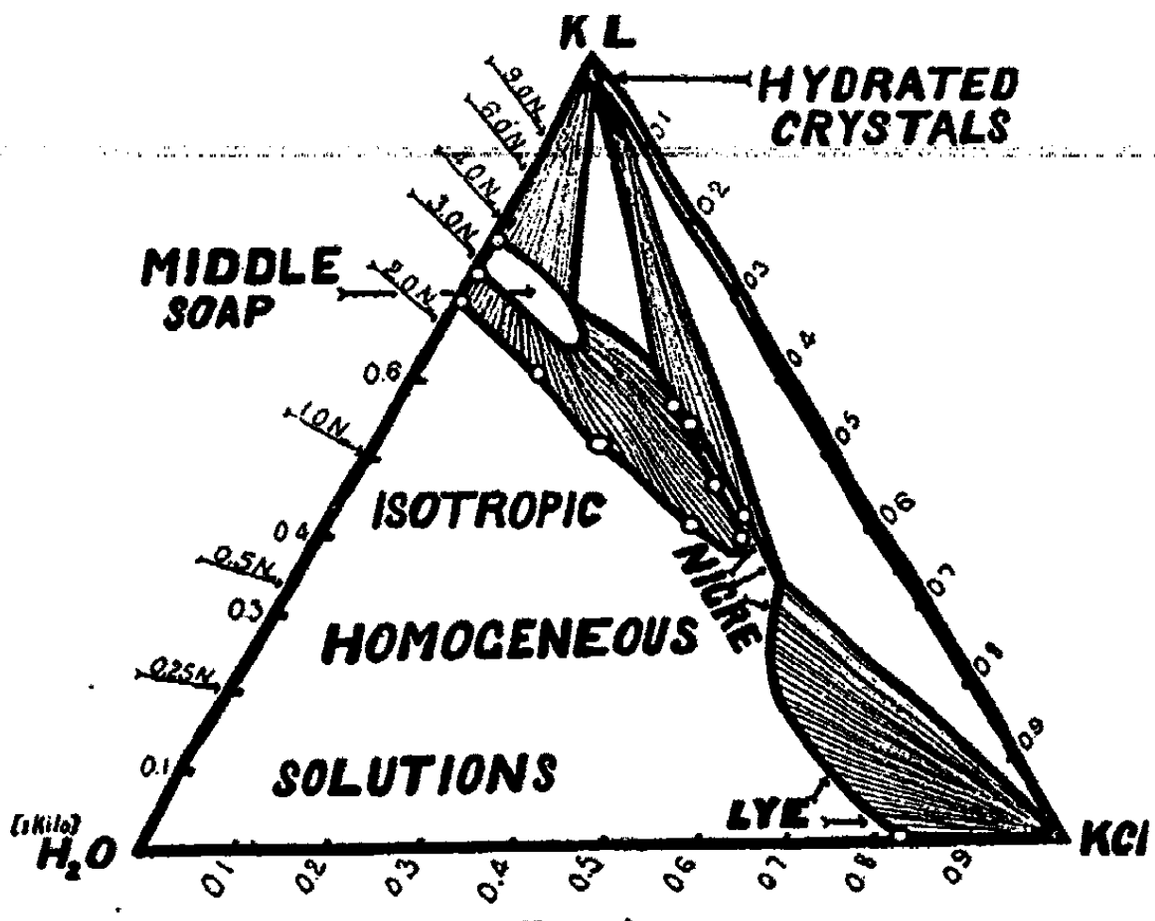



FIG. 4*

Phase rule diagram at 18°. Potassium laurate-potassium chloride-water; concentrations are expressed in fractions of mols of potassium laurate and potassium chloride, and in fractions of one kilogram of water. The shaded areas represent the approximate direction of the tie lines in the two-layer systems.

isotropic liquid, then slowly allowed to cool until hydrated soap crystals separated; the temperature at which these dissolve was determined in the same manner as has already been discussed for the two component aqueous potassium laurate systems.

Table IV gives the results thus obtained, although they are not by any means complete. From these data, for each fixed concentration of potassium chloride, a cross sectional graph may be constructed, in which temperature is plotted against weight normality of potassium laurate and from this point on the upper neat soap isotherms can be read off for any temperature. Table V gives these readings for 90°.

* See page 1560.

TABLE IV

Effect of addition of concentrated solutions of potassium laurate to 0.5, 1.0 and 2.0$N_w$ potassium chloride; $T_c$, the temperature, at which the last trace of hydrated soap crystals dissolves, forming neat soap

| Conen. KCl ($N_w$) | Conen. K Laurate ($N_w$) | $T_c$ (visual) |
|---|---|---|
| 0.5 | 6.006 | (21.0°) |
| | 6.987 | 29.0 |
| | 7.461 | 35 |
| | 8.756 | 50 |
| | 9.766 | 65 |
| | 12.62 | 100 |
| | 19.96 | 175 |
| 1.0 | 6.010 | 24.5 |
| | 7.907 | 50.5 |
| | 8.928 | 79.0 |
| | 14.96 | 98.0 |
| 2.0 | 5.020 | 33.5 |
| | 5.967 | 35.2 |
| | 7.698 | 41.5 |

TABLE V

| Temp. of isotherm | Weight normalities KCl | Weight normalities K Laurate | Fractional proportion KCl | Fractional proportion K Laurate |
|---|---|---|---|---|
| 90° | 0.5 | 11.2 | 0.0394 | 0.8818 |
| | 1.0 | 9.8 | 0.0847 | 0.8305 |

Homogeneous neat soap does not exist at room temperature (18°C) because so much laurate crystallises out that only sufficient soap is left in solution to form middle soap. Neat soap first appears at approximately 25° as is represented by a point in the aqueous two-component potassium laurate system. The width of the boundary becomes a maximum at 264°, and then progressively decreases until at 376° it is again represented by a point in the aqueous potassium laurate system and above this temperature neat soap again does not exist.

Fig. 4 represents the equilibria and stable phases at room temperature plotted on the triangular type of diagram which is most suitable for representing these three-component systems.

Fig. 5 represents the same equilibria plotted on the rectangular type of diagram using commercial units. The most striking features about these representations are the absence of neat soap, and the inability to obtain nigre-lye separations owing to equilibria existing with solid potassium chloride.

Figs. 6 and 7 represent the equilibria and stable phases at 90°. At this temperature nigre and lye can be separated as two isotropic layers. Three layer separations are only represented by a single line; if a triangular region exists (see McBain and Elford, loc. cit.) it is sufficiently narrow to be repre-

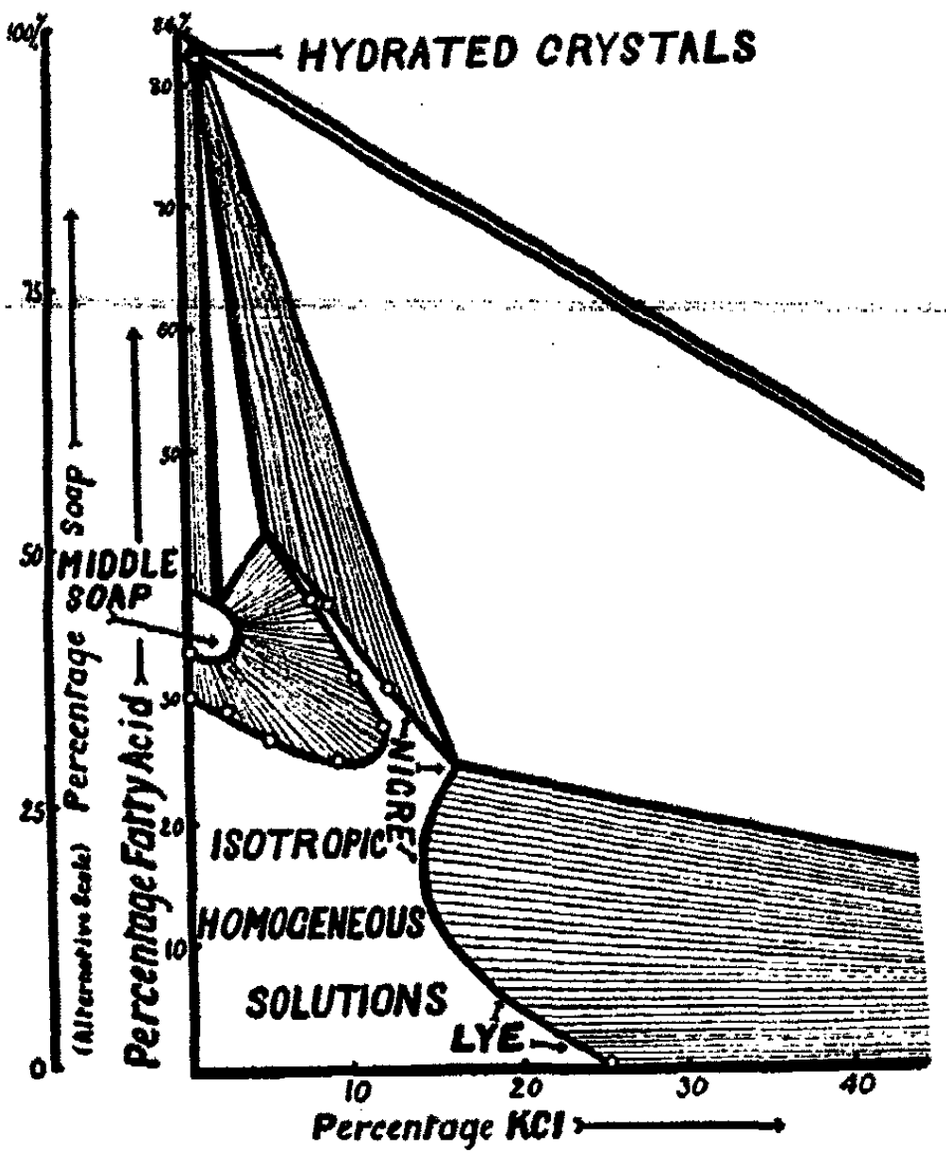



FIG. 5*

Phase rule diagram at 18°, potassium laurate-potassium chloride-water; concentrations are expressed in grams of fatty anhydride and grams of potassium chloride per 100 grams of total system. The areas correspond to those in Figure 4.

*Footnote to Figs. 4 and 5). At room temperature it will be noticed there is no nigre-lye two-layer system. However, in place of this, two phase equilibria exist between homogeneous isotropic soap solutions containing salt (nigre or lye) and solid potassium chloride. The solubility of potassium chloride in these soap solutions has not been determined with the same degree of accuracy as the remainder of the isotherm but the error involved in its delimitation is unimportant.

sented by a single line. It should be possible working at 90° to obtain neat soap and lye; neat soap, nigre and lye; neat soap and nigre; if separation of layers were sufficient the neat soap boundary could be determined by analysing the layers.

Fig. 8 represents the equilibria and stable phases at 200°; the middle soap phase is now absent, the triangle representing three phase systems of constant composition, hydrated potassium laurate crystal, neat soap and lye

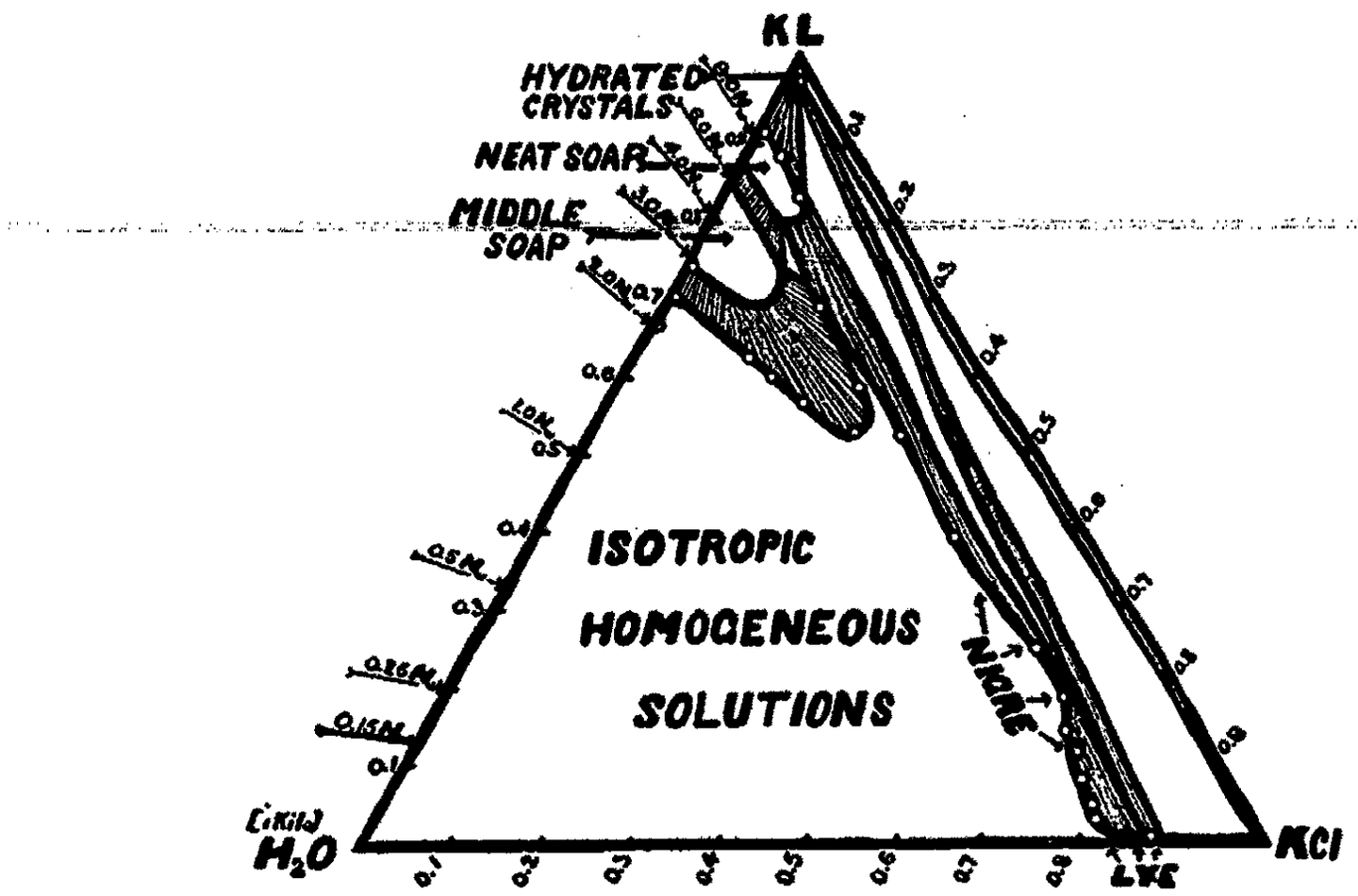



FIG. 6

Phase rule diagram at 90°. Potassium laurate-potassium chloride-water; concentrations are expressed in fractions of mols of potassium laurate and potassium chloride, and in fractions of one kilogram of water. The shaded areas represent the direction of the tie lines in two-phase systems. Homogeneous phases and three-phase systems are left clear.

has become very narrow. Figs. 4 to 8 are partly diagrammatic, but give a general indication of the boundaries of the different phases and of the direction of the tie lines.

Comparing the diagrams obtained with potassium laurate with the diagrams for sodium palmitate (McBain and Langdon: loc. cit.) and potassium oleate (McBain and Elford: loc. cit.) two striking dissimilarities are observed. The region of homogeneous isotropic soap solutions containing salt is much greater than for either of the two soaps previously studied. The heterogeneous region between middle soap and isotropic soap solution extends over a much greater area for potassium laurate than for either sodium palmitate or potassium oleate, and this is doubtless the reason for some of the troubles met with in the manufacture of certain soaps containing large quantities of coconut and palm kernel oil. The diagrams indicate how such trouble may be avoided.

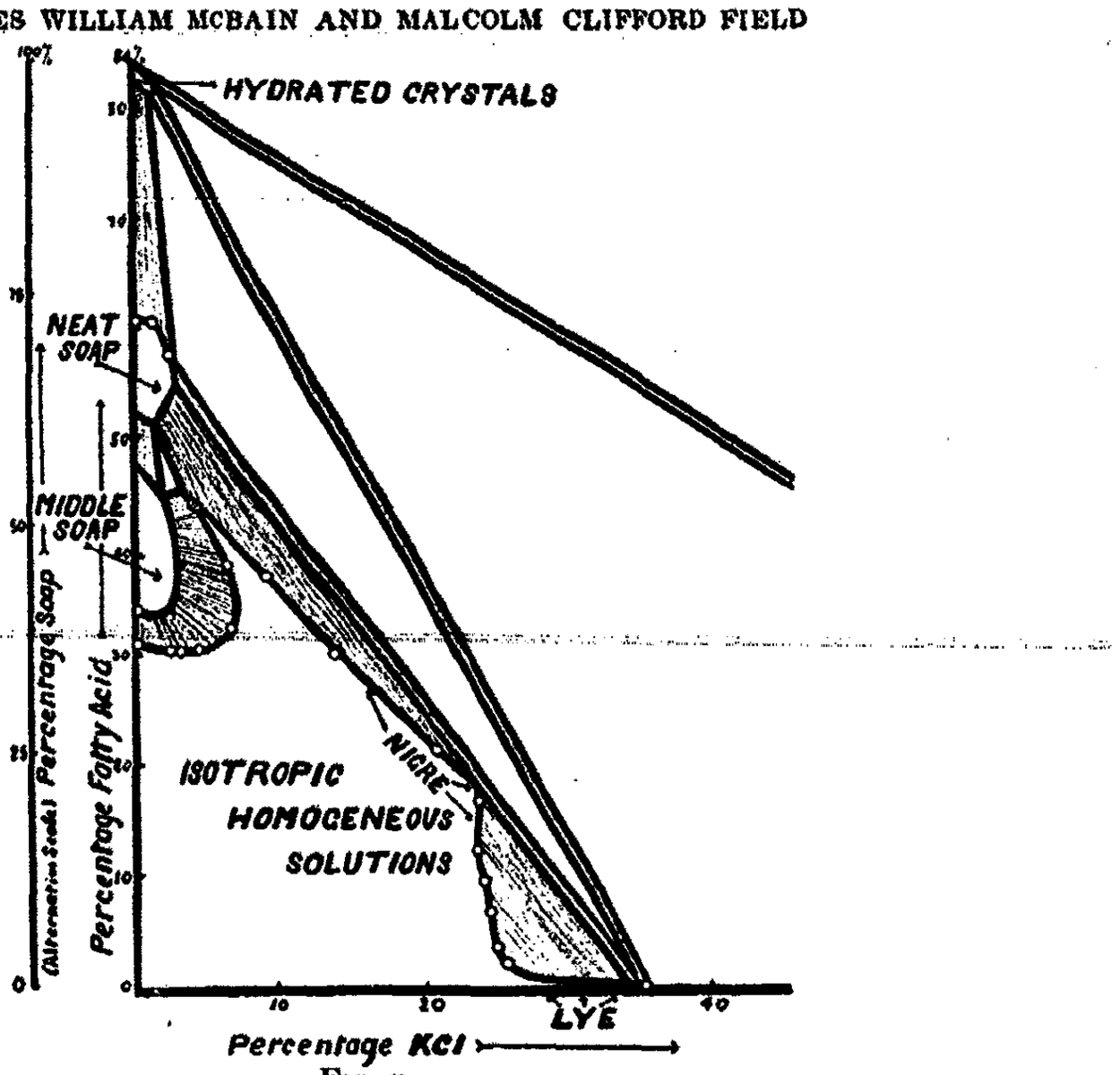



FIG. 7

Phase rule diagram at 90°, potassium laurate-potassium chloride-water; concentrations are expressed in grams of fatty anhydride and grams of potassium chloride per 100 grams of total system. The areas correspond to those in Figure 6.

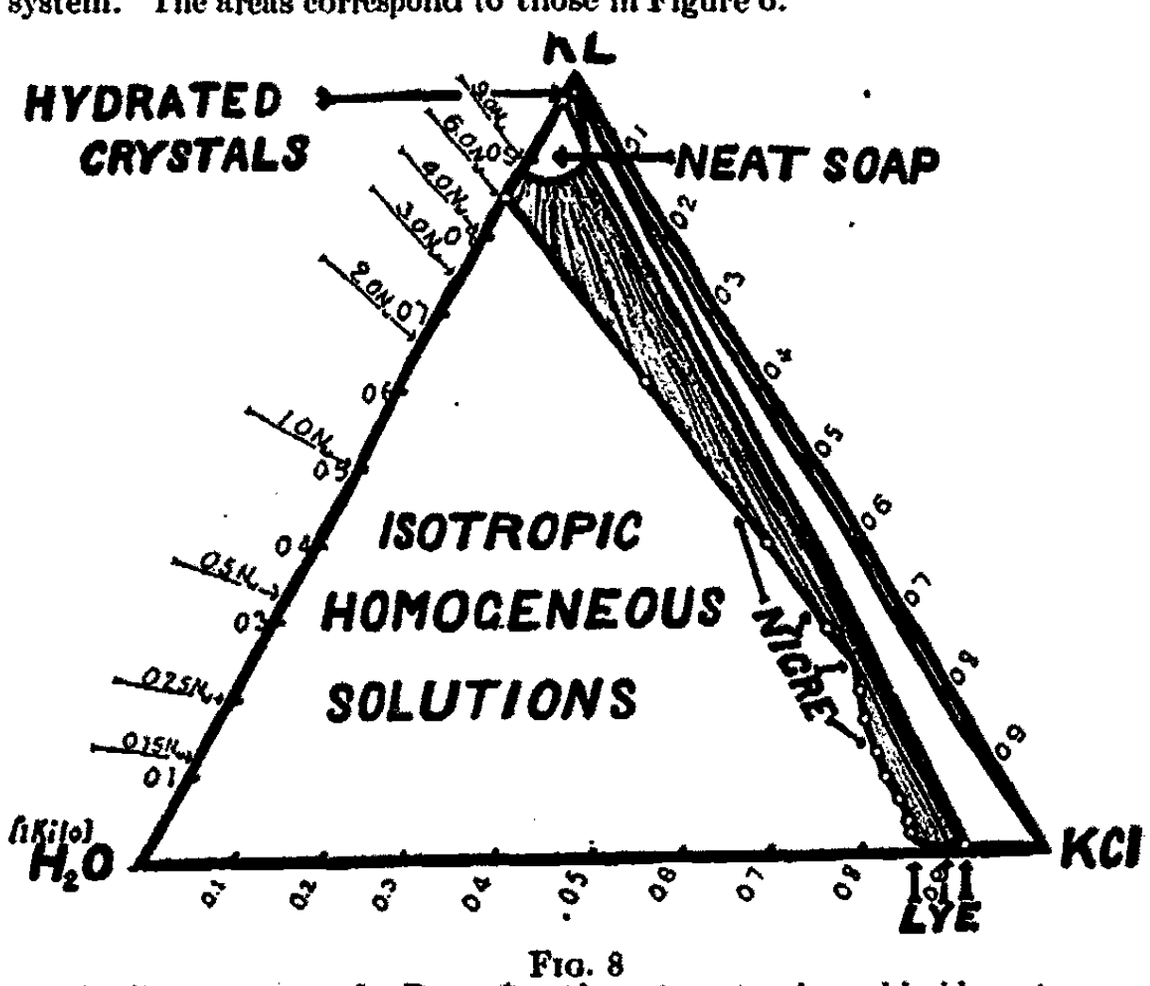



FIG. 8

Phase rule diagram at 200°. Potassium laurate-potassium chloride-water; concentrations are expressed in fractions of mols of potassium laurate and potassium chloride, and in fractions of one kilogram of water. The shaded areas represent the direction of the tie lines in two-phase systems. At this temperature middle soap does not exist.

## Summary

1. The forms or phases in which soaps can exist are very similar for such different soaps as potassium laurate, potassium oleate and sodium palmitate. The chief phases are crystals, isotropic liquid, and two anisotropic liquids (liquid crystals) middle soap and neat soap. The equilibria between these phases are quantitatively similar for the various soaps although they differ in their quantitative aspect.

2. All the soap phases that exist in the three-component system which includes salt, are found in the simpler system, soap and water, where also their separation is spontaneous; that is, they "salt out" in the absence of salt and may even be observed at room temperature.

3. The limits of the field of existence of isotropic liquid solutions of potassium laurate have been accurately determined for temperatures up to 376° in the absence of potassium chloride and up to 225° in the presence of potassium chloride. This single phase includes solutions which are wholly crystalline as well as those which are colloidal electrolytes, and ranges at sufficiently high temperatures from pure water up to pure anhydrous potassium laurate, the two being miscible in all proportions above 376°. Conditions of existence of the two important anisotropic liquids, neat soap and middle soap, have been determined both in the presence and absence of potassium chloride. Both are typical conic anisotropic liquids. Middle soap is much more prominent with potassium laurate than for the higher soaps and is therefore much more liable to disturb the normal course of soap making.



*Department of Physical Chemistry,*
*University of Bristol,*
*Bristol, England.*

*September 2, 1926.*

# INFLUENCE OF 'AGEING' OF A SOL ON ITS COAGULATION

BY S. GHOSH AND N. R. DHAR

In one of the papers[1] published from this laboratory we have investigated the influence of ageing on arsenious sulphide sol towards its coagulation by various electrolytes and the following results were obtained:—

TABLE I

Concentration of the sol = 0.922 grm. $As_2S_3$ per litre.
Volume = 10 c.c.; Time = ½ hour.

| Salt | | Amount necessary for coagulation in c.c. | Amount necessary for coagulation in c.c. after one month. |
|---|---|---|---|
| KCl | N/2 | 2.0 | 1.80 |
| $K_2SO_4$ | N | 1.25 | 1.15 |
| $BaCl_2$ | N/50 | 1.30 | 1.25 |

These results prove that arsenious sulphide sol becomes slightly unstable when coagulated by either a monovalent or a bivalent cation, but the sol becomes more unstable for the electrolytes KCl and $K_2SO_4$ than for the electrolyte $BaCl_2$.

We have now made further experiments on the coagulation of an 'aged' sol of arsenious sulphide. The results are given in Table II.

TABLE II

Concentration of the sol = 0.2804 grm. $As_2S_3$ per litre
Amount of sol taken each time = 4 c.c.
Volume = 10 c.c.; Time = 1 hour.

| Salt | Conc. | Amount necessary for coagulation in c.c. on 22nd Jan., 1925. | Amount necessary for coagulation in c.c. on 25th July, 1925. |
|---|---|---|---|
| KCl | N/2 | 1.60 | 1.45 |
| $BaCl_2$ | N/100 | 2.60 | 2.50 |
| $Al(NO_3)_3$ | N/1000 | 3.10 | 3.00 |
| $C_1H_5NH_2HCl$ | M/50 | 2.70 | 2.50 |
| Quinine hydrochloride | M/500 | 2.0 | 2.60 |
| Strychnine hydrochloride | M/120 | 0.8 | 0.90 |
| Crystal violet | M/660 | 2.90 | 2.70 |

The foregoing results show that arsenious sulphide sol becomes unstable on ageing when coagulated by KCl, $BaCl_2$, $Al(NO_3)_3$, aniline hydrochloride and crystal violet. On the other hand, the sol becomes stable on ageing when coagulated by quinine hydrochloride or strychnine hydrochloride. The un-

[1] Kolloid-Z., 36, 129 (1925).

stability[1] of arsenious sulphide sol on ageing towards its coagulation by various electrolytes is in the following decreasing order, KCl > aniline hydrochloride > crystal violet > $BaCl_2$ > $Al(NO_3)_3$.

It has been emphasised repeatedly in several publications[2] from these laboratories that precipitates like $(FeOH)_3$, $Cr(OH)_3$, $Al(OH)_3$, etc., which possess a high adsorptive power when freshly prepared, lose much of their chemical reactivity and their adsorptive power when aged. It has been further observed that precipitated $Fe(OH)_3$, $Cr(OH)_3$, etc., prepared a year ago and kept under water change colour, the deep brown colour of ferric hydroxide becomes deep red and green chromium hydroxide becomes greyish. The aged precipitates do not dissolve in HCl at the ordinary temperature, whilst the freshly precipitated substances dissolve very readily in HCl.

We have shown in previous papers that sols of substances like $As_2S_3$, $Sb_2S_3$, etc., can appreciably adsorb anions like $Cl'$, $SO''_4$, etc., from the added electrolyte due to chemical affinity of these sols for the anions. Now, when these sols are allowed to age, they lose much of their chemical affinity for anions ($Cl'$, $SO''_4$, etc.), and, therefore, their adsorptive power for an ion bearing the same charge as the sol is considerably diminished. Hence, when an aged sol of substances like $As_2S_3$, $Sb_2S_3$, etc., is coagulated by KCl, $BaCl_2$, etc., the adsorption of similarly charged ions is considerably less from these electrolytes and consequently the stabilisation due to this adsorption is smaller for an aged sol than a freshly prepared one, which possesses a greater adsorptive power. In other words, if the charge on the colloidal particles of arsenious sulphide and antimony sulphide is not much decreased on ageing, the aged sols require smaller quantities of KCl, $BaCl_2$, etc., than those required for freshly prepared ones, because the capacity for the adsorption of ions carrying the same charge as the sol is appreciably decreased. Moreover, it is expected that the influence of similarly charged ions on the coagulation of these sols being more prominent with monovalent electrolytes like KCl, NaCl, etc., than bivalent and trivalent electrolytes like $BaCl_2$, $Al(NO_3)_3$, etc., the effect of ageing will be more pronounced with the sols of arsenious sulphide, antimony sulphide, etc., when coagulated by KCl, NaCl, etc., than that observed with either $BaCl_2$ or $Al(NO_3)_3$. Se have already proved that marked adsorption of cations takes place when arsenious sulphide sol is coagulated by an alkaloid or a dyestuff. Hence an aged sol, which has lost its adsorptive power appreciably, cannot adsorb these alkaloids and dyestuffs as markedly as a freshly prepared sol. Consequently, greater amounts of these substances are required to coagulate an aged sol than a freshly prepared one.

Our results on the coagulation of an aged sol of arsenious sulphide prove that as reasoned above, the sol really becomes unstable for KCl, $BaCl_2$ and $Al(NO_3)_3$, and it is more marked for KCl than for either $BaCl_2$ or $Al(NO_3)_3$.

[1] If 'a' is the amount of an electrolyte required to coagulate a freshly prepared sol, and 'b' is the amount required to coagulate the aged sol, then the relative degree of unstability may be measured by the ratio (a − b)/a.

[2] J. Phys. Chem., 29, 435 (1925); Z. Elektrochem., 31, 261 (1925).

Similarly, the sol becomes stable on ageing towards quinine hydrochloride and strychnine hydrochloride, but the sol becomes unstable for crystal violet, a dyestuff which is known to be highly adsorbed by arsenious sulphide sol.[1]

We are of opinion that this discrepancy in the observed results is due to the fact that arsenious sulphide decomposes markedly on standing, giving out $H_2S$ and thionic acids. Colloidal sulphur, as well as a precipitate of sulphur, is also obtained from the oxidation of $H_2S$. We have observed that a considerable amount of sulphur may be extracted by carbon disulphide from an aged sample of arsenious sulphide after its coagulation. Hence an aged sol of arsenious sulphide has changed its constitution, because of the presence of colloidal sulphur and other intermediate products formed from the oxidation of $H_2S$ liberated as a product in the hydrolysis of arsenious sulphide sol. Consequently, it is difficult to find a consistent explanation of all the diverse facts observed in the coagulation of an aged sol of arsenious sulphide, which is far from being in a pure condition.

We shall now present our results on the coagulation of ferric hydroxide sol, and prove that the adsorption of similarly charged ions by a sol is primarily due to the chemical affinity existing between the sol and the similarly charged ions.

The results in Table III have been obtained in the coagulation of an aged sol of ferric hydroxide.

TABLE III

Concentration of the sol = 1.43 grm. $Fe_2S_3$ per litre.
Amount of sol taken each time = 2 c.c.
Volume = 6 c.c.; immediate turbidity is observed.

| Salt | Conc. | Amount necessary for coagulation in c.c. on the 15th Aug., 1925 | Amount necessary for coagulation in c.c. on on the 15th Nov., 1925 |
|---|---|---|---|
| KCl | N/5 | 0.95 | 0.95 |
| $K_2SO_4$ | N/400 | 0.60 | 0.60 |
| $K_2C_2O_4$ | N/400 | 0.65 | 0.65 |
| HCl | N | 1.90 | 1.25 |
| $Al(NO_3)_3$ | N | 1.35 | 0.85 |

The amounts of KCl, $K_2SO_4$ and $K_2C_2O_4$ required to coagulate the sol are the same for an aged as for the freshly prepared sol, whilst the amounts of HCl and $Al(NO_3)_3$ required to coagulate a freshly prepared sol are far greater than the amounts of these electrolytes necessary to coagulate an aged sol. In other words, ferric hydroxide sol shows no change in its stability when coagulated by KCl, $K_2SO_4$ and $K_2C_2O_4$; on the other hand, the sol becomes very unstable on ageing when coagulated by HCl or $Al(NO_3)_3$. This is certainly, because ferric hydroxide sol, which possesses a great chemical affinity for similarly charged $H^{\cdot}$ and $Al^{\cdot\cdot\cdot}$ ions, loses much of its adsorptive power on ageing and consequently an aged sol now requires smaller amounts of HCl and $Al(NO_3)_3$ for coagulation. We have often emphasized that the high

[1] Freundlich: "Kapillarchemie," 576 (1922).

precipitation value of either HCl or $Al(NO_3)_3$ is due to high adsorption of similarly charged $H^{\cdot}$ or $Al^{\cdot\cdot\cdot}$ ions by the sol and its consequent stabilisation.

It has been shown by us that far greater quantities of KCl are necessary to coagulate a sol of ferric hydroxide in presence of HCl, because the sol is appreciably stabilised by the adsorption of $H^{\cdot}$ ions. Hence, it is obvious that this stabilisation of a ferric hydroxide sol by the adsorption of $H^{\cdot}$ ions from HCl will be less marked with an aged sol than with a freshly prepared one.

In Table IV the results are given.

TABLE IV

Concentration of the sol = 1.43 grm. $Fe_2O_3$ per litre.
Amount of sol taken each time = 2 c.c.
Volume = 6 c.c.; Immediate turbidity is observed.

| N/100 HCl added in c.c. | N KCl for complete coagulation in c.c. | |
|---|---|---|
| | On the 18th Aug., 1925 | On the 16th Nov., 1925 |
| 0.1 | 0.85 | 0.80 |
| 0.2 | 1.30 | 1.20 |
| 0.4 | 1.70 | 1.35 |
| 0.6 | 1.95 | 1.30 |
| 0.8 | 1.95 | 1.30 |

These results on the coagulation of ferric hydroxide sol prove conclusively that the sol loses its adsorptive power markedly on ageing, and that therefore the influence of ions bearing the same charge as the sol on its coagulation diminished considerably.

It will be interesting to point out now that we have been able to coagulate by HCl a sol of ferric hydroxide which was prepared by hydrolysing $FeCl_3$ solution with hot water, whilst a sol of aluminium hydroxide obtained by washing a precipitate of $Al(OH)_3$ at the ordinary temperature could not be coagulated by the same acid. The sol dissolves partially in HCl. The sol also could not be coagulated by aluminium nitrate. This shows that the chemical reactivity of ferric hydroxide sol, which is prepared in the hot condition, has been considerably diminished, whilst aluminium hydroxide sol, which is prepared at the ordinary temperature possesses a far greater chemical affinity for $H^{\cdot}$ or $Al^{\cdot\cdot\cdot}$ ions. It has been shown clearly in a separate paper that aluminium hydroxide can be stabilised to a far greater extent than ferric hydroxide sol by a definite amount of HCl. Graham[1] found that a sol of ferric hydroxide prepared by dialysing a solution of ferric acetate in the cold could not be coagulated by acids like HCl, $HNO_3$, $CH_3COOH$, etc., and easily dissolved in these acids. On the other hand, Graham found that a colloid of ferric hydroxide obtained by the method of Péan de St. Gilles[2] by boiling a dilute solution of ferric acetate, coagulated when poured in either HCl or $HNO_3$ and is insoluble in these acids. Hence, it is evident that the adsorptive power and

[1] J. Chem. Soc., 15, 249 (1862).
[2] Compt. rend., 40, 568, 1243 (1855).

chemical reactivity of a substance become less when it is heated; in other words, the phenomenon of 'ageing' which also consists in the decrease of the chemical reactivity of a substance, will be greatly increased when heated.

In a recent paper Gessner[1] has observed that vanadium pentoxide sol becomes unstable when coagulated by either NaCl or $CaCl_2$ on ageing. This is probably due to the formation of larger aggregates of vanadium pentoxide colloid particles on standing.

We are of opinion that a sol, which does not form larger aggregates when kept for some time, and does not decompose on keeping into new constituents as arsenious sulphide sol does, becomes unstable only towards such electrolytes as possess a stabilising influences on the sol when added in small quantities, because the colloid particles lose theor chemical reactivity, and, therefore, the adsorptive power for similarly charged ions is also greatly decreased on ageing.

It must be emphasised here that the sols of cupric ferrocyanide and prussian blue are markedly decomposed on standing, forming the corresponding hydroxides and ferrocyanic acid, which in its turn is decomposed in presence of light into HCN and ferrous hydroxide. Hence, when a sol of prussian blue or cupric ferrocyanide is left to the action of light, considerable decomposition occurs, and, when the stabilising acid $H_4Fe(CN)_6$ is all decomposed, the sol becomes unstable and finally coagulates. Similarly, we have observed that a sol of cadmium sulphide free of $H_2S$ decomposes markedly on standing, thus:—

$$CdS + 2\ H_2O \rightleftharpoons Cd(OH)_2 + H_2S.$$

This decomposition gives out $Cd^{\cdot\cdot}$ ions from slightly soluble $Cd(OH)_2$, which possess a high coagulating power.[2] In a recent paper Piccard and Thomas[3] have shown that a precipitate of CdS can be dissolved completely by passing a current of carbon dioxide through a suspension of the sulphide in cold dilute acid.

We have already observed that the sols of prussian blue and cupric ferrocyanide are decomposed on ageing, forming the corresponding hydroxides and the acid $H_4Fe(CN)_6$, which possess a stabilising effect . Hence it is expected that these sols should become stable on standing for some time; but the sols finally become unstable when kept for a long time because $H_4Fe(CN)_6$ also decomposes into $Fe(OH)_2$ and HCN.

Now, in this connection it will be interesting to note that we have observed that these sols of ferrocyanides are coagulated when exposed to sunlight, because $H_4Fe(CN)_6$ decomposes rapidly in presence of light. We have found that a sol of cadmium sulphide free from $H_2S$ is highly sensitive to light and is coagulated within ten minutes when exposed to sunlight. Similarly, vanadium pentoxide sol has been found to be very sensitive to light. We also have observed that sunlight has a coagulating effect on sols of arsenious sulphide,

---

[1] Kolloidchem. Beihefte, 19, 213 (1923).
[2] Compare Prost: Chem. Centr., 1888, 32.
[3] Helv. Chim. Acta., 6, 1046 (1923).

antimony sulphide, gold and positively charged ferric hydroxide sol. Ganguly and Dhar[1] have also observed that sunlight possesses a coagulating effect on many colloidal solutions.

Several years ago Young and Pingree[2] investigated the influence of light from a carbon arc on many colloidal solutions. They have shown that the sols of arsenious sulphide and ferric hydroxide show a diminution in the electric charge when exposed to light; on the other hand, colloidal solutions of mastic and chlorophyll showed a marked increase of electric charge when exposed to light. Dreyer and Hanssen[3] have observed that coagulation sets in different samples of albumen in presence of ultraviolet light. Similarly, Bobie[4] has found that fresh egg-white and ox-serum are coagulated into feathery flakes by ultraviolet light, and some chemical change similar to those on heating takes place.

We are of the opinion that the marked influence of light on the coagulation of a sol is due in most cases to the decomposition of colloidal solutions by light, yielding an electrolyte, which has a marked coagulating effect. On the other hand, as shown by Young and Pingree the increase in electric charge on a mastic sol when exposed to light is due to the greater hydrolysis of this sol in presence of light, yielding a complex organic acid, which has a stabilising influence.

## Summary

1. Arsenious sulphide sol becomes unstable on ageing when coagulated by KCl, $BaCl_2$, $Al(NO_3)_3$, aniline hydrochloride, and crystal violet. The same sol becomes stable on ageing when coagulated by quinine hydrochloride and strychnine hydrochloride.

2. The stability of ferric hydroxide sol does not change appreciably on ageing when coagulated by KCl, $K_2SO_4$, and $K_2C_2O_4$, whilst it becomes unstable on ageing when coagulated by HCl or $Al(NO_3)_3$.

3. It has been proved that the stabilisation of ferric hydroxide sol by HCl, will be less marked with an aged sol than with a freshly prepared one, because the chemical affinity and adsorptive power for hydrogen ions become less on ageing.

4. A sol, which does not form larger aggregates and does not decompose into new constituents on keeping will become unstable only towards such electrolytes as possess a stabilising influence on the sol when added in small quantities, because the colloid particles lose their chemical reactivity and, therefore, their adsorptive power for similarly charged ions is also decreased on ageing.

---

[1] Kolloid-Z., **31**, 16 (1922).
[2] J. Phys. Chem., **17**, 668 (1913).
[3] Compt. rend., **145**, 234 (1907).
[4] Science, **37**, 24 (1913).

5. The marked influence of light on the coagulation of sols is in most cases due to the decomposition of the sols by light, yielding an electrolyte, which exerts a high coagulating influence.

5. The coagulation of sols of prussian blue, cupric ferrocyanide, arsenious sulphide, etc., by light is very likely due to the decomposition of stabilising electrolytes under the influence of light.

*Chemical Laboratory,*
*University of Allahabad,*
*Allahabad, (India).*

# NEW BOOKS

**A Manual of Radioactivity.** *By George Hevesy and Fritz Paneth. Translated by R. W. Lawson. 24 × 16 cm, pp. xix + 252. New York: Oxford University Press, American Branch,* 1926. *Price:* $5.00. The chapters are entitled: introduction; the alpha rays; the beta rays; the gamma rays; secondary rays; recoil rays; constitution of the atom and radioactive rays: applications of the theory of disintegration; mathematical treatment of disintegration processes; the transformation series of uranium, actinium and thorium; determination of very short half-value periods—relation between half-value period and velocity of the rays emitted; chemical properties of the radio-elements—isotopy; isotopy and the periodic classification—alteration of chemical characteristics within a transformation series—the displacement laws; the chemical behavior of extremely small quantities of a substance; application of the radio-elements as indicators in physical and chemical investigations; isotopy and the displacement laws in the light of atomic constitutions—the current representation of the periodic classification; electronic and nuclear properties of the atom; isotopy as a general property of matter; separation of isotopes; mixed elements and pure elements—combining weights and atomic weights; disruption of the chemical elements; structure of the atomic nucleus: the preparation of radio-substances; the properties of the individual radio-elements; effects of the rays from radium: radioactivity in geology and in geophysics; the historical development of the science of radioactivity.

"The production of secondary beta rays appears to be connected with the presence of a gas layer. For example, with zinc that has been freed from gas by distillation in a high vacuum this effect is absent. It returns, however, when air is admitted to the surface of the zinc," p. 58.

"As a result of recent investigations with very pure helium, the possibility of the existence of an anomalous state has been discovered, and in this state the atom can persist permanently, in contrast to the short-lived transitory states of electrons not in their normal orbit. Helium atoms can be converted into this "excited" state by bombardment with electrons of 20 volts "velocity." A reversion from this metastable state into the normal state can be brought about by chemical influences, such as the presence of traces of hydrogen and the like. From the point of view of the theory of the atom referred to above, this metastable state is identical with one of the stationary states, the existence of which is shown by the spectrum of helium. Here both electrons move in the same plane—the inner one in a one-quantum orbit, and the outer in a two-quantum orbit, or more precisely, in a 21-orbit," p. 69.

"Whereas the classical theory required a simple relation to exist between the frequency of the electron in the atom and that of a spectral line, we find that, according to the quantum theory, no such direct relation exists between these two magnitudes, for the frequency of a spectral line is determined by the difference in the energy content of the atom in the respective stationary states (*e. g.* between state 3 and state 2). But it is an interesting fact that, in spite of this, there exists a deep-seated *correspondence* between the rays emitted during the orbital transitions and the motion of the electron in the atom. This correspondence enables us to draw certain conclusions about the transitions from one stationary orbit to another and about the radiation sent out during these transitions. These conclusions far transcend the results directly obtainable from the two hypotheses above-mentioned, and amongst other things, they have led to the views already referred to about the structure of the higher atoms," p. 72.

"One of the most striking differences between Röntgen and optical rays lies in the fact that no absorption lines occur in Röntgen radiation. If, for instance, we pass white light through sodium vapour, the characteristic D-line of sodium is strongly absorbed by the vapour. With Röntgen lines there is no analogy to this behaviour; the $K\alpha$-line of an element is no more strongly absorbed by a layer of the same element than are the lines of

slightly greater or lesser frequency. Not until much shorter wavelengths have been reached do we find a sudden increase in the absorption, and simultaneously we find that the *Ka*-line is now emitted by the layer. In optics, fluorescent substances show a similar behaviour, in that they convert light of shorter into light of longer wavelengths, and for this reason the characteristic Röntgen radiation of the elements is also sometimes called "fluorescent radiation."

"On the basis of the current model of the atom, we can readily understand the difference in behaviour. In order to produce a Röntgen absorption line, we must remove an electron from one of the inner orbits of the atom to one more remotely situated; but all the inner electron groups are completely occupied by electrons, and only when the energy of the incident waves is sufficient to remove the electron to the periphery of the atom is it possible to have absorption. In contrast to optical absorption spectra, for the production of which outlying electrons only need to be slightly raised in level, we require a much shorter wavelength than that corresponding to the emission line, in the case of Röntgen rays, in order to supply the necessary energy. But once an electron has been removed from the innermost orbit to beyond the limits of the atom, in the manner described above, it is then possible for an electron from the successive second, third, etc., orbits to spring into the resulting gaps, and the *Ka*-, *Kb*-, etc., emission lines then make their appearance," p. 76.

"But apart from the influence of the nucleus of the atom penetrated, the $\alpha$-particles also suffer scattering by the extra-nuclear electrons in the atom. Thus, during their passage through the atoms, the individual $\alpha$-particles encounter a somewhat varying number and arrangement of electrons, and their respective losses in energy are not all the same, so that this manifests itself as a scattering of the particles. The scattering produced by the electrons is much smaller than that due to the nuclei, but still, the value found experimentally is appreciably in excess of that to be expected theoretically," p. 78.

"When Röntgen rays are scattered by a light substance such as graphite, they can be divided into two parts, one of which possesses the same wavelength as the primary rays, whereas the other has a somewhat greater wavelength. The scattering without change in wavelength is produced by a fairly large number of electrons, whilst that accompanied by a change in wavelength is caused by a single electron. In the latter case the scattering electron suffers recoil, and thereby takes up a part of the energy quantum of the Röntgen ray; thus the energy quantum of the scattered ray must be smaller, and the wavelength of the ray correspondingly longer than that of the primary ray. If the scattering is caused by an appreciable number of electrons, the total mass of which is relatively large, the quantity of energy removed from the Röntgen rays by recoil is insignificant, and the wavelength of the scattered rays is identical with that of the primary rays.

"The main features of the absorption and scattering of $\gamma$-radiation may be described in the following manner. When $\gamma$-rays traverse matter, the characteristic radiations of the absorbing medium are excited. The atomic absorption coefficient of the fluorescent radiation varies as the cube of the wavelength of the incident radiation, and as the fourth power of the atomic number of the absorber. The pure atomic absorption coefficient of scattering is proportional to the atomic number of the absorber. For light elements, the absorption is almost wholly due to scattering," p. 79.

"Only a few of the radioactive elements, *e. g.* thorium, uranium, and radium, can be obtained in weighable quantities. The determination of the properties of these elements is carried out by means of the usual chemical methods, for the radioactive nature of the element does not affect its chemical properties, and during the time of its stability an atom of radium, to take one example, is quite analogous to the atoms of the typical metals of the alkaline earths. From the moment of its disintegration, however, we are no longer dealing with an atom of radium, but with an atom of a new element—the emanation produced from radium—which, so long as it lasts, behaves entirely like the atoms of the other rare and inert gases.

"The large majority of the radio-elements can only be obtained in unweighable quantities, and in many cases the amounts of them available are vanishingly small. The determin-

ation of the chemical properties of these elements is rendered possible by the application of two facts which are of fundamental importance in radiochemistry. (*a*) It has been observed that the behaviour of the elements in extreme dilution is essentially the same as that shown at concentrations usually employed. (*b*) It has been established, and this involves a principle quite new in chemistry, that a chemical element can occur in different types, the chemical properties of which are identical, in spite of differences in atomic weight that are often considerable. Furthermore, many of the radioactive substances have been found to be none other than radioactive types of chemical elements that have been known for a long time. Such types of one and the same element are called *isotopes*," p. 107.

"An interchange of the atoms and molecules within a homogeneous substance can be readily followed by means of radioactive indicators. The simplest example of such a kinetic problem is presented by the addition of an activated $Pb(NO_3)_2$ solution to an inactive solution of $PbCl_2$ of equivalent strength. By crystallising from this mixture a sample of lead chloride, we can determine whether it only contains those lead atoms that were combined with chlorine before the mixing, or whether it also contains lead atoms which were originally combined in the form of nitrate. As we should expect, the result of such a determination demonstrates that the lead atoms of the lead chloride were derived in equal quantities from the two initial solutions. On the other hand, if, say, activated lead nitrate and inactive tetraphenyl-lead, or another compound in which the lead atom is linked with carbon in a non-ionisable form, be simultaneously dissolved and then separated by crystallisation, we are unable to detect any interchange of the lead atoms between the lead nitrate and the organic compound of lead.

"The interchange between the solid and liquid phases, as between metal and ion, or between a salt and its saturated solution, is more difficult to picture, and for this reason more important to investigate than the positional interchange in solutions. These processes can be readily traced in their dependence on time by means of radioactive types of lead and bismuth, and the observed behaviour can be made the basis of a method of measuring the absolute surface of powders, which is of importance in many experiments on adsorption. Even when we are only dealing with the relative comparison of surfaces, radio-elements can be applied with advantage. By means of radioactive indicators, we can study the simple, and, from the theoretical view-point, the very important case, which Maxwell termed "self-diffusion," and which he frequently carried out in the form of a mental experiment. We only need to measure the velocity of diffusion of molten or solid active lead in inactive molten or solid lead, in order to obtain the constant of self-diffusion of lead," p. 123.

"In the modern theory of the atom, a distinction is drawn between the nucleus and the electrons. This brings us face to face with the question as to which physical and chemical properties are primarily determined by the nucleus and by the electrons respectively. As already mentioned, the emission of spectral lines is brought about by the return of electrons into their original orbit, after they have been removed from their normal orbit to a distance by the action of an external agency, such as the absorption of radiation, electron collision, etc. In the chemical reactions of the atoms, also, it is the electrons situated in the electron groups, particularly the outer ones, that are involved. Thus in the simplest case of ionisation, positive ions are formed when electrons leave the atom, and negative ones when the atom embraces additional electrons. It can be readily seen, by means of a simple consideration, that the gravitational forces within the atom are negligible as compared with those of an electrostatic nature. For example, the electrostatic attraction between the electron and the nucleus in the hydrogen atom is $10^{41}$ times greater than the gravitational attraction. The extensive independence of the chemical and spectroscopic properties of the atom, previously discussed, on the mass of the atom, and their exceedingly similarity in the case of isotopes, follows directly from the theory of the atom. They are called *electronic properties* because of their dependence on the number and arrangement of the electrons in the extra-nuclear system," p. 130.

"In chemical reactions it thus appears that only the outside electrons of an atom play a part, whereas in the excitation of characteristic Röntgen rays the innermost electrons also are involved. But in all these processes, the nucleus is not in the least influenced; and

as long as it remains intact, the nature of the element is not altered, since changes in the electron configuration are always reversible. In this we have an explanation of the fundamental law of chemistry, according to which chemical elements can be neither produced *nor destroyed*. Radioactive transformations, however, alter the nucleus—for the ejected $\alpha$- and $\beta$-particles are constituents of the nucleus—and we perceive a corresponding transmutation of elements in operation as a consequence of radioactive processes. We are only able to call forth this transformation artificially when we make an effective attack on the nucleus. In recent years, such experiments have actually met with success," p. 131.

"When we speak of a "chemical element" in general, it is not clear whether we are dealing with a pure element, or with a mixed element, as in the case of, say, mercury and chlorine. The mixed elements mentioned are composed of isotopes, and these cannot be separated by the usual chemical methods of separation. But, as we have seen in the previous chapter, they can be more or less completely separated by various physical processes. Consequently, we can no longer define a chemical element as a substance which cannot by any means be broken up into simpler substances. The following may be regarded as a convenient "practical definition" (1): *A chemical element is a substance which cannot be resolved into simpler substances by any chemical process.* For all practical purposes the chemical inseparability of isotopes retains its validity, and this is the sole reason why chemistry is obliged to adhere to the old elements as the constituent bricks of its chemical system. Moreover, for practical and didactic purposes the above definition is also sufficiently precise, since all the successful methods of separating isotopes are typically mechanical ones, inasmuch as in them we always make use of the differences in mass and never of the differences in chemical properties. When substances enter into no chemical reactions whatsoever, as in the case of the rare gases, it is of course not possible to apply the criterion of chemical inseparability, and we must test the unitary nature of the nuclear charge (cf. the definition above) by other methods such as spectroscopy. But it was the impossibility of chemically resolving elements like gold, mercury, etc., and not the exceptional cases of the rare gases that led to the formulation of the chemical conception of an element. Even to-day, exactly as at the time of its conception by Boyle, its value lies in the fact that "corpuscles of a compound nature may *in* all the *wonted examples of chymists* pass for elementary."

"A more exact and more "theoretical definition," even though it is more removed from the chemical meaning of the conception of an element, can be given by having recourse to the ideas of atomic theory. We may say quite rigorously:

"*A chemical element is a substance, all of the atoms of which have the same nuclear charge.* Examples: hydrogen (nuclear charge 1), chlorine (nuclear charge 17), lead from an arbitrary mineral (nuclear charge 82), lead from disintegrated radium emanation (nuclear charge 82)," p. 1431.

"The mechanism of the action of the rays from radium on the silver bromide of the photographic plate is certainly akin to that of light, and the same theories (quantum theory, colloido-chemical ideas, etc.) must be applied here for an explanation of the effects. In this connection, it is probable that the $\gamma$-rays do not act directly, but that here the same peculiar fluorescence of the silver or bromine atoms manifests itself, as makes the plates so particularly sensitive to Röntgen rays. With $\alpha$-rays it has been established that every silver halide nucleus struck by a single $\alpha$-particle becomes blackened after development, whereas on the average 6 to 8 $\beta$-particles are necessary to make a silver halide capable of development.

"At those places on the gelatine film that are most strongly bombarded by $\alpha$-particles, indentations occur; the swelling capacity of the gelatine is reduced. Moreover, marked solarisation effects are observed on those parts of the plate that have been subjected to the action of strong sources of $\alpha$-rays. After a certain duration and intensity of the action has been exceeded, the plates are found to be blackened even before they have been developed.

"Bunsen and Roscoe's law of blackening holds not only for the $\beta$- and $\gamma$-rays, but also for the $\alpha$-rays," p. 191.

"The rays from radium, themselves invisible, possess the striking ability of being able to excite substances to emit visible light. This subject has already been mentioned briefly on p. 1, in the case of so-called *autoluminescence*. Thus, when we subject a barium salt containing radium to fractional crystallisation, the mixed barium and radium salt becomes self-luminous in the dark, when the concentration of radium in the mixture has reached a certain value. The colour depends on the proportion of radium relative to barium present in the mixture, and can, in fact, serve for the approximate estimation of the radium content of the preparation. When a 100% preparation of radium chloride is fused, and thus completely freed from water, it emits a bluish light which is so intense that it can be seen even in bright daylight. Investigations of the spectrum of this light have shown that it consists of the band spectrum of nitrogen. Correspondingly, we obtain the helium lines in an atmosphere of helium. The phenomenon of self-luminescence has also been observed with strong solutions of radium salts, and with strong preparations of polonium, ionium, mesothorium and actinium," p. 193.

"Most fluorescing substances become coloured under lengthy exposure to the rays; simultaneously the fluorescence diminishes, and "*fatigue*" occurs. This fact is of practical and theoretical interest. By heating only slightly above room temperature, or by illumination with light, the colouring can frequently be annulled, and at the same time the ability to fluoresce restored. This decoloration by means of heat or light is generally accompanied by luminescence and the emission of electrons (thermo-luminescence and photo-electric effect), as, for instance, with kunzite, the original rose-colour of which is changed to green by the rays, or with fluorspar, which is transformed from a green to a blue colour under the action of the rays. New vessels and tubes of glass luminesce much more strongly under the action of radioactive solutions or gases than those that have been in use for a long time. This is a striking illustration of the fact that glass fatigues or loses its ability to fluoresce under the action of the rays. Glass apparatus that has been long subject to the rays always has a brown or violet colour, and also shows the phenomenon of thermo-luminescence very clearly (in the well-known characteristic green glow of Röntgen tubes). Quartz that has assumed a violet colour also shows the same luminescence during its decoloration by means of heat.

"A unitary theoretical explanation of the phenomena described is possible on the basis of the electron theory. The $\beta$-rays, *i. e.*, free electrons, are the most effective in the production of the majority of colorations; moreover, the $\gamma$-rays also always liberate secondary electrons. The incident electrons, or indirectly the $\gamma$-rays, discharge the positive metal ions of the minerals and glasses, which latter are constituted like salts, or else they bring individual atoms composing the crystal into anomalous quantum states. In these cases, where the electrons have the opportunity of establishing themselves in the crystal edifice, these disturbances may persist under certain circumstances for considerable periods, in contrast to the disturbances, say, in gaseous media (reasonance disturbances), which always have an exceedingly short life. The return from the metal-ionic or from the anomalous ionic state to the normal state, which is hastened by heating, may be associated with the emission of light (thermo-luminescence) and simultaneous decoloration, and the former process may also be accompanied by the liberation of electrons (photo-electric effect). The colour assumed by salts under the action of the rays has often been found to agree with that of their colloidal liquid solutions (sols). This suggests that in these cases, *e. g.* when sodium chloride is irradiated, the colour is due to the separation of the metal; thus borax beads containing lithium become brown, with sodium violet, with potassium blue, and with rubidium greenish-blue, just like the corresponding sols. Salt that was originally colourless, and has become yellowish-brown under the action of the radiation from radium, and subsequently violet by heating at 200°C., behaves like the violet salt of natural occurrence. Colour changes and thermo-luminescence do not always run a parallel course, as is shown by the case of glass that has been coloured violet. This may lose its thermo-luminescence completely at 200°C., but it only loses its colour above 400°C. It is only the brown coloration of glasses that disappears at the low temperatures sufficient for the manifestation of thermo-luminescence," p. 195.

"Great strides have been made in the theoretical treatment of photo-chemical processes during recent years. By using thermodynamic principles as a basis, the tendency of a few years ago was to introduce a strict differentiation between those processes which take place as a result of the absorption of energy from the light, and those in which the light accelerates the action in a catalytic fashion. But it has now been recognized that reactions which run a quite similar course must often for some reason or other be treated separately. The mechanism of the processes was first revealed by considering them from the atomistic viewpoint, by means of Einstein's "photo-chemical law of equivalence." If we divide the absorbed energy of radiation by the value of Planck's element of energy corresponding to the wavelength used, then by the equivalence law we must obtain the number of the elementary processes involved in the experiment. In point of fact, it was found, *e. g.*, when oxygen is subjected to ultraviolet radiation, that the number of elementary processes calculated in this manner is of the same order of magnitude as the number of molecules of ozone formed. To be more exact, twice as many ozone molecules are formed, and hence we may assume that in every elementary process one $O_3$ molecule is split up, and the resulting $2O$ combine with two additional $O_3$ molecules to form $2O_3$.

"The idea suggests itself of interpreting the elementary process as the separation of an electron from the atom, or as the elevation of an electron to a higher quantum orbit, and in this way to establish a relation between the amount transformed and the number of the electrons taking part in the reaction. This relation was clearly revealed in an electro-chemical investigation akin to the photo-chemical one described. In this work we recognise in a particularly striking manner, the close connection with the reactions produced by the rays from radium. The formation of ozone from oxygen under the influence of Lenard rays was here also investigated. Cathode rays were passed through an aluminium window into a vessel containing oxygen, and the amount of ozone formed was determined; moreover, by measuring the saturation current, it was also possible to determine the total number of ions produced in the reaction vessel. Whereas the number of primary electrons shot into the vessel was one hundred to one thousand times smaller than the number of ozone molecules formed, a good agreement was found to exist between the number of the ozone molecules and the number of secondary pairs of ions produced in the reaction vessel. A single electron can give rise to many thousands of ions when it ionises by collision, and it is obviously these secondary ions which call forth an equally large number of elementary chemical processes in accordance with the photochemical law of equivalence. The fact that the number of ozone molecules was always found to be somewhat larger than the number of pa rs of ions speaks in favour of the idea mentioned above, according to which even those electrons that are not separated from the atom but only slightly raised to a higher quantum level, and which therefore do not contribute to the saturation current, are nevertheless to be taken into account for the law of equivalence," p. 204.

"This equivalence between the number of molecules entering into chemical reaction and the total number of ions formed by the $\alpha$-rays has been proved not only in the formation of ozone, but also in the formation of water, ammonia and hydrobromic acid from the constituent elements, and also in the decomposition of hydrochloric acid, ammonia, CO and $CO_2$. Moreover, it has also been established in liquid systems, *e. g.* in the decomposition of water, liquid hydrobromic acid, and in an acid aqueous solution of potassium iodide. In accordance with this equivalence, it has been possible to show that a definite chemical transformation is associated with the presence of a definite number of ions, in a similar manner as in Faraday's law. In contrast to Faraday's law, however, these ions must not participate in the transport of current, and hence in this case we generally only speak of an *'iono-chemical equivalence,'* " p. 206.

"In this section we shall discuss individual effects produced by the rays from radium, in so far as they stand in particularly close relation to questions in colloidal chemistry. It is of course not possible to delineate a sharp boundary with respect to the topics hitherto dealt with. Thus it is known that the photographic process, of which we have previously spoken, must also be considered from the colloido-chemical viewpoint, and the colorations dealt with on p. 196 likewise present certain colloido-chemical problems for solution.

"The study of the action of the rays from radium on the stability of colloidal solutions belongs to colloido-chemical investigations in the narrower sense. In this connection, the following interesting result has been established, namely, that positive colloids are precipitated, whereas negative ones survive the radiation. The experimental arrangement was so chosen that almost exclusively $\beta$-rays were involved in the action, and since these carry negative charges, we can understand why they deposit the positive colloids. Thus, if we add to a colloidal solution of iron hydroxide a quantity of, say, sodium acetate solution, just insufficient to produce a change, we can then obtain turbidity of the colloid by means of radium rays, whereas a control sample that has not been subject to radiation will remain unchanged. With a sol of cerium hydroxide it is not even necessary to sensitize it previously by means of an electrolyte; by subjecting the sol to radiation it is transformed into a coherent gel even after a period of 24 hours, whereas it remains unchanged for years when not submitted to the action of radiation.

"None of the electro-negative colloids gold, molybdenum blue (an oxide of molybdenum containing water), and vanadium pentoxide, the last of which tends to form a gel just like cerium hydroxide, were influenced when subject to radiation. Albumin, which also forms electro-negative colloidal solutions, is deposited in flocculent masses, but it is probable that this is not simply a phenomenon of discharge, but rather that the albumin first loses its original nature," p. 208.

"The velocities of radioactive decay are independent of all external conditions, and constitute natural constants characteristic of the disintegration process concerned. For this reason they can be utilised for the measurement of time. Since they supply us with the functional relation between the amount of the substance transformed and the time, it is clear that the velocity of decay enables us to calculate quantity when the former is known. Thus, we can readily recognise the lapse of an hour without the aid of a clock, if we notice that the activity (measured, say, by a method of steady deflection) of a preparation of ThC falls to 49% of its initial value during this time. Such methods for the measurement of time have actually attained great importance in geology," p. 213.

"From amongst the minerals the ages of which have been determined by the method described, a uraninite of Carboniferous age has been found to be one of the youngest (320 millions of years). This number gives us the age of the Carboniferous System, if we make what appears to be quite a plausible assumption, namely, that the uraninite concerned is a primary mineral, and has not gained access into the formation in the course of a subsequent epoch, in which case it would be secondary. The oldest mineral hitherto investigated was a zircon from Mozambique, the age of which was found to be 1500 millions of years," p. 215.

"The aurora is associated with the periodic variations in the activity of sun spots, and encircles the magnetic north and south poles of the earth. These facts suggest that we can interpret it as being due to electrically charged corpuscular rays emitted by the sun, which, when they arrive in the neighbourhood of the earth, are deflected by its magnetic field. Those corpuscular rays are presumably of radioactive origin. Groups of rays of different velocity have been detected in the aurora, but it is still an open question whether they are high-speed electrons or positive atomic rays of moderate velocity," p. 223.

*Wilder D. Bancroft*

**Chemistry of the Proteins and its Economic Applications.** *By Dorothy Jordan Lloyd. 20 × 15 cm; pp. xii + 279. Philadelphia: P. Blakiston's Son and Co., 1926. Price: $3.00.*
In the introduction Gowland Hopkins says: "The subject falls, of course, naturally, into two main divisions: the constitutional chemistry of proteins, and their physical chemistry. In a formal sense these are dealt with separately in this book, but the bearing of one upon the other is kept clearly in view, and the somewhat unhappy choice which these two aspects of chemical knowledge are apt to suffer is not to be found here. Few, I think, could have dealt with both aspects with the grasp and mastery of essentials which the author displays.

. . . I am so assured of the merits of Dr. Jordan Lloyd's work, that I take great pride in being allowed to write this foreword."

The chapters are entitled: the nature and constitution of the proteins; the methods of protein analysis; the different classes of proteins; the identification of proteins and the structure of the protein molecule; the proteolytic enzymes and the linkages in the protein molecule; the chemistry of protein foods; the problems of food preservatives; the combination of proteins with acids and alkalies; the properties of protein solutions; the absorption and loss of water by gels and tissues; the influence of salts on protein solutions; the theory of protein solutions; denaturation and coagulation; irreversible protein gels; the industrial uses of the proteins.

Some quotations will give an idea of the value of this book to physical chemists.

"A full analysis of a protein and an estimation of its content of amino acids can be used to obtain an idea of the molecular weight of the original protein. Calculations of molecular weights on amino acid content are based on three assumptions: firstly, that the amino acid used for the basis of the calculation was originally present in the protein, and is not merely in the mass of hydrolyzed material as the result of an admixture with an unrecognised impurity; secondly that the determination of the amino acid is an accurate estimate of the original amount of the precursor present in the protein; and finally, that the result obtained is to be regarded as a minimum value only, and subject to multiplication by a factor $n$, where $n$ may be any integer.

"In this way the writer (1920) calculated the minimum molecular weight of gelatine to be of the order of 10,000. Dakin's estimation of the histidine present was used as the foundation of the calculation. Loeb (1922) by a similar calculation based on Dakin's figure for phenylalanine obtained 11,800. A molecular weight obtained by a similar calculation is that of haemoglobin calculated on the assumption that the molecule contains one atom of iron. The value obtained is 16000. Cohn, Hendry and Prentiss (1925) have gathered together all the available evidence on the determination of special groups or atoms in certain proteins, and have used these figures, together with the combining weights for acids and alkalis, obtained by titration, and certain physico-chemical measurements, such as osmotic pressure determinations, for estimating the molecular weights of proteins. Their paper gives a full review of the literature," p. 31.

"The origin of the proteins in milk and the problem of their identity has been further studied by Dudley and Woodman (1915, 1918), and by Woodman (1921). Their work was based on an observation of Dakin (1912-13) that in strongly alkaline solutions the specific rotation of a protein drops slowly from its original value to a much lower one, at which it remains stationary. Dakin called this change "racemisation." His work will be described in detail later. Woodman (1921) found that every protein has a definite rate of racemisation under fixed conditions which can be followed by plotting the curve of specific rotation against time, and therefore that the racemisation curves could be used to test the identity of proteins," p. 62.

"To return to the problem of the linkages in the protein molecule—the existence of the peptide link has been recognised since the time of Fischer, and the strength of the link has now been shown by Levene and his co-workers to depend on the ionisation constants of the amino and carboxylic groups which take part in its formation. The existence of anhydride rings in the protein molecule and the possibility of the formation of internal salts has also long been recognised; collagen, for instance, has for many years been recognised as an anhydride of gelatin. It seems very probable that the strength of the anhydride ring (diketopiperazine) also will be found to depend on the nature of the groups which form it. Many peptide linkages resist the action of trypsin, and possibly many anhydrides resist the action of pepsin—the keratins, for instance, are remarkable for the power of resisting enzymes, yet hydrolyse to amino acid mixtures under the action, both of acids and alkalis. Boiling in water seems an efficient method of opening anhydride rings. After boiling with water, collagen is hydrolysed by trypsin. A few of the plant globulins, when prepared by dialysis, are remarkably resistant to the action of the digestive enzymes. Waterman and Breeze Jones (1921) showed that the globulins (stizolobin) from both the Chinese and the Georgia velvet bean, when prepared by dialysis were only digested *in vitro* to the extent of about 30 percent by pepsin followed by trypsin. When the dialysed proteins were boiled,

or when the globulins were prepared by a coagulation method, the digestibility rose to nearly 60 percent and it seems possible therefore that both these processes lead to an opening up of anhydride rings," p. 75.

"Pellagra is a disease which only appears among the poorest classes in tropical countries, and is nearly always associated with a meagre diet of maize. It is characterized by emaciation, by a painful rash on the exposed parts of the body, by general oedema, and by nervous symptoms which may end in definite insanity. It can be cured, at any rate in its early stages, by giving fresh animal protein, though in its later stages the damage inflicted on the body seems to be permanent. Half the protein of maize consists of zein, and the whole maize contains very little tryptophane and lysine, both of which are present in fair quantity in all animal proteins. The deduction seems justifiable, therefore, that these two protein units are essential in the diet of man and that their absence leads to ill-health. During the recent war, particularly in Austria, under acute conditions of underfeeding which prevailed there, many people developed a condition known as war-oedema. These cases disappeared rapidly after the arrival of the American Relief Commission, and the disease was undoubtedly due more to serious deficiencies in the nature of the war diet than to actual shortage in quantity. Chick and Hume (1920) give an account of the experimental results obtained by feeding monkeys for a prolonged period on diets in which the proteins supply was a mixture of zein and maize glutelin. This mixture contains only traces of tryptophane and lysine. In spite of the diet being adequate in all other respects, the monkeys lost weight rapidly and developed erythematous rashes on the face and parts of the body, and, in one case, marked oedema. The loss in weight ceased in two cases immediately tryptophane was added to the diet, and both the oedema and the face rash diminished, after the addition of tryptophane and lysine, in the form of commercial casein. Restoration of weight, however, only took place after the return to a normal mixed diet," p. 86.

"Many of the vegetable proteins become more digestible after cooking, and the same is true of the ovalbumin of egg white. Ovalbumin is a protein constitutionally closely applied to lactalbumin, yet in the raw state it has practically no food value. Mendel and Lewis (1913-14) have shown that in man, after a standard meal containing protein in the form of meat, there is a rise in the hourly secretion of nitrogen in the urine. This rise is due to the amino acids from the hydrolysed protein having been absorbed by the body, with the subsequent deamination in the liver. After a meal containing raw egg-white instead of meat, the nitrogen excretion only rises slightly. Raw egg-white is only digested to a very small extent, and therefore is evacuated in an almost unchanged condition. Cooked egg-white, however, is digested and absorbed by the body and its nitrogen starts to appear almost immediately in the urine," p. 92.

"It therefore follows that, in calculating a scientific basis for diet, the "percentage of protein" is a value which has very little meaning. Every protein has its own feeding value. This is well shown in the curves taken from Osborne and Mendel's paper which shows the growth of young rats obtained on a diet containing 4.5 percent of proteins. At this low concentration lactalbumin, with its high content of tryptophane, cystine and lysine groupings, promotes good growth, and so does casein when supplemented by cystine, but neither casein alone, nor any one of the three vegetable globulins, is able to promote growth, glycinin giving especially poor results. It is important to notice that not only is there a necessary minimum value for protein in the diet, but also that a certain maximum must not be exceeded. With dogs and cats a heavy protein meal is dealt with by vomiting; with other animals, like rats, which do not vomit so easily, if at all, the ingestion of too much protein is followed by serious symptoms," p. 95.

"The balance of proteins in the diet, especially of the young growing animal, is obviously of the greatest importance, both from the point of view of health and of economy. Analysis and feeding experiments have shown that the best amino acid balance for the young animal is found in the proteins of milk, which is thus proved to be a social necessity. Among the cereals, the best amino acid balance is found in the proteins of wheat. Economic necessity demands that in general the best proteins should be reserved for human consumption. It is essential, therefore, in order to obtain the best results in stock feeding from the

proteins available on the market after the demands of man have been satisfied, that a very careful study of these should be undertaken so that any deficiencies in any one type of product could be remedied or balanced by suitable mixing with other material. Many difficulties, both major and minor, in raising young animals satisfactorily will, undoubtedly, be found due to unsatisfactory diets. Hartwell (1925) for instance, records that young rats, on a diet in which slow growth is being achieved, frequently suffer from loss of fur. She concludes that the quality or quantity (or both) of the dietary protein is the factor responsible and finds that the cure lies in adding more or better protein. There is no doubt that much work still remains to be done on the scientific feeding of stock. For instance, it was long thought impossible to raise chickens intensively in captivity; but Plimmer and Rosedale (1922) have shown that if a diet containing the essential vitamins and a supply of "good" protein rich in tryptophane is used, the chickens grow rapidly and healthily, and become mature even sooner than those which have been brought up running on a free range according to the usual method," p. 96.

"An interesting case where bacterial contamination can lead to serious economic waste occurs in the condition of "rope" in bread. Two severe epidemics of this occurred during the late war, and have been reported on in a paper by the writer, Clarke and McCrea (1921). Rope is a condition in which the bread becomes discoloured, sticky, and develops a strong and most unpleasant smell. Its occurrence during the war was due to the use of a quantity of inferior wheat with badly-filled grains that could not be cleaned properly by the scourers of the milling machines. The resulting flour was therefore highly infected with various types of the common saprophytic organism, B. *mesentericus*. As a war regulation insisted that all bread must be kept for twenty-four hours before sale, this heavy infection resulted in a number of instances during the summer months of the bread putrefying under the action of the bacteria. This putrefaction was accompanied in all cases by a breakdown of the wheat protein, and in a few cases only by decomposition of the starch. The bread, although quite harmless, became useless as food owing to the unpleasant physical characteristics which it developed," p. 106.

"The limiting reaction for the growth of nearly all bacteria is pH 5.0-5.5, and for most moulds is about 3.5-3.0. By raising the acidity, therefore, it is possible to inhibit autolysis and the growth of micro-organisms. This is the principle of pickling. The reaction of a pickling liquid may be as high as pH 2.8. It will be seen later that all tissues swell in acid solutions, and to prevent this salt is always added to a pickling liquor. Acetic acid is always used for pickling, and to be effective must be present to the extent of 15 percent. It is usually added as vinegar. Pickling was one of the early methods of preserving food for long journeys, especially in the days of the sailing ship. It has the advantage of requiring no accessory apparatus. It can be used to preserve meat, fish and vegetables. There is still a large trade in pickled herrings between the Scottish ports and Central Europe. Meat and vegetables are not usually pickled nowadays for the sake of storage and transport, but a number of methods of pickling in which spices are added are in common use for preparing special table delicacies, such as the Bismarck herring, soused mackerel, pickled cabbage, etc., etc. Pickles of this type are cooked before pickling. The pickled pork and beef of a former era were pickled before cooking," p. 109.

"A four percent concentration of salt in the tissues noticeably retards autolysis and bacterial growth. A twenty percent concentration inhibits both to such an extent that the food can be preserved for long periods at ordinary temperatures. Salting is sometimes followed by smoking as a method of cure," p. 112.

"Preservation of food by drying it by evaporation in the sunlight is the most obvious and the most primitive method. It is not a very much further step to preserving it by drying in the smoke of a wood fire. When fish or meat is cured by smoking, partial dehydration takes place, but in addition the surface of the tissue undergoing treatment becomes impregnated with phenolic substances present in the smoke. These substances inhibit the growth of micro-organisms, and smoked food therefore is preserved both by the drying action and by chemical treatment of the surface. Bacon, Scotch kippers, and Finnan

haddocks are examples of foods where smoking is a part of the method of cure. Smoked foods have only a limited resistance to contaminating bacteria or moulds. Vegetables are never preserved by this method," p. 113.

It is not easy to make out what Miss Lloyd's attitude is towards Loeb and his school. The paragraph on p. 142 is distinctly not enthusiastic. "The examples given above are typical of the behaviour of proteins towards acids, bases and neutral salts. It would perhaps be useful to add a note on the use of such expressions as "gelatin chloride" and "sodium gelatinate." These phrases are convenient short expressions, particularly useful for writing on diagrams and distinguishing curves, several of which may be plotted together on one figure. Wherever they are used, however, it must always be borne in mind that they are not names of definite chemical entities. There are probably at least ten "gelatin hydrochlorides," all of which may be present together, and no one of which has yet been isolated or probably ever will be isolated as a single individual; and at least four "sodium gelatinates" of which the same is true. The need for a brief terminology justifies the use of these terms, but the bestowal of a name does not create a definite substance where none exists."

The paragraph at the bottom of the same page hedges a bit. "The theory that proteins form ionisable salts with acids and bases rather than adsorption compounds has in its favour the fact that it is a mental tool easily available to most chemists, and that inductively and deductively it fits in very fairly with experimental observations. Like most scientific theories, it should be recognised that it only holds between certain limits."

The paragraph on p. 188 might have been written by Loeb himself. "The swelling of gelatin and other protein systems, which occur when these are transferred from neutral solutions to those of a more acid or alkaline reaction, is due to the formation of soluble protein salts, which ionise to form one colloidal and one diffusible ion, and so set up an internal osmotic pressure."

"It is difficult to estimate to what extent the buffer action is of importance in the living animal or plant body. It has been shown, for instance, that the plasma proteins take part in maintaining a steady pH value in the blood, and the muscle proteins also interact with the lactic acid produced during the course of muscular work and so prevent the hydrogen ion activity in the fibre from reaching too high a value. In living cells the reaction is never very far removed from the iso-electric points of the cell proteins, and it seems probable that the very labile system resulting with its possibilities of readily changing from uncharged, slightly soluble protein to electrically active, highly soluble protein salt is one which is particularly well adopted for maintaining the equilibrium of the body fluids," p. 143.

"In the living animal body the blood, which is the source of water supply to all the tissues, is kept in the circulatory system by what is essentially a system of membranes, and is, like the cell contents, under a definite head of pressure, the arterial, or blood pressure. Substances which increase the permeability of either the cell membranes or the capillary walls will allow the contents to ooze away, and to accumulate in the interstices between cells or tissues. The work of Dale and his co-workers (1918, 1919) has shown that an oedematous condition of this type can be produced by the action of histamine, a substance which causes capillary distension with increased permeability of the capillary walls and is produced under certain conditions in the body. The pathological accumulation of fluid in the lymph spaces of the limbs and body cavity, which is a clinical symptom for dropsy, is more probably due to a constant leakage from the circulatory system than to the development of an acid reaction in the caelom, as postulated by Bechhold," p. 187.

"There is at present no satisfactory theory to account for the antagonistic action of salts on the behaviour of living protoplasm. There is no doubt, however, that it is fundamentally due to the influence of the salts on the cell proteins. There is sufficient evidence of antagonistic action in the domain of non-living colloids to make this much at least certain. Pieton and Linder (1895) showed that in the precipitation by salts of colloidal arsenic sulphide, while two mono-valent cations or two divalent cations have an influence equal to the sum of each separately, when mono-valent and divalent cations are present together the precipitating action of the salts is less than the sum of the mono-valent effect and the divalent effect, or, in other words, that the ions act antagonistically. Similarly, Fenn

(1916) has shown that in the precipitation of gelatin by alcohol in the presence of chlorides the effect of sodium and potassium chlorides is additive, but that the following salt pairs are antagonistic:

$$NaCl + CaCl_2;\ NaCl + MgCl_2;\ CaCl_2 + MgCl_2.$$

, "It is an interesting fact that all the work on antagonistic salt action has been on the action of the cations. As far as the writer is aware, there is no evidence of antagonistic action among anions," p. 207.

"The type of denaturation which has been studied in greatest detail is that which occurs under the action of heat. This is characteristic of the two groups, albumins and globulins. Under many conditions it is accompanied by the coagulation of the denatured protein. The commonest example of this is, of course, the setting of the white of an egg which takes place on boiling. Denaturation and coagulation are both influenced by temperature, time, and reaction of the solution, the presence of water, and by the nature and concentration of the electrolytes present, but the effect of these factors is different for each of the two processes.

"Denaturation is a process which cannot occur except in the presence of water. Chick and Martin (1910, 1913) showed that crystals of egg albumin, squeezed as dry as possible between filter paper, could be heated for five hours in a current of dry air at 120° without losing their solubility. Heated with steam at 120° the protein became totally insoluble in a few minutes. Heated in aqueous solution under conditions arranged to ensure a constant hydrogen ion concentration, it was found that the concentration of the unchanged albumin in the solution was a logarithmic function of the time of heating, *i. e.*, the denaturation rate at any moment is proportional to the concentration of the unchanged protein," p. 229.

"It has long been known that proteins precipitated from aqueous solutions by the addition to these of either alcohol or acetone, are converted into a form completely insoluble in water, *i. e.*, they are denatured. The relationships of the proteins thus denatured to proteins denatured by the catalytic action of hydrogen or hydroxyl ions, heavy metal ions or heat, has not yet been studied. There is no doubt that temperature plays an important rôle in the denaturation by alcohol or acetone, since Hardy and Gardiner (1910) have shown that at temperatures lower than 5°, this action does not occur, or only so with extreme slowness," p. 241.

"It is not at present easy to form a satisfactory theory of the cause of denaturation, and it is not yet certain that the different types of denaturation, *i. e.*, by heat, light, mechanical means, action of strong acid or alkali, action of alcohol, are brought about by the same types of change in the molecule or by different mechanisms. Denaturation by light and heat seem to be undoubtedly of a similar nature, and the evidence concerning them may be summed up as follows: This type of change seems to be confined to the albumins and globulins. It leads to loss of the power of passing into solution as electrically neutral particles, to greater combining capacity for both acids and bases, to an appearance of fresh reactive groups, to a change in the specific optical rotation, to a greater ease of attack by the proteolytic enzymes (see Chapter VI. on the influence of cooking on the digestibility of egg albumin and stizolobin), and it only occurs in the presence of water. Chick and Martin suggest that denaturation consists of an opening up of internal anhydride rings with combination with the elements of water at the point of cleavage. This theory would account for all the known facts on denaturation with the exception of the loss of solubility, anhydrides being in general less soluble than the bodies from which they are derived. Young suggests that denaturation consists of the closing of rings and formation of internal anhydrides. This theory would explain the loss of solubility in water and dilute salt solutions, but leaves the appearance of the sulph-hydryl group in denatured egg albumin, of the disulphide group in denatured serum albumin, and the greater digestibility by the proteolytic enzymes, entirely unexplained," p. 242.

"It is important in cheese-making to have the right micro-organisms (bacteria and moulds) growing in the cheese, and to ensure successful work in any new factory it has been

the practice to rub the shelves with the rind of a cheese brought from an old factory. This ritual, suggestive at first sight of sympathetic magic, is now recognised to have a sound scientific justification," p. 250.

"Wislicenus and Lorentz (1924) find that gelatins and glues can be graded satisfactorily by determining the percentage that is adsorbed from aqueous solution by fibrous alumina. This material adsorbs the intact gelatin molecules, but leaves all stages of degraded protein in solutions," p. 262.

*Wilder D. Bancroft*

**Metallographie.** *By W. Guertler. Vol. II, Part IV. Gewerbliche Metallkunde. 20 + 18 cm; Berlin: Gebrüder Borntraeger. Price: 38 marks.* Part IV. of the second volume of Guertler's handbook on Metallography, concerned with the properties of Metals and their alloys, deals in particular with the compositions of the alloys used in industry up to the present time. Every alloy of which a description has been published has its composition and properties given in this volume. The book therefore is "uncritical" in the sense that the author makes no attempt to examine whether the alloys in question possess either the compositions or the qualities ascribed to them.

The book consists of a series of tables in which are given the composition of the alloy, its trade name, application, and properties, together with the name of the originator. The alloys fall into three main classes. The largest is that of the high-melting heavy alloys, to which group belong all the steels, brasses, and bronzes. Then follows a group containing the low-melting heavy alloys which include all the white metals, and this is succeeded by a group of the light alloys containing as their principle constituent either manganese or aluminium. These alloys are grouped in a series of tables at the end of each of which there is a short paragraph dealing briefly with the properties of the alloys as a whole. In addition, wherever possible, the compositions are shown graphically. The ternary alloys lend themselves particularly well to this method of representation. The corners of the triangle represent each of the pure metals, the sides the binary alloys and any point within the triangle a ternary alloy. These tables enable the compositions of the alloys to be observed at a glance and it is generally found that the industrial alloys in any given series are grouped fairly near together in the triangle, and as a rule near either one or two of the metals in question.

It would appear from this book that excluding straight carbon steels about 3500 industrial alloys have been invented, whose properties have been described. It may well be doubted whether anything like this number are really needed. As an example one may take the alloys of copper, nickel and zinc which used to be known as the "German silvers". No less than 123 different alloys are described. An inspection of the diagram in which their compositions are graphically represented shows that the great majority of them cluster in an area in which the composition of copper varies from about 40 to 67, while the nickel and zinc vary within limits of about the same magnitude. It is probalbe that not more than about 20 of these 123 alloys are really needed. Under the heading of modern aluminium alloys there are no less than 183 different compositions set forth.

One of the services that this book will render will be to show how unecessary are a considerable number of the alloys described within its pages. It will be of undoubted use as constituting evidence of the date on which a particular alloy was invented and of the name of its inventor. It will no doubt be consulted in law cases in connection with patent litigation concerned with the origin of particular alloys. It is, however, by no means so certain that it will be useful to the technical man, for the properties attributed to the alloys in question are in the great majority of cases merely those claimed by the inventors, and not those found in actual practice. The author wisely recognises that some sort of testing of the properties claimed will have to be carried out, and he indicates that in the future editions he will only incorporate alloys which have been thoroughly tested and whose properties have shown them to be valuable for some definite purpose.

*H. C. H. Carpenter.*

**Untersuchung und Nachweis organischer Farbstoffe auf spektroskopischem Wege** *By J. Formanek and J. Knop. Second, completely rewritten and enlarged edition. Part II, Section III. 24×17 cm; pp. 367-574. Berlin: Julius Springer, 1926. Price: 36 marks.* This instalment deals with the yellow dyes, which are classed in nine groups with some subdivisions: I. Dyes which give only one symmetrical absorption band in dilute aqueous, ethly alcoholic, and amyl alcoholic solutions. This group consists chiefly of acridine dyes together with a few azo dyes and with quinoline yellow. II. Dyes which in dilute solutions give an absorption consisting of one strong band and one weak band to the right. The dyes of the fluorescein group belong here and also some acridine and azo dyes. III. Dyes which in dilute solution give an absorption consisting of a strong, symmetrical band with a weak symmetrical one to the left of it. These dyes are all azo colors. IIIa. Dyes which are like those in Group III in dilute aqueous solutions, but giving two symmetrical and almost equally strong bands when dissolved in ethyl alcohol or amyl alcohol. These dyes are chiefly azo colors. IV. Dyes which give two nearly equal bands whether dissolved in water, ethyl alcohol, or amyl alcohol. These dyes are chiefly azo colors and phosphines. IVa. Dyes which give two approximately equal bands in aqeuous solution; but a strong, symmetrical band and a weaker symmetrical band to the right of it in alcoholic solutions. These dyes are chiefly azo colors.

In Group V are the dyes which give three bands in the dilute alcoholic solutions, the middle one being much the stronger. The dyes of the purpurin class belong here. When made water-soluble by treatment with alkali or by sulphonation, the aqueous spectrum is similar to the alcoholic one. VI. Dyes which show a unilateral absorption in the violet with no bands, but which turn red and show one symmetrical or one unsymmetrical band when acidified. These are all azo colors. VIa. Dyes like those in Group VI except that they give two nearly equal bands in acid solution. These are also azo colors. VII. Dyes giving unilateral absorption in the violet, the solution becoming red and giving one band when made alkaline. Most dyes in this group are azo colors. VIIa. Dyes like Group VII but showing two absorption bands when the solution is made alkaline. A few azo and triphenylmethane dyes fall in this group. VIIb. Dyes like Group VII but showing in alkaline solution three bands with the strongest one in the middle. The alizarine dyes containing hydroxyl groups belong here.

In Group VIII are the dyes which give unilateral absorption in the violet and which are decolorized by acids. Most of the dyes of this type are nitro colors. IX. Dyes like Group VIII except that they are decolorized by alkali. In this class belong dyes of the auramine, flavinduline, and primuline groups, and also a few azo dyes.

*Wilder D. Bancroft*

**An Introduction to the Physics and Chemistry of Colloids.** *By Emil Hatschek. Fifth edition. 18×13 cm; pp. xii+183. Philadelphia: P. Blakiston's Son and Co., 1926. Price: $2.25.* The fourth edition was reviewed about four years ago (26, 600). This new edition "has been carefully revised and the author has again included recent important advances, as far as they fall within the purview of a short introduction to an ever-growing subject. The additional matter includes the work of Porter and Hedges on the vertical distribution of particles in suspension, recent investigations on non-aqueous systems, on the correct interpretation of adsorption experiments, and on the origin of the electric charge on colloid particles."

*Wilder D. Bancroft*

# THE SOLUBILITY OF STRONG, SIMPLE ELECTROLYTES IN WATER*

BY GÖSTA ÅKERLÖF

## I. Introduction

The solubility of a chemical compound in water is of great importance for its synthesis and purification or its use for the purpose of synthesizing other compounds. On account of the necessity for a practical knowledge of solubilities, they have been determined for a large number of compounds in different solvents. Especially for aqueous solutions, they are known at least qualitatively for all more important classes of compounds. A summary of our present knowledge of this subject and the attempts to give a general theory of solubility have been given by Rothmund[1] and Hildebrand. Solubility in non-aqueous solvents has been treated very carefully by Walden.[2] In the present note a discussion of the relative merits of the present theories will not be attempted. A uniform theoretical description of the solubilities of a larger class of compounds seems to meet with very great difficulties. It is for that reason the intrinsic value of the existing theories can not easily be determined. The purpose of this communication is a discussion of an idea regarding the solubilities of some strong simple electrolytes in water.[3]

## II. Theoretical Considerations

The solubility of strong electrolytes has always been a very puzzling problem. Silver and lithium nitrates are both very soluble in water but the solubility of lithium fluoride is very small in comparison with the value for silver fluoride. Potassium fluoride is deliquescent and calcium fluoride has a very small solubility but both the corresponding chlorides are easily soluble in water. The solubilities of the alkali halides decrease rapidly in solutions of hydrochloric acid with increasing acid concentration as would be expected but the silver halides are more soluble in solutions of the alkali halides than in pure water when according to all simple rules the reverse should be true.

A large number of similar peculiarities might be mentioned. How have they been explained? It may safely be said that a reasonable explanation has not yet been given. It is easy to understand that the activity coefficients of the electrolytes can not be directly related to the solubilities, because then increasing activity coefficients would in one case give increasing and in others decreasing solubilities which must be impossible. Nor can other more important properties of the electrolytes as melting point, heat of fusion *et cetera* be connected in a reasonable, simple way with the observed values for the

*Contribution from the John Harrison Laboratory of Chemistry of the University of Pennsylvania.

[1] Rothmund: "Löslichkeit und Löslichkeitsbeeinflussung," (1907); Hildebrand: "Solubility," (1924).

[2] Walden: "Elektrochemie nichtwässriger Lösungen," (1924).

[3] Compare also McAulay: J. Phys. Chem. **30**, 1202 (1926).

solubilities. Exceptions from the so called laws for the solubility of salts in salt solutions have always been said to be due to the formation of complex ions and usually another explanation has seemed to be impossible.

Is it then so very difficult to give a uniform, simple qualitative explanation for the variations in the solubilities of the electrolytes? In the following will be discussed an idea which seems to give in a simple way a clue to an explanation which may possibly be applied to the solubility of any strong electrolyte.

*A. An Assumed Difference between the Solubility of Strong and Non-Electrolytes.* For the present purpose we may divide all chemical compounds in three classes: strong, weak and non-electrolytes. A very large number of the last group we find among the organic compounds. We shall assume that the solubilities of these compounds in water are determined by the relatively greater or smaller number of groups which have a structural similarity common with water or are able to react as oxygroups. Thus we shall regard the high solubilities of the carbohydrates or the polyvalent alcohols as due to their oxygroups. The non-solubility of hydrocarbons, ethers or alkyl halides in water must then be due to the absence of the same group. They are on the other hand more or less easily soluble in ethylalcohol, which contains a group built up in the same general way as their alkyl groups.

Then we shall also assume that the strong electrolytes do not possess any structural solubility in water, even if they should give hydroxyl or hydrogen ions. Their entire solubility should then be due to the action of the electrical field, which belongs to their ions, upon the water or any other solvent. The high solubility of sodium chloride in pure glycerine or sodium iodide in absolute ethyl alcohol must then be caused by the great influence of the ions of these salts upon the respective solvents.

These simple assumptions may not cover all possible cases and should only be considered as a convenient working hypothesis. Later it will be evident, that it was necessary to distinguish between solubility of strong electrolytes and of non-electrolytes. It would then be insignificant for our purpose if the assumption regarding the solubility of non-electrolytes is correct or not.

*B. The Influence of the Change of the Dielectric Constant of the Medium upon the Solubility of Strong Electrolytes* Hückel[1] assumed for his extension to the more concentrated solutions of the Debye-Hückel[2] theory for strong electrolytes that the dielectric constant of the medium changed with increasing concentration of the electrolyte according to a linear formula. It is known through the investigations of Harned and Åkerlöf[3] that this assumption for the specific change produced by an ion gives values, which for some ions are positive for others negative. In other words some electrolytes may cause an increase, others a decrease of the dielectric constant of the solution.

[1] Hückel: Physik. Z., **26**, 93 (1925).

[2] Debye und Hückel: Physik. Z., **24**, 185, 305 (1923); compare further Debye: Physik. Z., **24**, 334 (1923); **25**, 97 (1924); A. A. Noyes: J. Am. Chem. Soc., **46**, 1080 (1924).

[3] Harned and Åkerlöf: Physik. Z., **27**, 411 (1926); compare further Harned: J. Am. Chem Soc., **48**, 326 (1926); Åkerlöf: **48**, 1160 (1926).

When an electrolyte is dissolved in water, the ions which before were arranged in a certain lattice structure very near each other move apart and each ion will be surrounded with water molecules. Every ion changes the previous equilibrium state of these water molecules in its own specific way. *We shall assume, that the ion with the greatest ability to change the state of the solvent in one way or the other is most easily dissolved.* If the specific changes of the state of the solvent caused by the positive and negative ions of the electrolyte both have the same sign, they must work together and a high solubility may result. On the other hand with opposite signs for the changes of the dielectric constant of the solvent caused by the positive and negative ions, the total effect may be very small and this must then give a low solubility.

We may therefore express our idea in the following way. *When the total influence of the ions of an electrolyte upon the dielectric constant of the solvent is zero the solubility of the electrolyte is zero. As the influence of the electrolyte increases, whether towards higher or lower dielectric constant of the medium the solubility always increases.*

At the present time it would be very difficult to carry out a quantitative test of this hypothesis regarding the solubility of electrolytes. Hückel assumed that:

$$D = D_o - \Sigma' c_i \cdot \delta_i$$

where D and $D_o$ are the dielectric constants of the solution and the pure solvent respectively. The assumed change of this constant by the ion with the concentration $c_i$ is denoted $\delta_i$. The calculations of Harned[1] showed that this assumption for a number of ions gave $\delta$ values which were far too high in the concentrated solutions, because at increasing concentration of the electrolyte the dielectric constant of the medium would soon be zero and change sign which must be impossible. The formula must therefore be changed in such a way, that the dielectric constant more or less rapidly approaches a specific limiting value. It is then also evident that the calculated $\delta$ values only possess a certain relative value to each other.

Beside these difficulties we do not know if their relative values are constant or not. It was shown by Harned and Åkerlöf[2], that some complex ions together with different ions may change their $\delta$ values to a very large extent. These changes must be caused by the interaction of the electrical field of the different ions upon each other. That such changes actually occur was found first for the hydroxyl ion and later by Åkerlöf[3] also for the cyanide ion. The sulfate and other similar complex ions with more than two atoms do not appear to change their $\delta$ values to any great extent, although they may have large negative $\delta$ values. The conclusion that some complex ions change their $\delta$ values was based on the assumption, that they were constant for the simple ions. This may approach the true conditions for a few simple ions with low atomic weight and small dimensions but with increasing diameter of the ions

[1] Harned: J. Am. Chem. Soc., 48, 326 (1926).
[2] Harned and Åkerlöf: Physik. Z., 27, 411 (1926).
[3] Åkerlöf: J. Am. Chem. Soc., 48 (1926).

larger deviations are to be expected. All we can do at the present time to test the hypothesis of the relation between the sum of the δ values of the ions of an electrolyte and the solubility of that electrolyte is to show whether it seems to have any probability of being approximately valid.

### III. Experimental Evidence

The δ values for a number of different ions have been calculated by Harned and Åkerlöf.[1] A summary of these calculations is given in Table I. Regarding

TABLE I

Debye-Hückel Constants for Some Electrolytes in pure Aqueous Solutions

| Electrolyte | A | a $10^8$ | B | $\bar{\delta}$ | $\delta_i^+$ | $\delta_i^-$ |
|---|---|---|---|---|---|---|
| KCl | 0.784 | 3.38 | 0.017 | 3.2 | 3.2 | 3.2 |
| NaCl | 0.84 | 3.62 | 0.028 | 5.5 | 7.8 | 3.2 |
| LiCl | 0.84 | 3.62 | 0.0698 | 11.5 | 19.8 | 3.2 |
| HCl | 0.784 | 3.38 | 0.0805 | 11.8 | 20.4 | 3.2 |
| KOH | 0.777 | 3.35 | 0.0632 | 9.65 | 3.2 | 16.1 |
| NaOH | 0.660 | 2.87 | 0.050 | 6.45 | 7.8 | 5.1 |
| LiOH | 0.500 | 2.15 | 0.0215 | 2.2 | 19.8 | −15.4 |
| $BaCl_2$ | 0.888 | 3.83 | 0.0285 | 7.14 | 15.0 | 3.2 |
| $SrCl_2$ | 1.018 | 4.39 | 0.030 | 8.93 | 20.4 | 3.2 |
| $CaCl_2$ | 1.008 | 4.35 | 0.060 | 14.61 | 37.4 | 3.2 |
| $K_2SO_4$ | 0.662 | 2.85 | −0.014 | −3.6 | 3.2 | −17.2 |
| $Na_2SO_4$ | 0.719 | 3.10 | −0.0053 | −1.4 | 7.8 | −19.7 |
| $Li_2SO_4$ | 0.767 | 3.31 | 0.0087 | 2.1 | 19.8 | −33.3 |
| $H_2SO_4$ | 0.40 | 1.72 | 0.031 | 2.4 | 20.4 | −33.4 |

In this table the mean δ value of the ions of an electrolyte with their signs is represented by $\bar{\delta}$. The constants A and B in the table are obtained empirically from the general formula:

$$\log \gamma = \frac{u \sqrt{\Sigma' c_i z_i^2}}{1 + A \sqrt{\Sigma' c_i z_i^2}} + B c_i z_i^2 - \log \left(1 + \frac{M}{1000} \nu m\right)$$

where γ is the activity coefficient of the electrolyte, u a theoretical constant, M the molecular weight of the solvent, $z_i$ the valence of the ion i, ν the number of ions per mol, c and m the concentrations in mol per 1000 cc. solution and 1000 gr. of the solvent respectively. The mean limiting distances of the ions are given by a.

Regarding the δ values of some other ions which are not represented in this table the following may be added. According to the investigation of Åkerlöf[2] it seems to be probable that the carbonate ion has a δ value numerically greater than the one for the sulfate ion and they have both as well

[1] Harned and Akerlöf: Physik. Z., 27, 411 (1926).
[2] Åkerlöf: J. Am. Chem. Soc., 48, (1926).

as the value for the fluoride ion the negative sign. The fluoride ion may be built up of two atoms and would then have an electrical moment variable to some extent. The measurements of Harned and James[1] with aqueous solutions of potassium bromide and iodide have shown that the $\delta$ values for the chloride, bromide and iodide ions together with potassium ions increase in the above order. An estimate of the $\delta$ value for the silver ion may be obtained from the activity coefficients for silver nitrate calculated by Lewis and Randall[2] from freezing point measurements. A summary of the results of the approximate calculation of the Debye-Hückel constants for silver nitrate with the general formula of Hückel[3] for the activity coefficient of an ion is given in Table II.

TABLE II

Activity Coefficients and Debye-Hückel Constants for Silver Nitrate

$A = 0.75$ $B = -0.054$ $\delta_{AgNO_3} = -7.9$

| conc. mol | 0.01 | 0.02 | 0.05 | 0.1 | 0.2 | 0.5 | 1.0 | 2.0 |
|---|---|---|---|---|---|---|---|---|
| $\gamma$ obs. | 0.902 | 0.857 | 0.783 | 0.723 | 0.655 | 0.526 | 0.396 | 0.280 |
| $\gamma$ calc. | 0.899 | 0.862 | 0.800 | 0.739 | 0.666 | 0.547 | 0.436 | 0.307 |

The nitrate ion has very probably a small $\delta$ value and therefore the $\delta$ value for the silver ion must be negative and numerically fairly large. This should explain the high solubility of silver nitrate. If the $\delta$ value of the nitrate ion is near zero this would account for the relatively high solubility of all nitrates, because whether the cation present has a positive or negative $\delta$ value an algebraic sum of the $\delta$ values of both ions near zero could not be obtained unless the $\delta$ value of the cation is near zero.

In the following discussion of the solubility of strong electrolytes in water it must always be remembered, that all our $\delta$ values for the simple ions have only a certain relative value. The $\delta$ values of the complex ions change numerically in the same direction but with opposite sign to the $\delta$ values for the simple ions in the same solution.

*A. The Solubility of the Alkali and Alkali Earth Halides in Water* A summary of the solubilities of these salts in molarity per 1000 gr. of water at 25° is given in Table III. All values are obtained from Landolt-Börnstein: Tabellen, 4th ed. (1912).

TABLE III

Solubility of the Alkali and Alkali Earth Halides in Water at 25°

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| KF | 17.5 | KCl | 4.81 | KBr | 5.58 | KI | 8.95 |
| NaF | 1.04 | NaCl | 6.15 | NaBr | 9.17 | NaI | 12.3 |
| LiF | 0.11 | LiCl | 19.5 | LiBr | 21.2 | LiI | 12.6 |
| $BaF_2$ | $0.91 \cdot 10^{-2}$ | $BaCl_2$ | 1.77 | $BaBr_2$ | 3.58 | $BaI_2$ | 5.28 |
| $SrF_2$ | $0.95 \cdot 10^{-3}$ | $SrCl_2$ | 3.59 | $SrBr_2$ | 4.18 | $SrI_2$ | 5.37 |
| $CaF_2$ | $0.19 \cdot 10^{-3}$ | $CaCl_2$ | 7.60 | $CaBr_2$ | 7.47 | $CaI_2$ | 7.14 |

[1] Harned and James: J. Phys. Chem., **30**, 1060 (1926); compare further Harned and Douglas: J. Am. Chem. Soc., **48**, (1926).

[2] Lewis and Randall: "Thermodynamics", p. 363 (1923).

[3] Hückel: Physik. Z., 27, 93, formulas 95 to 85 c (1926).

The solubilities of the alkali fluorides are a good example for a qualitative test of our hypothesis. The $\delta$ value for the potassium ion is comparatively small and as the $\delta$ value for the fluoride ion is large and negative the sum of these values for both ions of potassium fluoride must be negative and it may also be numerically large, which according to our hypothesis should give a high solubility. With increasing $\delta$ value for the sodium and lithium ions their sum with the one for the fluoride ion must decrease numerically and the solubility of sodium and lithium fluoride should then also decrease rapidly, which Table III shows to be the case. The behavior of the alkali earth fluorides can not yet be interpreted in detail but solubilities of the same order of magnitude as for lithium fluoride could be expected, because their cations have similar $\delta$ values as the lithium ion.

The solubilities for all the chlorides and bromides represented in Table III seem to follow our general solubility rule except the value for calcium bromide as is clearly seen through a comparison with the mean $\delta$ values given for the chlorides in Table I. Among the iodides there seems to be several exceptions. The $\delta$ values for lithium, strontium and calcium ions are very high and these exceptions as it may seem could be due to distortion in the fine structure of the ions of these salts. This would lower the $\delta$ values of the ions of these electrolytes and thus explain, that the observed solubilities are not as high as expected.

*B. The Solubility of the Alkali and Alkali Earth Carbonates, Sulfates, Hydroxides, and Nitrates* A summary of the solubilities of these salts in molarity per 1000 gr. of water at 25° is given in Table IV. Some of the values are obtained from Abegg-Auerbach. The accuracy of the values for salts with a very small solubility is a little uncertain, because they are to a great extent dependent on the size of the particles and the crystal form.[1] These errors are however insignificant for the present purpose.

TABLE IV

Solubility of the Alkali and Alkali Earth Carbonates, Sulfates, Hydroxides, and Nitrates at 25°

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $K_2CO_3$ | 8.22 | $K_2SO_4$ | 0.69 | KOH | 21.3 | $KNO_3$ | 3.83 |
| $Na_2CO_3$ | 2.82 | $Na_2SO_4$ | 1.97 | NaOH | 28.5 | $NaNO_3$ | 10.8 |
| $Li_2CO_3$ | 0.18 | $Li_2SO_4$ | 3.11 | LiOH | 5.41 | $LiNO_3$ | 10.6 |
| $BaCO_3$ | $0.46\ 10^{-4}$ | $BaSO_4$ | $0.98\ 10^{-5}$ | $Ba(OH)_2$ | 0.28 | $Ba(NO_3)_2$ | 0.40 |
| $SrCO_3$ | $0.68\ 10^{-4}$ | $SrSO_4$ | $0.82\ 10^{-3}$ | $Sr(OH)_2$ | 0.082 | $Sr(NO_3)_2$ | 3.74 |
| $CaCO_3$ | 0.015 | $CaSO_4$ | 0.015 | $Ca(OH)_2$ | 0.021 | $Ca(NO_3)_2$ | 9.28 |

The structure of all these electrolytes is far more complicated than the structure of the corresponding halides. Many of them form a long series of different hydrates and have a number of transition points for the solubility.

[1] Compare for instance the solubilities of aragonite and calcite, Bäckström: Z. physik. Chem., 97, 179 (1921).

The relative solubilities are therefore to a certain degree dependent on the temperature chosen for the comparison. A few of these electrolytes have a great tendency to form supersaturated solutions.

The solubilities of the alkali carbonates change in the same way as the values for the alkali fluorides and they must therefore follow our solubility rule, because also the carbonate ion has a large, negative $\delta$ value as previously mentioned. The sum of the $\delta$ values for the ions of the alkali carbonates must then change in a similar way as for the corresponding alkali fluorides and cause similar solubilities. The values given for the alkali sulfates seem to contradict our rule, because the mean $\delta$ value as given in Table I is numerically greater for potassium than for sodium sulfate. At the present time the theory for the $\delta$ values is too uncertain for a decision for or against, but it should be noted, that the solubilities of these three sulfates follow the change in the sum of their $\delta$ values very well. The alkali earth sulfates have very small solubilities, which agrees in general with our rule, because the corresponding fluorides and carbonates are very slightly soluble.

A difference between the solubilities of the alkali fluorides and sulfates should be pointed out, which will make clear the very large difficulties a general theory of solubility for strong electrolytes has to face. For the fluorides as for the carbonates the solubility decreases from the potassium to the lithium salt but for the sulfates it is reversed, the solubilities increase in the same order. All the three anions have undoubtedly negative $\delta$ values and it seems therefore as if the only way to explain this reversal is, that the electrostatic moments of these ions behave in two different ways in the presence of different ions. For one anion the electrical moment may vary to a large extent, for the other it may be nearly constant.

The behavior of the alkali hydroxides is complicated through the number of different hydrates formed. The great decrease for the solubility of lithium hydroxide as compared with potassium and sodium hydroxide is however in good agreement with our solubility rule, because the mean $\delta$ value has also decreased to a great extent as shown in Table I. Barium hydroxide has the greatest solubility of the alkali earth hydroxides, which probably is due to the smaller distortion of the hydroxyl ions, than when these ions are together with strontium or calcium ions, which both have very high $\delta$ values. These hydroxides follow therefore our rule very well.

The solubilities given for the nitrates follow in general the rule except the value for lithium nitrate. The solubility of this salt increases very rapidly with increasing temperature and a comparison at a slightly higher temperature would have been more favorable.

*C. The Solubility of the Silver, Thallous, Cuprous, Mercurous Halides*

The solubility of these compounds in weight normality at 25° is given in Table V. A value for cuprous fluoride could not be obtained, because it immediately decomposes with water and cupric fluoride is formed. Mercurous fluoride seems to be easily soluble, because it can be recrystallized in concentrated hydrofluoric acid, but in pure water it decomposes very rapidly.

TABLE V

Solubility of the Silver, Thallous, Cuprous and Mercurous Halides in Water at 25°

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| AgF | 10.7 | AgCl | $1.6\ 10^{-5}$ | AgBr | $7.1\ 10^{-7}$ | AgI | $1.0\ 10^{-8}$ |
| TlF | 3.6 | TlCl | $1.6\ 10^{-2}$ | TlBr | $1.8\ 10^{-3}$ | TlI | $2.0\ 10^{-4}$ |
| CuF | — | CuCl | $1.1\ 10^{-3}$ | CuBr | $2.0\ 10^{-4}$ | CuI | $2.3\ 10^{-6}$ |
| HgF | — | HgCl | $1.3\ 10^{-5}$ | HgBr | $1.0\ 10^{-7}$ | HgI | $0.6\ 10^{-9}$ |

The behavior of these electrolytes seems to be almost opposite that of the alkali earth halides. The cations of the alkali earth halides had large positive $\delta$ values but the cations for the salts represented in Table V must evidently all have negative $\delta$ values as was shown to be the case for the silver ion. According to our solubility rule this would cause their fluorides to possess a high solubility, because the $\delta$ value for the fluoride ion was negative and thus numerically increased the mean $\delta$ value of these electrolytes. In all cases this could be tested a high solubility was also found for the fluorides.

The chloride, bromide and iodide ions have positive $\delta$ values increasing in the above order. The sum of these values with the negative $\delta$ value for the cation must give a numerically small mean $\delta$ value and thus their low solubility is easily explained. In all cases the solubility of the chloride is highest and for the iodide the lowest, which also is in accord with our hypothesis.

*D. Comparison of Solubilities of Strong Electrolytes at Increasing Temperatures* We have so far made a qualitative comparison of the solubilities and mean $\delta$ values for 64 electrolytes. There was not found any case, which could with certainty be considered as a contradiction for our solubility hypothesis, that when the value for the change of the dielectric constant of the solvent caused by an electrolyte increases the solubility of the electrolyte also increases. The activity coefficients of the electrolytes which have been used for the determination of the $\delta$ values for the individual ions have all been measured at 25°. Very little is at present known about the changes of the activity coefficients of strong electrolytes at increasing temperatures. It might however still be of some interest to compare the solubilities of these electrolytes at other temperatures than 25°. If our solubility rule holds there ought to be maintained at all temperatures in general about the same ratio between the solubilities for electrolytes of the same class and with simple ions, for instance the alkali bromides or iodides. A summary of the solubilities for a few electrolytes in weight molarity at increasing temperatures is given in Table VI. The values are obtained partly from Landolt-Börnstein, partly from Abegg-Auerbach.

The solubility for all electrolytes with simple ions seems to change in a nearly uniform way at increasing temperatures. The solubility ratio for two electrolytes of the same kind may in some cases be approximately constant at all temperatures as in the case of calcium bromide and iodide. In other cases the differences became more pronounced with increasing temperature and generally they seem to increase in the same direction to a similar ratio as the ratio of the mean $\delta$ values given in Table I.

TABLE VI

Solubility of Some Electrolytes at Increasing Temperatures

| Temp. | KBr | NaBr | LiBr | KI | NaI | LiI |
|---|---|---|---|---|---|---|
| 0 | 4.54 | 7.73 | 16.4 | 7.70 | 10.6 | 11.3 |
| 20 | 5.46 | 8.77 | 20.1 | 8.68 | 11.9 | 12.4 |
| 40 | 6.39 | 10.3 | 23.3 | 9.64 | 13.7 | 13.4 |
| 60 | 7.23 | 11.4 | 25.8 | 10.6 | 17.1 | 15.0 |
| 80 | 8.07 | 11.6 | 27.6 | 11.6 | 19.7 | 32.5 |
| 100 | 8.82 | 11.8 | 30.4 | 12.6 | 20.1 | 36.0 |
| | $BaBr_2$ | $SrBr_2$ | $CaBr_2$ | $BaI_2$ | $SrI_2$ | $CaI_2$ |
| 0 | 3.30 | 3.55 | 6.26 | 4.35 | 4.68 | 6.55 |
| 20 | 3.50 | 4.33 | 7.14 | 5.07 | 5.24 | 6.94 |
| 40 | 3.84 | 4.90 | 10.7 | 5.93 | 5.74 | 7.76 |
| 60 | 4.15 | 5.83 | 13.9 | 6.14 | 6.73 | 11.5 |
| 80 | 4.54 | 7.06 | 14.6 | 6.33 | 8.49 | 13.6 |
| 100 | 5.01 | 9.08 | 15.4 | 6.88 | 10.8 | 14.6 |
| | KOH | NaOH | LiOH | $Ba(OH)_2$ | $(SrOH)_2$ | $Ca(OH)_2$ |
| 0 | 17.3 | 10.5 | 5.25 | 0.098 | 0.034 | 0.023 |
| 20 | 20.0 | 27.2 | 5.36 | 0.25 | 0.066 | 0.022 |
| 40 | 23.7 | 32.2 | 5.47 | 0.48 | 0.145 | 0.019 |
| 60 | 26.2 | 43.5 | 5.79 | 1.22 | 0.30 | 0.016 |
| 80 | 28.9 | 78.9 | 6.39 | 5.92 | 0.68 | 0.013 |
| 100 | 31.7 | —— | 7.30 | —— | 2.21 | 0.011 |
| | $KNO_3$ | NaNO | $LiNO_3$ | $K_2CO_3$ | $Na_2CO_3$ | $Li_2CO_3$ |
| 0 | 1.32 | 8.58 | 7.74 | 7.60 | 0.67 | 0.208 |
| 20 | 3.13 | 10.5 | 10.0 | 8.10 | 2.02 | 0.180 |
| 40 | 6.32 | 12.3 | 21.4 | 8.47 | 4.59 | 0.166 |
| 60 | 10.9 | 14.6 | 25.4 | 9.19 | 4.37 | 0.146 |
| 80 | 16.7 | 17.4 | 30.5 | 10.1 | 4.26 | 0.139 |
| 100 | 24.3 | 20.6 | —— | 11.3 | 4.26 | 0.124 |

Strong electrolytes with complex ions show in some cases the normal behavior of electrolytes with simple ions as the alkali carbonates and alkali earth hydroxides. In other cases there may seem to be increasing deviations from the normal behavior as for solutions of the alkali hydroxides and nitrates. The thermodynamic properties of these electrolytes at higher temperatures are at present completely unknown.

*E. Solubility of Salts in Salt Solutions* The effect of one electrolyte upon the solubility of another has been given a detailed study by A. A. Noyes[1]

[1] A. A. Noyes: Z. physik. Chem., **6**, 241 (1890); A. A. Noyes and W. C. Bray: J. Am. Chem. Soc., **33**, 1643; A. A. Noyes, Boggs, Parrell and Stewart: 1650; Bray and Winninghoff: 1663; Bray: 1673; Harkins: 1807; Harkins and Winninghoff, 1827; Harkins: 1836 (1911); Harkins and Paine: **41**, 1155 (1919); Harkins and Pierce: **37**, 2679 (1916); compare further Forbes: **33**, 1937 (1911); Kendall, Davidson and Adler: **43**, 1481 (1921).

and his collaborators and more recently by Brönsted.[1] If the added electrolyte is homoionic the solubility should decrease and if heteroionic increase. In the former case the activity of one of the ions increases but as the activity product must be constant, because the activity in the solid phase is constant, the concentration of the other ions or the solubility of the electrolyte decreases. With heteroionic electrolytes the logarithm of the activity coefficient in dilute solutions is proportional to $\sqrt{\Sigma c_i z_i^2}$ and an increase in the concentration of one of the electrolytes must therefore decrease the activity coefficient and increase the concentration of the other.

Just as often as agreements there has been found a large number of exceptions from these rules. One of the best known is the increasing solubility of the silver halides in solutions of the alkali halides at increasing salt concentrations. To explain this and similar cases it has always been the custom to assume the presence of complex ions. In some cases this seems to be probable and sometimes it may even be necessary to make the assumption of the formation of complex ions. It might however be of some advantage if an explanation of the behavior of the silver halides in salt solutions could be given without this assumption.

Their behavior in alkali halide solutions might qualitatively be explained as due to the distortion of the silver ions in the intense electrical fields existing in these solutions. This explanation seems to be probable, because it would increase the numerical sum of the $\delta$ values of the ions of the silver halides, which according to our solubility rule must give them a higher solubility. It should also be noted that the solubility of the silver halides in alkali halide solutions at a given salt concentration increases nearly proportionally to the activity of the salt present.[2]

## IV. Discussion

The whole problem of solubility for strong electrolytes is very difficult. Many theories have been offered. The most successful so far seems to be the theory of Bodländer.[3] He was able to show, that the solubility of a strong electrolyte with simple ions could approximately be calculated from the assumption that the heat of formation was proportional to the sum of the potential of the ions of the electrolyte in a saturated solution. The potentials of the ions were referred to a reference state with the standard electrode potentials. For slightly soluble electrolytes activities may be exchanged for concentrations and the formula would be:

$$(E_s^+ - E_o^+) + (E_s^- - E_o^-) = -\frac{RT}{NF} \ln c$$

where $c$ is the concentration of the saturated solution and the index $s$ and $o$ denote potentials of the ions in the saturated solution and the standard

[1] Brönsted: J. Am. Chem. Soc., 42, 761 (1920); 43, 2265 (1921); 44, 877, 938 (1922); Brönsted and LaMer: 46, 555 (1924); compare also Brönsted: Kgl. Danske Videnskabs Selskab Meddel., 2, 10 (1919).

[2] Harned: J. Am. Chem. Soc., 40, 1461 (1918).

[3] Bodländer: Z. physik. Chem., 27, 55 (1898); Abegg and Bodländer: Z. anorg. Chem., 20, 453 (1899).

electrode potentials respectively. It was shown by Bodländer that this formula for electrolytes with simple ions generally gives the order of magnitude for the solubility very well as long as the electrolyte is slightly soluble. When the ions present are complex or the solubilities higher large deviations are often found. A further extension of the theory of Bodländer would therefore offer very large difficulties as pointed out already by Rothmund.[1]

In this communication an idea is presented regarding the solubility of a strong electrolyte as a function of the changes of the dielectric constant of the medium. The solubility should not be directly related to the dielctric constant of the medium as such. Since the probability for a change of sufficient mangitude to dissolve the electrolyte must decrease rapidly with decreasing dielectric constant of the solvent our solubility hypothesis might be brought in agreement with the rule found by Walden[2]. According to Walden the solubility of an electrolyte in different solvents is proportional to the cube root of the dielectric constants of these solvents. Our idea for the solubility of strong electrolytes in water was obtained from an experimental test by Harned and Åkerlöf of the extension by Hückel of the Debye-Hückel theory. It was shown that in all cases a somewhat simplified form of Hückel's general formula for the activity coefficient of an ion, when applied to the measurements gave a very good agreement between observed and calculated values through the entire concentration range used.

It was first found upon the examination of the empirical constants that the difficulties of Hückel's theory were seen. The $\delta$ values of many simple ions were too large in the concentrated solutions and for the complex ions they varied with the nature of the ions present. Any certainty of the constancy of the $\delta$ values of the simple ions could not be obtained. It might then be regarded as hazardous to use the $\delta$ values obtained and draw conclusions for their relation to the solubility of strong electrolytes. We have therefore only pointed out, that there seems to be a certain parallellism between the algebraic sum of the $\delta$ values for the ions of an electrolyte and the solubility of the same. At the present time a step further would be very uncertain.

## V. Summary

This note is written as a suggestion towards a probable hypothesis regarding the solubility of strong electrolytes, because a more careful test can not yet be carried out.

According to this hypothesis the solubility of a strong electrolyte in water is dependent on the ability of the ions of the electrolyte to change the dielectric constant of the solvent.

Every ion influences individually the solubility, which is a function of the total algebraic sum of all the individual changes of the ions on the dielectric constant of the solvent.

---

[1] Rothmund: "Löslichkeit und Löslichkeitsbeeinflussung," p. 132 (1907).
[2] Walden: "Elektrochemie nichtwässriger Lösungen," p. 430 (1924).

This gives the following rule for the solubility of strong electrolytes: The solubility increases with increasing value for the total change of the dielectric constant of the solvent. As a special case follows that for the change zero, the solubility is zero.

The calculated values for the changes of the dielectric constant for a number of different electrolytes were compared with the observed solubilities of the same electrolytes and in general an agreement with our hypothesis was found, which owing to the extreme complexity of the phenomena encountered, we regard as encouraging.

This paper has been thoroughly discussed with Dr. Herbert S. Harned. The author wishes to express his sincere thanks to Dr. Harned.

*Philadelphia, Pennsylvania, U. S. A.*

# DECOMPOSITION POTENTIALS AND METAL OVERVOLTAGES IN LIQUID AMMONIA AND IN WATER[1]

BY A. A. GROENING WITH H. P. CADY

Decomposition potentials and overvoltages have been measured in two ways. The one called the direct method and the other the indirect or the commutator method. The former was first suggested by Fuchs[2] in 1875 and has since been extensively employed by others.[3] The latter or the indirect method with rotating commutator was first used by LeBlanc[4] and has lately been used by Newbery.[5] The results obtained by the two methods are not in very close agreement and hence a controversy has arisen between the adherents of the two methods. It has however, been definitely shown by Ferguson and Van Zyl[6] and Knobel[7] that the direct method is the correct method.

## Apparatus and Method

In this investigation the direct method has been used. It has been customary to use stationary electrodes but this permits of great concentration polarization near the electrodes. This then adds the potential due to the difference in concentration near the electrodes to the values of decomposition voltage and overvoltage that are to be measured. To avoid this change in concentration the electrodes in this investigation were rapidly rotated.

After much experimenting the cell shown in Fig. 1 was adopted. The electrodes a′ and b′ are platinum plates, approximately one-half square centimeter in size, sealed into a glass tube by means of platinum wires and in direct metallic connection with the brass rings d and d′. The brushes a and b make electrical contact with the rings d and d′ and hence also with electrodes a′ and b′. They are also connected to a and b of Fig. 2. The electrodes and the rings are mounted on an iron rod which passes through a bearing to a pulley so that they may be rotated at any desired speed by a motor with variable speed. The glass tube f is open at the bottom and has an opening on the side away from the reference electrode c. This reference electrode c is of the same metal as the cation of the salt under investigation and is in direct contact with c of Figure 2. The large test tube g contains the solution under investiga-

---

[1] An abstract of a thesis submitted by A. A. Groening in partial fulfilment of the requirements for the degree Doctor of Philosophy in the Graduate School of the University of Kansas.

[2] Pogg. Ann., **156**, 158 (1875).

[3] Caspari: Z. physik. Chem., **30**, 89 (1899); Dannenberg and Coehn: **38**, 609 (1901); Tafel: **50**, 641 (1905); Möller: **65**, 226, (1909); MacInnes and Adler: J. Am. Chem. Soc., **41**, 194 (1919); Knobel, Caplan and Eiseman: Trans. Am. Electrochem. Soc., **43**, 55 (1923).

[4] Z. physik. Chem., **5**, 469 (1890); **8**, 299 (1891); **12**, 333 (1893); "Text Book of Electro-Chemistry," pp. 287-320, English translation by Whitney and Brown.

[5] J. Chem. Soc., **105**, 2419 (1914); **109**, 1051, 1066, 1107, 1359 (1916); **111**, 470 (1917); **119**, 477 (1921); **121**, 7 (1922).

[6] Trans. Am. Electrochem. Soc., **45**, 311 (1924).

[7] J. Am. Chem. Soc., **46**, 2613 (1924).

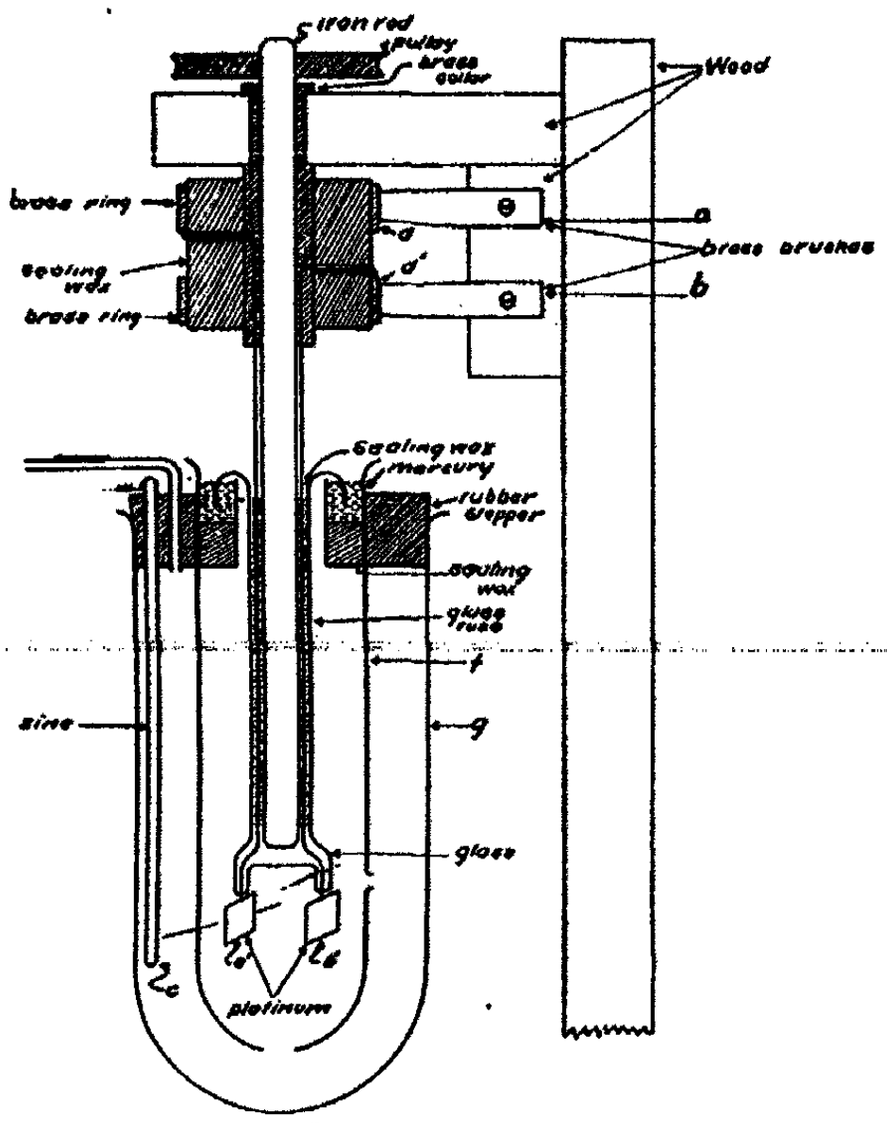



FIG. 1
The Cell

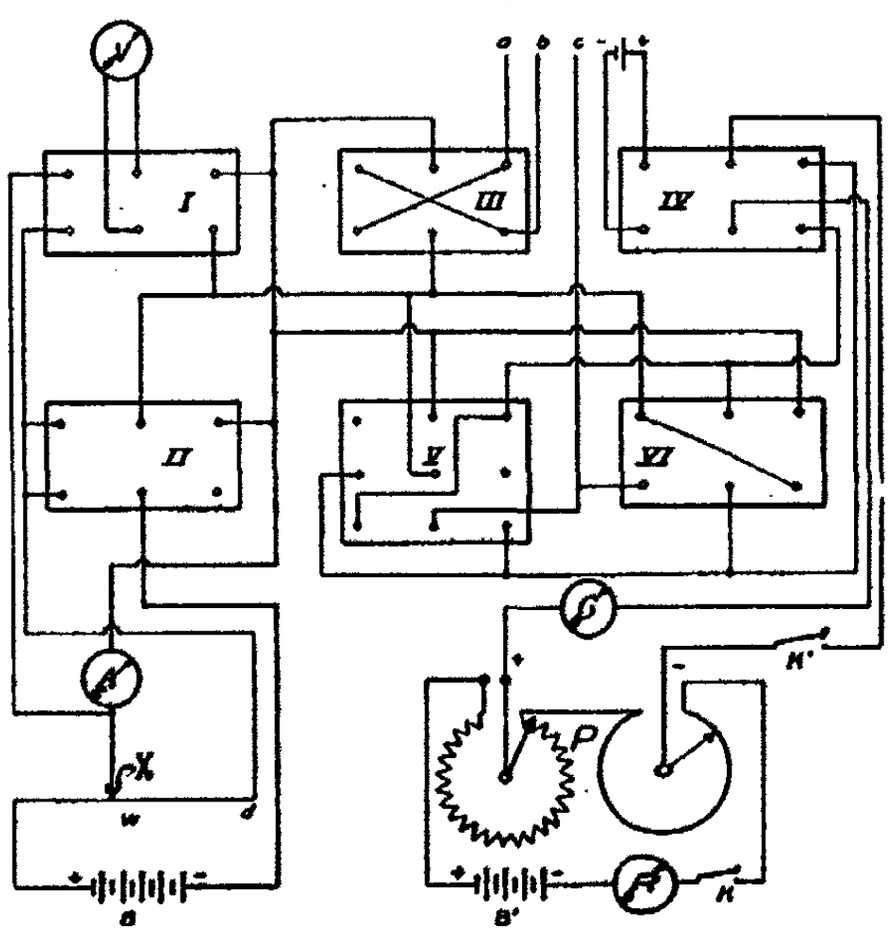



FIG. 2

Diagram of circuits employed. V—a voltmeter; A—a milliammeter; G—a d'Arsonval galvanometer; R—a variable resistance; P—a potentiometer; W—a resistance with sliding contact; I to VI are double throw knife switches; S—a Weston Standard cell; K and K′—contact keys; B and B′—dry cells; a, b, and c are leads to the cell Fig. 1.

tion and is immersed in a Dewar flask containing liquid ammonia when working with this solvent and is thus kept at or slightly below the boiling point of this liquid. When salts in water are investigated the tube g is immersed in a vessel containing ice and water to keep it at 0° C.

The apparatus as finally arranged is diagrammed in Fig. 2. The voltage impressed upon the electrodes is determined by the voltage drop between X and d. For the benefit of the reader the position of the switches in making the various measurements is shown below:

(A) *Adjusting the Potentiometer.* IV, left; all others open; the potentiometer P set at the voltage of the standard cell S and the resistance R adjusted until there is no throw in the galvanometer G when the keys K and K′ are closed. This makes the potentiometer direct reading.

(B) *Charging the Cell.* III, left or right; I, left; II, left; others open.

(C) *Measurement of Voltage applied.* Switches closed as in (B); IV, right; VI, right, K and K′ closed and the potentiometer adjusted for zero throw.

(D) *Measurement of Voltage between Cathode and the Reference Electrode.* Switches closed as in (B); IV, left; V, left (if the reference electrode is the more negative then V is left open and VI is thrown to the left); K and K′ are closed and the potentiometer adjusted for zero throw.

Pure dry liquid ammonia was obtained by condensing the vapors of ammonia from a cylinder containing the liquid and metallic sodium. About fifty cubic centimeters were condensed at a time, this amount being sufficient for a run. The salts used were of the best c. p. salts obtainable. They were dried in vacuum over phosphorus pentoxide. Copper nitrate with ammonia of crystallization was obtained by fractional crystallization from liquid ammonia. This salt was dried as above and completely dehydrated as shown by the ordinary tests. Ferric nitrate was not completely dehydrated.

Enough salt to make an approximately N/1c solution was weighed, put into the test tube (g Figure 1) and fifty cubic centimeters of the dry liquid ammonia or water introduced and placed into position.

The potentiometer was now adjusted as in (A) above.[2] The switches were set as in (B) and slide X moved to the left until the milliammeter showed a current flowing. The voltage applied was measured (C) and recorded, after which the cathode overvoltage was measured (D) and recorded. By this time the milliammeter had generally become nearly stationary and the current was read. The interval of time between the application of the current and the reading of the milliammeter was about one-half minute. The slide X was now moved a little to the left and another series of readings made. This was continued until the limit of the voltage was reached or the milliammeter became erratic.

The metal deposited on the cathode was dissolved with nitric acid. The cell was thoroughly washed with distilled water and dried before the next

[1] Many salts were found not to be sufficiently soluble to make a solution of this strength in liquid ammonia.

[2] After a run the potentiometer always showed perfect adjustment.

run. After using electrode a as cathode for one of a pair of runs, switch III was thrown the other way and electrode b was used as cathode. Any difference in the two electrodes was thus compensated.

After a run the current was plotted against the corresponding voltage applied and also against the cathode overvoltage. The upper straight parts of the curves obtained were extrapolated upon the line of zero current. These points are called the dynamic[1] decomposition voltage and the metal overvoltage respectively. The curves are shown on the Figs. 3-6. The letters refer to the Tables from which the data was taken. Capital letters refer to liquid ammonia and small letters to water solution.

## Data

The data are shown in the Tables A to R, Table T being a Summary of the values obtained. The "volts applied" is the voltage between the electrodes a′ and b′ when the current was flowing and measured by the potentiometer. The "volts reference" is the potential that existed between the reference electrode and the cathode also measured by the potentiometer. An undervoltage whenever the reference electrode was negative with respect to the cathode, is designated with a minus (−) sign. The "current" in milliamperes is the reading of the milliammeter during the above interval. To save space only a few points on a curve are given but in each case from five to fifteen points fell smoothly on the straight portion of the curve. Only one set of readings is given for a given salt although a check run was always made and generally three or four.

*Silver Nitrate* was composed of pure white crystals and formed clear solutions both in ammonia and in water.

TABLE A
Silver Nitrate

| In Ammonia | | | In Water | | |
|---|---|---|---|---|---|
| Current | Volts applied | Volts reference | Current | Volts applied | Volts reference |
| 0.15 | 0.779 | 0.225 | 0.07 | 0.702 | 0.002 |
| 0.96 | 0.988 | 0.308 | 0.50 | 0.880 | 0.040 |
| 4.95 | 1.274 | 0.408 | 1.20 | 0.984 | 0.060 |
| 19.0 | 1.738 | 0.682 | 7.40 | 1.354 | 0.228 |
| 43.0 | 2.478 | 1.144 | 15.0 | 1.800 | 0.458 |
| (See Fig. 3 A and A′) | | | (See Fig. 3 a and a′) | | |

*Silver Nitrite* is not sufficiently soluble in ammonia to form a N/10 solution.

[1] The term dynamic is used because the decomposition voltage is obtained when there is actual electrolysis taking place. The decomposition voltage obtained at the beginning of electrolysis we would call the "static" decomposition voltage.

## Table B
### Silver Nitrite

| In Ammonia | | | In Water | | |
|---|---|---|---|---|---|
| Current | Volts applied | Volts reference | Current | Volts applied | Volts reference |
| 0.99 | 0.984 | 0.238 | 0.05 | 0.197 | 0.037 |
| 4.10 | 1.200 | 0.332 | 0.42 | 0.294 | 0.066 |
| 17.0 | 1.778 | 0.636 | 1.03 | 0.388 | 0.104 |
| 35.0 | 2.530 | 1.000 | 4.75 | 0.734 | 0.252 |
| 48.0 | 3.118 | 1.292 | 9.50 | 1.184 | 0.480 |
| (See Fig. 3 B and B′) | | | (See Fig. 3 b and b′) | | |

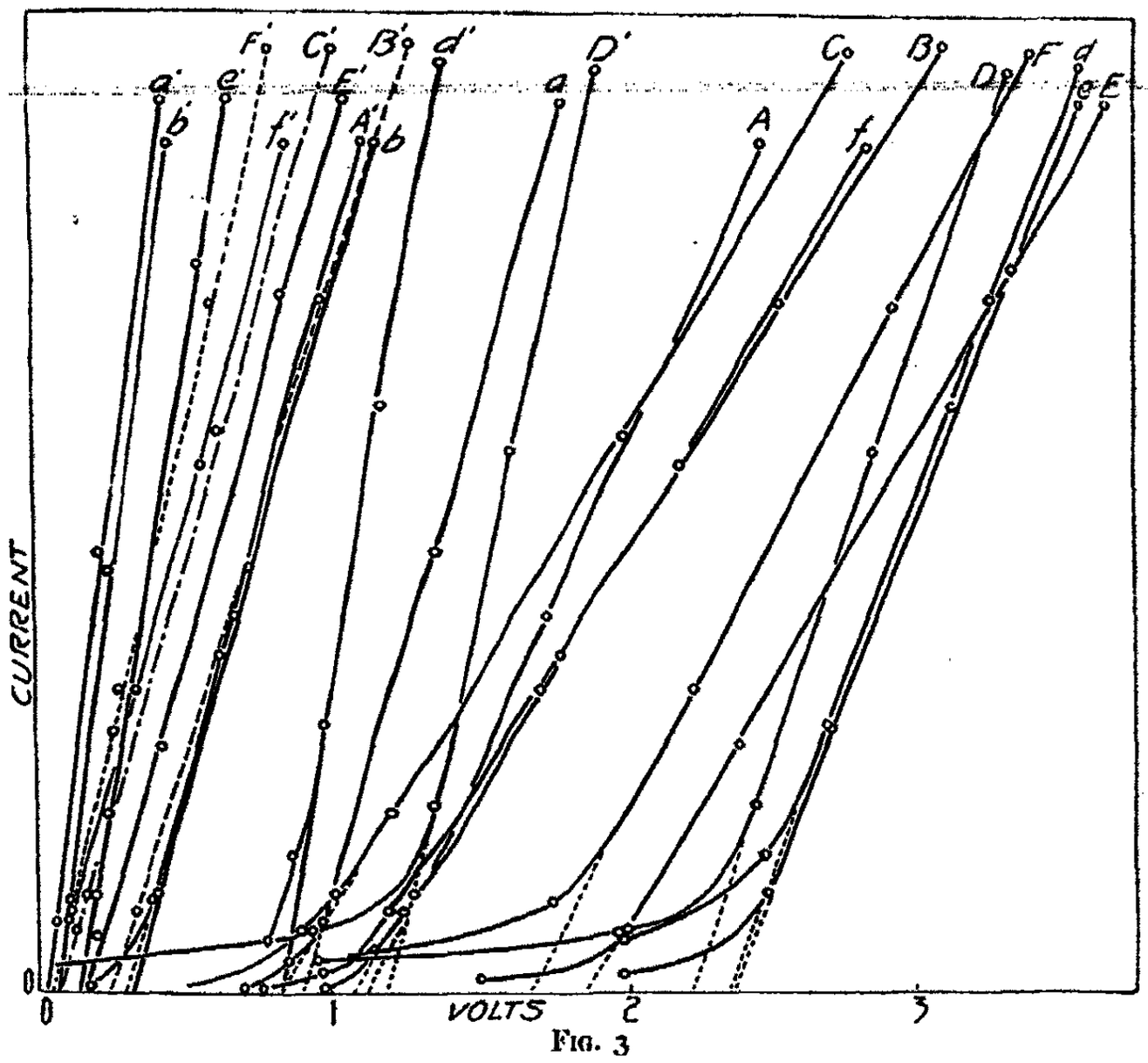



FIG. 3

*Silver Iodide* is rather soluble in ammonia but insoluble in water. One would expect free iodine to be liberated at the anode during electrolysis but none was observed and instead there was a gas liberated.

## Table C
### Silver Iodide in Ammonia

| Current | Volts applied | Volts reference | Current | Volts applied | Volts reference |
|---|---|---|---|---|---|
| 0.70 | 0.914 | 0.130 | 6.30 | 2.006 | 0.632 |
| 1.10 | 1.022 | 0.174 | 10.6 | 2.794 | 1.046 |
| 2.00 | 1.212 | 0.246 | (See Figure 3 C and C′) | | |

*Nickel Nitrate* formed a bright red solution in dry liquid ammonia. The deposit of nickel was smooth and the overvoltage high. When a trace of water is present the color changes to the characteristic blue.

TABLE D
Nickel Nitrate

| In Ammonia | | | In Water | | |
|---|---|---|---|---|---|
| Current | Volts applied | Volts reference | Current | Volts applied | Volts reference |
| 0.30 | 0.970 | 0.070 | 0.50 | 1.984 | 0.780 |
| 0.60 | 1.996 | 0.934 | 1.50 | 2.476 | 0.890 |
| 1.80 | 2.440 | 1.366 | 2.65 | 2.704 | 1.000 |
| 5.20 | 2.870 | 1.616 | 5.80 | 3.148 | 1.200 |
| 8.90 | 3.354 | 1.923 | 9.20 | 3.594 | 1.380 |

(See Fig. 3 D and D′) (See Fig. 3 d and d′)

*Cadmium Nitrate* did not form a basic salt in ammonia as in water.

TABLE E
Cadmium Nitrate

| In Ammonia | | | In Water | | |
|---|---|---|---|---|---|
| Current | Volts applied | Volts reference | Current | Volts applied | Volts reference |
| 0.24 | 1.486 | −0.200 | 0.20 | 1.986 | 0.076 |
| 1.13 | 1.972 | +0.200 | 1.10 | 2.470 | 0.202 |
| 5.00 | 2.396 | 0.434 | 2.95 | 2.718 | 0.264 |
| 14.0 | 3.280 | 0.874 | 8.15 | 3.354 | 0.570 |
| 18.0 | 3.712 | 1.084 | 10.0 | 3.596 | 0.680 |

(See Fig. 3 E and E′) (See Fig. 3 e and e′)

*Cadmium Iodide* is not sufficiently soluble to form a N/10 solution in ammonia. There was again no indication of free iodine at the anode in ammonia while in water the solution turned brown due to its liberation.

TABLE F
Cadmium Iodide

| In Ammonia | | | In Water | | |
|---|---|---|---|---|---|
| Current | Volts applied | Volts reference | Current | Volts applied | Volts reference |
| 0.10 | 1.000 | −0.448 | 0.05 | 0.998 | −0.012 |
| 0.50 | 1.742 | +0.104 | 0.90 | 1.240 | +0.110 |
| 1.70 | 2.220 | 0.282 | 3.40 | 1.708 | 0.344 |
| 3.85 | 2.944 | 0.612 | 5.90 | 2.180 | 0.578 |
| 5.30 | 3.424 | 0.834 | 9.50 | 2.858 | 0.894 |

(See Fig. 3 F and F′) (See Fig. 3 f and f′)

*Mercuric Nitrate* is also insufficiently soluble to form a N/10 solution in ammonia.

TABLE G

Mercuric Nitrate

| In Ammonia | | | In Water | | |
|---|---|---|---|---|---|
| Current | Volts applied | Volts reference | Current | Volts applied | Volts reference |
| 0.17 | 0.738 | 0.082 | 0.70 | 1.480 | 0.092 |
| 1.10 | 0.984 | 0.162 | 1.75 | 1.720 | 0.172 |
| 2.50 | 1.224 | 0.274 | 2.90 | 1.950 | 0.268 |
| 6.90 | 1.912 | 0.616 | 5.45 | 2.414 | 0.480 |
| 15.5 | 3.274 | 1.300 | 9.20 | 3.106 | 0.814 |

(See Fig. 4 G and G′) (See Fig. 4 g and g′)

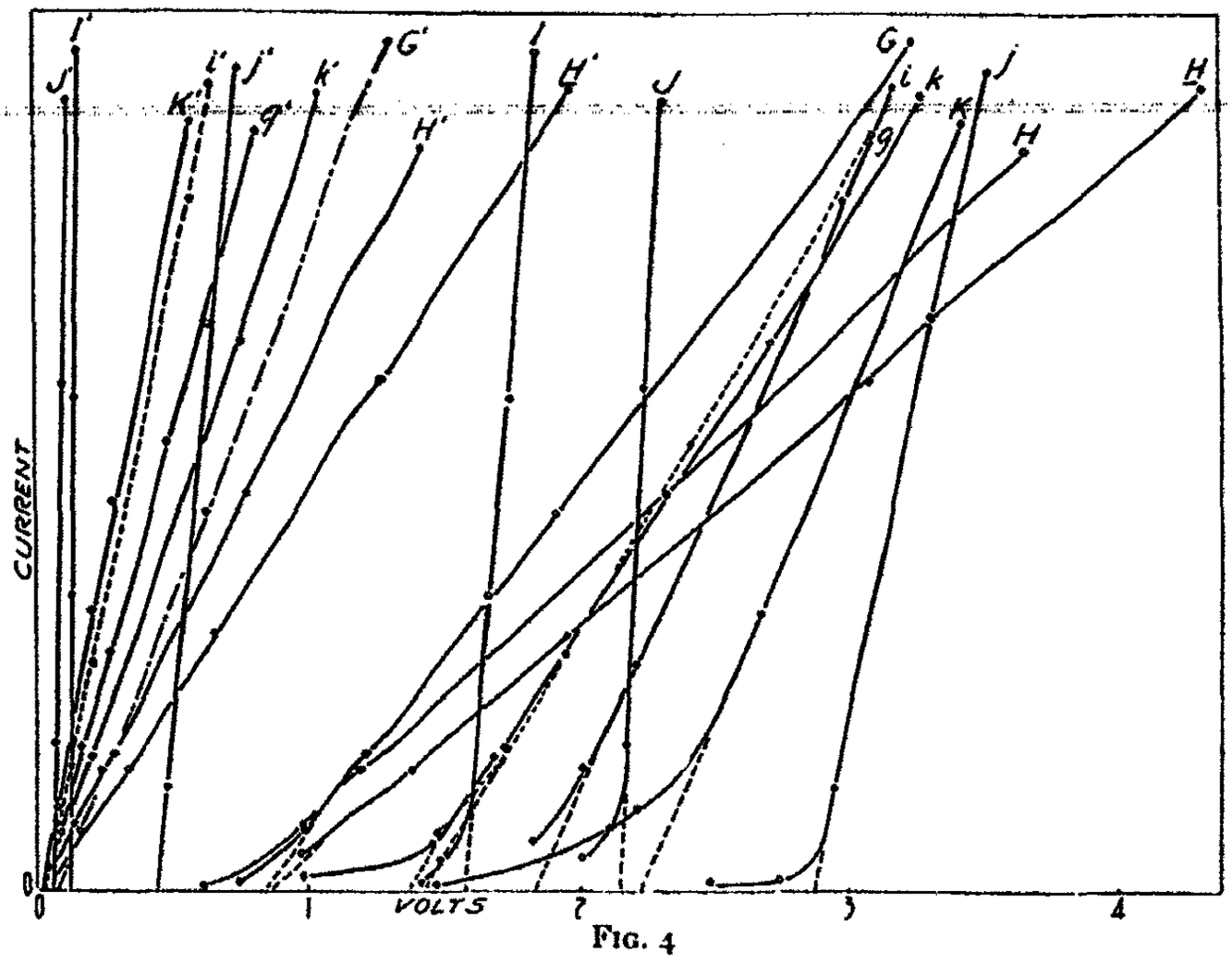



FIG. 4

TABLE H

Mercuric Iodide

| In Ammonia | | |
|---|---|---|
| Current | Volts applied | Volts reference |
| 0.13 | 0.600 | 0.030 |
| 2.40 | 0.976 | 0.150 |
| 4.40 | 1.208 | 0.232 |
| 14.5 | 2.328 | 0.772 |
| 27.0 | 3.674 | 1.412 |

(See Fig. 4 H and H′)

Mercuric Chloride

| In Ammonia | | |
|---|---|---|
| Current | Volts applied | Volts reference |
| 0.29 | 0.972 | 0.106 |
| 0.98 | 1.372 | 0.324 |
| 2.08 | 1.958 | 0.648 |
| 4.15 | 3.094 | 1.280 |
| 6.50 | 4.332 | 1.970 |

(See Fig. 4 *H* and *H′*)

*Lead Nitrate* is readily soluble and forms clear solutions. To avoid the formation of an alloy between the lead and the platinum the cathode was silver plated. Unless this was done it was with great difficulty that the lead could be removed.

TABLE I
Lead Nitrate

| In Ammonia | | | In Water | | |
|---|---|---|---|---|---|
| Current | Volts applied | Volts reference | Current | Volts applied | Volts reference |
| 0.10 | 1.410 | 0.068 | 1.00 | 1.824 | 0.072 |
| 0.37 | 1.494 | 0.094 | 2.50 | 2.012 | 0.138 |
| 3.60 | 1.662 | 0.138 | 4.60 | 2.216 | 0.216 |
| 6.00 | 1.740 | 0.156 | 14.0 | 2.986 | 0.562 |
| 10.2 | 1.842 | 0.170 | 16.3 | 3.192 | 0.632 |

(See Fig. 4 I and I′) (See Fig. 4 i and i′)

*Zinc Nitrate* has a lower dynamic decomposition voltage in ammonia than in water. The metal overvoltage, however, is much greater in water. Four different samples of zinc nitrate and the metal dissolved in nitric acid all gave the same high metal overvoltage.

TABLE J
Zinc Nitrate

| In Ammonia | | | In Water | | |
|---|---|---|---|---|---|
| Current | Volts applied | Volts reference | Current | Volts applied | Volts reference |
| 0.40 | 2.012 | −0.024 | 0.16 | 2.482 | 0.166 |
| 0.78 | 2.102 | +0.046 | 0.20 | 2.738 | 0.390 |
| 1.80 | 2.176 | 0.074 | 1.65 | 2.948 | 0.472 |
| 6.15 | 1.236 | 0.108 | 8.95 | 3.348 | 0.628 |
| 9.60 | 2.312 | 0.132 | 13.0 | 3.560 | 0.740 |

(See Fig. 4 J and J′) (See Fig. 4 j and j′)

*Zinc Iodide* is not very soluble in ammonia. This may be the cause of its high decomposition voltage. The metal overvoltage is not as high in water as in the case of the zinc nitrate.

TABLE K
Zinc Iodide

| In Ammonia | | | In Water | | |
|---|---|---|---|---|---|
| Current | Volts applied | Volts reference | Current | Volts applied | Volts reference |
| 0.10 | 1.474 | −0.380 | 0.50 | 0.986 | −0.330 |
| 1.50 | 2.210 | +0.080 | 1.70 | 1.462 | +0.070 |
| 5.10 | 2.670 | 0.210 | 4.90 | 1.682 | 0.206 |
| 7.10 | 2.850 | 0.286 | 20.0 | 2.702 | 0.750 |
| 14.0 | 3.470 | 0.564 | 29.0 | 3.310 | 1.046 |

(See Fig. 4 K and K′) (See Fig. 4 k and k′)

*Copper Nitrate with Ammonia of Crystallization* gives only one decomposition voltage in liquid ammonia and at this copper was not deposited, the decomposition potential of the cuprous ion to metallic copper evidently not having been reached under the conditions of the experiment. In water there is a break in the curve giving two values for the dynamic decomposition voltage.

TABLE L

Copper Nitrate with Ammonia of Crystallization

| In Ammonia | | | In Water | | |
|---|---|---|---|---|---|
| Current | Volts applied | Volts reference | Current | Volts applied | Volts reference |
| 1.10 | 0.994 | 0.062 | 1.30 | 1.206 | −0.036 |
| 2.90 | 1.230 | 0.162 | 3.20 | 1.416 | +0.076 |
| 5.10 | 1.454 | 0.264 | 6.40 | 1.808 | 0.314 |
| 14.5 | 2.352 | 0.694 | 8.00* | 2.002 | 0.444 |
| 29.0 | 3.656 | 1.326 | 9.90 | 2.190 | 0.554 |
| (See Fig. 5 L and L′) | | | 18.0 | 2.968 | 0.960 |
| | | | 24.2 | 3.560 | 1.290 |
| *Metallic copper appeared at this point. | | | (See Fig. 5 l and l′) | | |

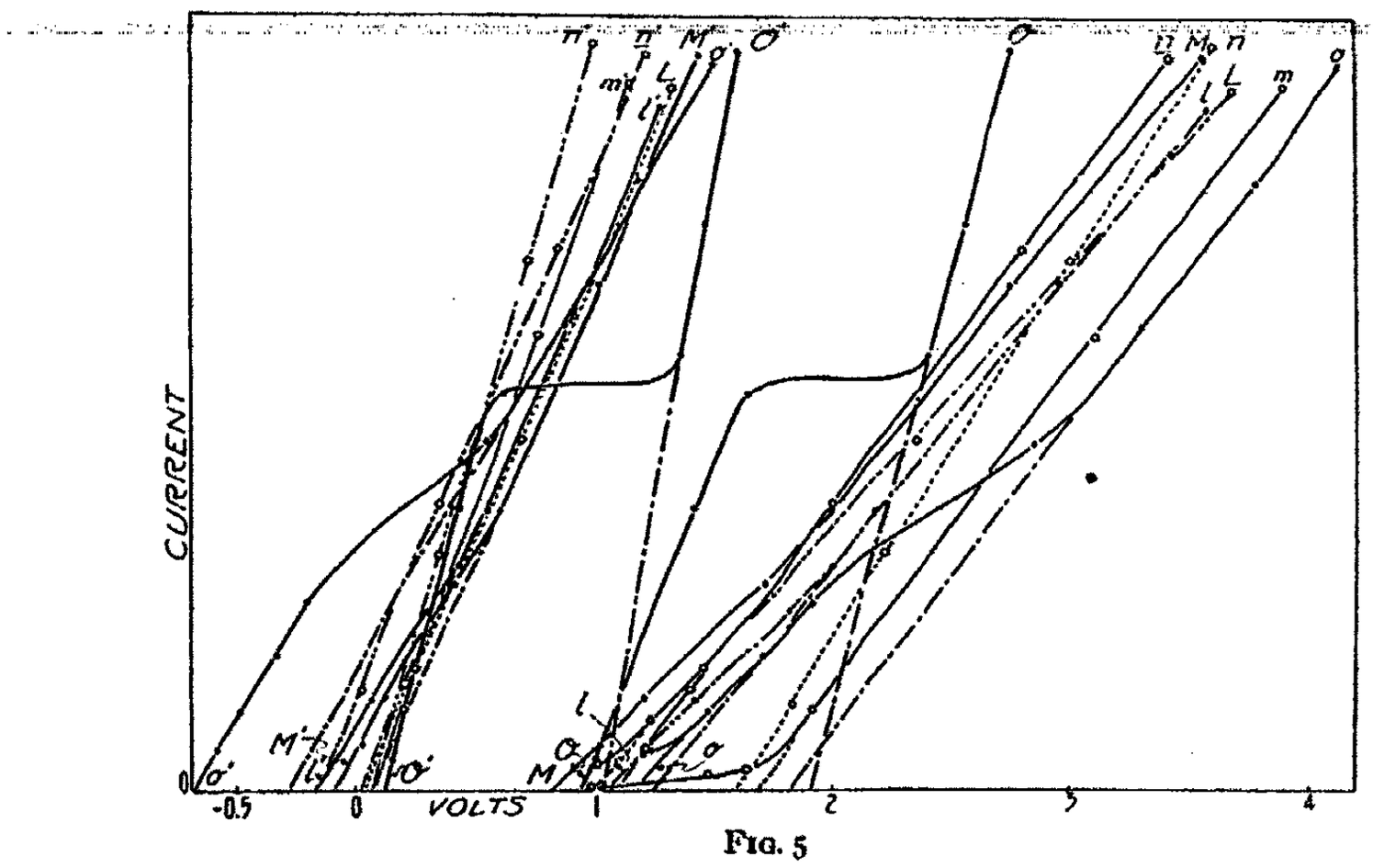



FIG. 5

*Copper Nitrate with Water of Crystallization* gives only one decomposition voltage in water and two in ammonia. This is in contrast to the above Table L.

TABLE M

Copper Nitrate with Water of Crystallization

| In Ammonia | | | In Water | | |
|---|---|---|---|---|---|
| Current | Volts applied | Volts reference | Current | Volts applied | Volts reference |
| 2.00 | 1.004 | 0.032 | 0.20 | 0.968 | 0.020 |
| 4.10 | 1.208 | 0.134 | 0.90 | 1.476 | 0.080 |
| 9.00 | 1.700 | 0.426 | 4.50 | 1.916 | 0.220 |
| 12.2* | 2.000 | 0.602 | 25.0 | 3.098 | 0.756 |
| 22.0 | 2.752 | 1.004 | 39.0 | 3.864 | 4.136 |
| 32.0 | 3.536 | 1.442 | (See Fig. 5 m and m′) | | |
| (See Fig. 5 M and M′) | | | | | |
| *Metallic copper appeared at this point. | | | | | |

*Copper Sulphate* was run in water with and without ammonia in order to determine the effect of the ammonia added. The decomposition voltage is considerably lower when ammonia is present than otherwise.

TABLE N
Copper Sulphate

| In Water without Ammonia | | | In Water with Ammonia | | |
|---|---|---|---|---|---|
| Current | Volts applied | Volts reference | Current | Volts applied | Volts reference |
| 0.30 | 1.626 | 0.144 | 1.20 | 1.200 | −0.082 |
| 1.20 | 1.826 | 0.220 | 3.00 | 1.400 | +0.028 |
| 3.30 | 2.222 | 0.368 | 8.50 | 2.000 | 0.366 |
| 7.30 | 3.000 | 0.714 | 16.0 | 2.800 | 0.836 |
| 10.3 | 3.588 | 0.986 | 21.7 | 3.400 | 1.214 |
| (See Fig. 5 n and n′) | | | (See Fig. 5 *n* and *n′*) | | |

*Ferric Nitrate* could not be completely dehydrated and the dried product was only slightly soluble in both ammonia and in water, possibly due to the formation of basic salts in both cases. There are two decomposition voltages evidently due to the changing of the iron from the active to the passive state. The difference between these decomposition voltages is about equal to the difference in the corresponding overvoltages.

TABLE O
Ferric Nitrate

| In Ammonia | | | In Water | | |
|---|---|---|---|---|---|
| Current | Volts applied | Volts reference | Current | Volts applied | Volts reference |
| 0.70 | 0.982 | 0.170 | 1.35 | 1.236 | −0.590 |
| 6.30 | 1.412 | 0.440 | 2.70 | 1.470 | −0.490 |
| 9.10 | 1.638 | 0.620 | 4.65 | 1.688 | −0.340 |
| 10.0 | 2.408 | 1.360 | 6.50 | 1.912 | −0.204 |
| 13.0 | 2.556 | 1.466 | 12.0 | 2.854 | +0.540 |
| 17.0 | 2.754 | 1.600 | 16.0 | 3.298 | 0.860 |
| (See Fig. 5 O and O′) | | | 21.0 | 3.750 | 1.170 |
| | | | 25.0 | 4.136 | 1.500 |
| | | | (See Fig. 5 o and o′) | | |

Different *Ammonium Salts* were run in liquid ammonia. These salts in ammonia correspond to acids in water.[1] The effect of temperature is small as is shown by the small difference in the dynamic decomposition voltage of ammonium chloride at the boiling point of ammonia (about −33.4° C.) and at −60° C. The ammonium nitrate shows several breaks in the current voltage curve (See R Fig. 6) evidently being caused by different products being formed at the electrodes at the different voltages. The nature of these products were not determined.

[1] Cady: J. Phys. Chem., 1, 707 (1897).

TABLE P

Ammonium Chloride in Ammonia

| At −33.4° C. | | At −60° C. | |
|---|---|---|---|
| Current | Volts applied | Current | Volts applied |
| 0.20 | 1.520 | 1.00 | 1.930 |
| 1.20 | 1.780 | 2.00 | 2.280 |
| 6.90 | 2.212 | 4.00 | 2.530 |
| 17.0 | 2.558 | 6.80 | 2.770 |
| 36.0 | 3.060 | 9.70 | 3.002 |
| 62.0 | 3.712 | 15.5 | 3.490 |
| (See Fig. 6 P) | | (See Fig. 6 P′) | |

TABLE Q

| Ammonium Bromide In Ammonia | | Ammonium Iodide In Ammonia | |
|---|---|---|---|
| Current | Volts applied | Current | Volts applied |
| 1.20 | 1.744 | 1.30 | 1.730 |
| 5.00 | 1.984 | 6.00 | 2.116 |
| 8.70 | 2.200 | 11.2 | 2.318 |
| 20.0 | 2.656 | 16.8 | 2.494 |
| 35.0 | 3.096 | 28.5 | 2.858 |
| 42.5 | 3.320 | 46.0 | 3.366 |
| (See Fig. 6 Q) | | (See Fig. 6 Q′) | |

TABLE R

Ammonium Nitrate in Ammonia

| Curent | Volts applied | Curent | Volts applied |
|---|---|---|---|
| 0.60 | 1.600 | 7.00 | 2.150 |
| 0.90 | 1.650 | 7.90 | 2.200 |
| 1.50 | 1.750 | 10.0 | 2.300 |
| 2.10 | 1.800 | 12.3 | 2.400 |
| 4.10 | 1.950 | (See Fig. 6 R). | |

## Discussion

Whenever we have a galvanic cell with the products on its electrodes in stable form and the solution at definite concentration, a definite difference of potential will be set up. If the processes are reversible, then the application of a slightly greater external potential will cause electrolysis. This potential then represents the static[1] decomposition voltage. When the voltage is increased and thereby also the current density, then, in general, the potential

[1] The term "static" decomposition potential, obtained only at the beginning of electrolysis, is used to differentiate it from the dynamic decomposition potential that would be obtained when considerable electrolysis were taking place.

necessary to continue electrolysis will be greater. This increase may be due to changes in concentration in the immediate vicinity of the electrodes and to irreversible processes taking place on them.

In this investigation the change in concentration near the electrodes was reduced to a minimum by rapidly rotating them. The irreversibility at the cathode was measured by determining the potential existing, during electrolysis, between the cathode and a reference electrode of the same metal as the

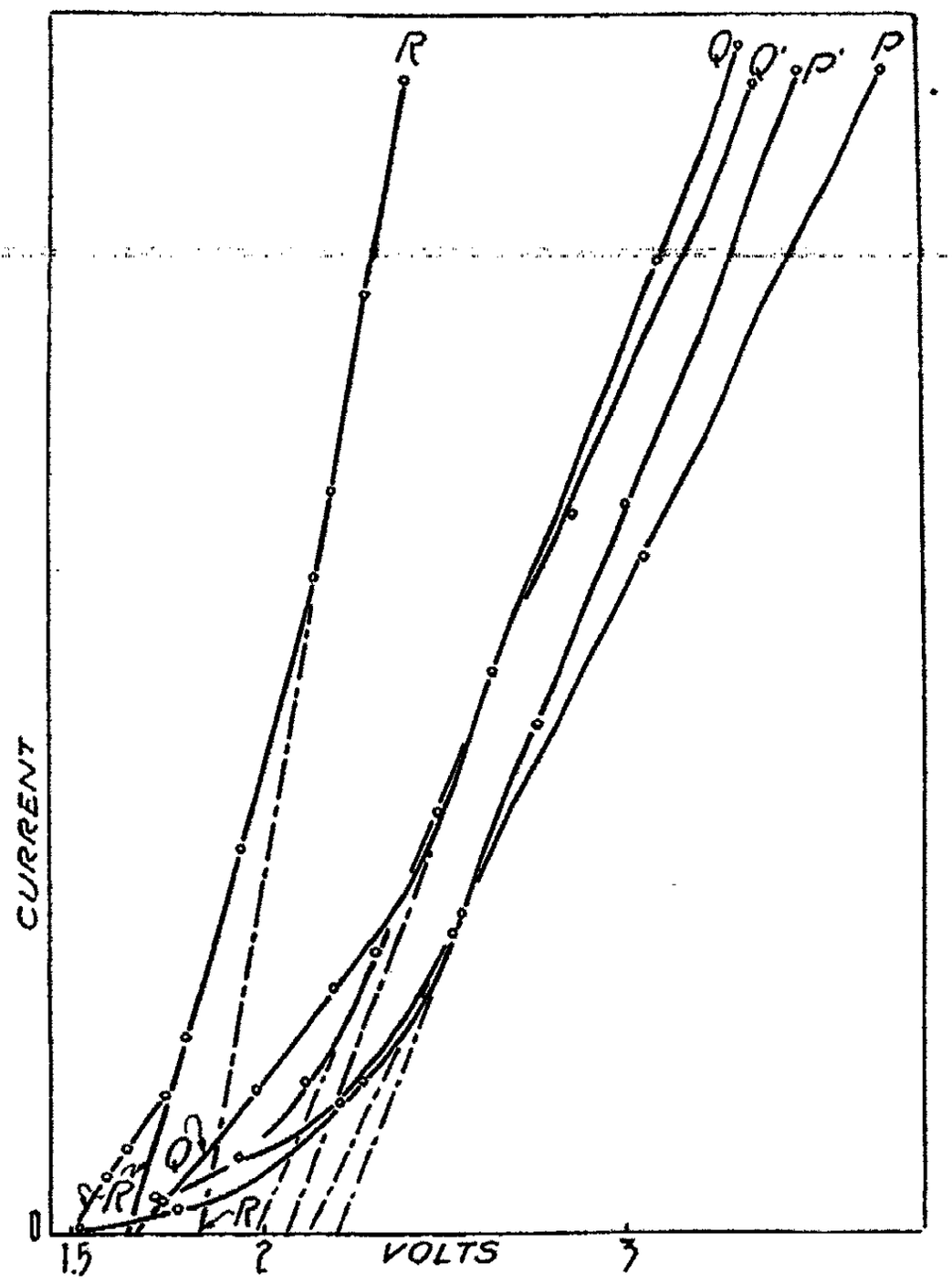



FIG. 6

cation under investigation, all in the same solution. This is known as the metal overvoltage when the metal is deposited on the cathode. An overvoltage of this kind would of necessity be meaningless unless the current density were also given or referred to zero current density (as is done in the present work).

LeBlanc[1] has determined the static decomposition voltages of many salts. He applied a gradually increasing potential and then noticed the potential

[1] Z. physik. Chem., 5, 469 (1890); 8, 299 (1891); 12, 333 (1892).

at which there was a sudden increase in the current. This voltage he then called the decomposition voltage.

Möller,[1] in plotting the current against the voltage applied, found a relation as shown in Fig. 7. The portion a is straight line which then gradually changes into the curved portion r. Later this again becomes straight as is shown by b. Le Blanc called the voltage at the beginning of r the decomposition voltage. This we would call the static decomposition voltage. It is

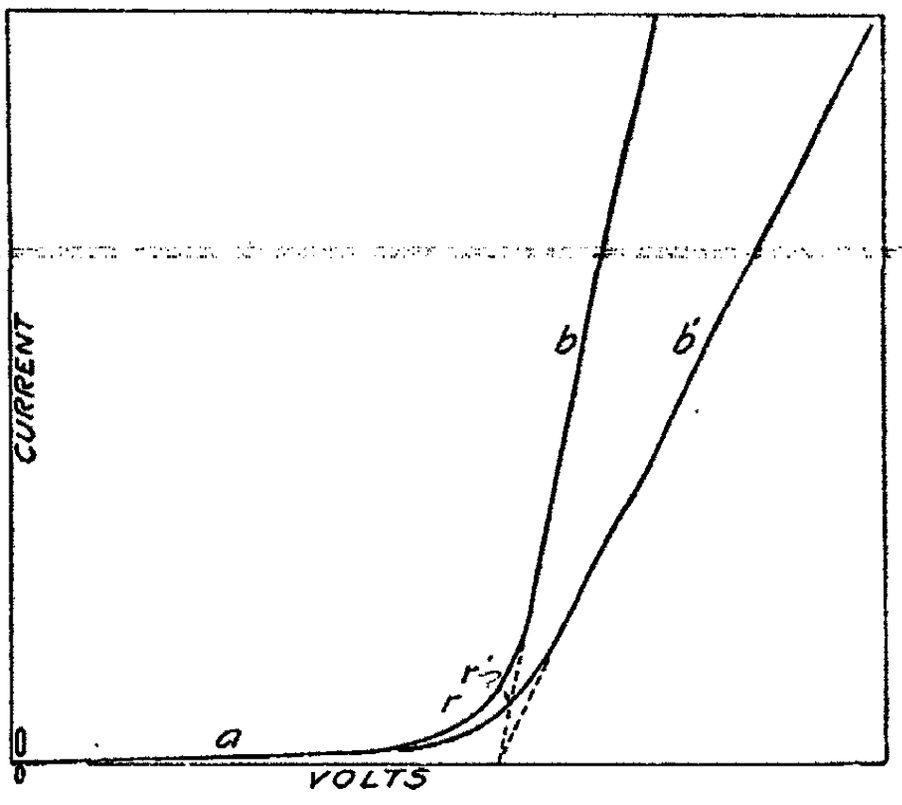



FIG. 7

familiar to investigators in this field that it is practically impossible to duplicate results on static decomposition voltage because the current flowing varies with time and other factors, as will be presently shown.

When a salt like silver nitrate is dissolved in water and a silver electrode immersed in this solution, then some of the silver will go into solution to form silver ions or the ions will be deposited on the metal. This process will continue until the silver has acquired a potential just sufficient to maintain the equilibrium represented by the equation

$$Ag \rightleftarrows Ag^{+}. \qquad (1)$$

On applying an external potential, slightly greater than the potential of the cell, the equilibrium of (1) will be upset, electrolysis will take place and silver will be deposited on the cathode. If equation (1) represented all that was going on, then the current should increase directly with the increase in voltage instead as represented by r Fig. 7. The current would rise sharply from the start and a and b Fig. 7 would meet in a point and show only a break.

What then is the cause of this gradual increase in the current when the potential is increased?

[1] Z. physik. Chem., **65**, 232 (1909).

Suppose that in addition to the equilibrium represented by equation (1) there were another equilibrium between the silver ions and water, like,

$$Ag^{+} + xH_2O \rightleftharpoons Ag(H_2O)_x^{+}. \qquad (2)$$

Suppose also that the concentration of the silver ion were small and that the rate of the above reaction were slow but increased by an increase in potential. Then whenever electrolysis is begun the silver ions in the immediate vicinity of the cathode will be deposited. This is represented by a considerable current for a short time which would of necessity decrease as these free ions were used up. Rotating the electrodes or stirring the solution in some other way will tend to keep up the current but will also prove to be insufficient. Increasing the applied potential still further, will increase the current for two reasons. In the first place the field from which free silver ions are drawn is increased. This would increase the current proportionally to the increase in potential. In the second place the current is increased due to an increase in the rate of the reaction (2) so that more free silver ions are produced. The results of these two factors would be to give us the curve as represented by r Fig. 7. When the rate of the reaction has reached a maximum then any further increase in the applied potential will cause a proportional increase in the current. This condition is represented by b Fig. 7 and is the condition that generally exists during electrolysis.

When measuring static decomposition voltage the processes are practically reversible. By carrying electrolysis a little farther the processes become more irreversible and the applied potential must be increased. This irreversibility is the overvoltage, the metal overvoltage when metal is deposited on the cathode and the oxygen overvoltage when oxygen is liberated at the anode. The dynamic decomposition voltage then is equal to the static decomposition voltage plus the cathode and the anode overvoltages.

In this investigation it was often impossible to continue the electrolysis until the current was steady. During electrolysis there was a change in concentration because of the removal of salt from solution. This would then affect the current. Also, the metal seldom deposited in smooth form. Often crystals would grow on the cathode and, due to the resulting decrease in resistance, the current would steadily increase. It was, therefore, necessary to read the ammeter before it had come to complete rest. Definite intervals of time were therefore used in making the readings.

TABLE S

The Effect of Time on the Current during Electrolysis
Ammonium Chloride in Liquid Ammonia

| Volts applied 1st and 2nd trials | Current, first trial | Current second trial |
|---|---|---|
| 2.200 | 5.2 | 4.0 |
| 2.400 | 8.9 | 8.2 |
| 2.600 | 13.6 | 12.6 |
| 2.800 | 17.2 | 16.8 |

If in a pair of runs the interval of time between the application of the voltage and the reading of the current is different, then there will be curves for each set of intervals. This is illustrated by the curves a, r, b, and a, r′, b′ of Fig. 7. The part b and b′ extrapolated to the line of zero current meet at R. This value is easily reproduced and it is what we have called the dynamic decomposition voltage.

Table S gives data to support this. The first trial was taken with one-fifth minute intervals and the second with three minute intervals between the application of the voltage and the reading of the current. In this investigation all readings were taken at one-half minute intervals.

The dynamic decomposition voltage is the lowest voltage at which, during electrolysis, the electrode processes are the same as they would be when electrolysis with considerable current density were taking place. The dynamic decomposition voltage cannot be measured directly but is obtained by extrapolating the upper straight part of the current-voltage curve upon the line of zero current.

It is customary to determine the metal overvoltage at definite current densities. There is a simple relation between the current density, or what amounts to the same thing in our case the current, and the overvoltage so that the overvoltage at zero current can be determined. This is the potential of the irreversible cell

M (depositing) | MX (solution) | M (reversible)

where M represents the metal under investigation and MX the salt used. The metal overvoltage at zero current density can be determined by extrapolating the upper straight part of the current-voltage (cathode-reference electrode) curve to the line of zero current. For curves of this type see Figs. 3-6.

It was our concern to determine the relation between the decomposition voltages and the metal overvoltages in the two solvents, ammonia and water. The physical nature of the surface of the electrodes was more or less immaterial and since smooth platinum electrodes are easier to clean they were used. Any differences that platinized electrodes would have caused would evidently have been similar in the two solvents and would have compensated each other.

Table T gives us a number of very interesting relations. In only five of the fourteen cases is the decomposition voltage greater in ammonia than in water. Two of these exceptions are iodides and one is a nitrate. In general, this shows that the ions of nitrates are less firmly held in the ammonia than in water solution.

The metal overvoltages are all higher in ammonia than in water with only one exception.[1] This is zinc nitrate which seems to behave abnormally. One would expect that the silver-ammonia, mercuric-ammonia, zinc-ammonia and the copper-ammonia ions would require more energy to desposit from solution in ammonia than the same metals in water. This is the case as the greater metal over-voltage in ammonia shows. In general, a high metal overvoltage in water will have a similarly high value in ammonia.

[1] At first sight it would seem as though copper nitrate with water of crystallization was also an exception but since copper was not depositing on the cathode it would not come in.

When the metal overvoltage is subtracted from the corresponding dynamic decomposition voltage in the same solvent then all the values of the nitrates and the chlorides are lower in ammonia and of the iodides and nitrates are higher. The apparent exceptions in the nitrates are entirely due to their greater metal overvoltage. Whether this difference in the two solvents is due to a difference in the anode overvoltages or an actual difference in static decomposition voltage we are unable to say at present. In the case of the iodides and the nitrites there might be stable ammoniated anions that would require a greater potential to be broken up.

Making comparisons between the values in column (E) of Table T one finds that the difference between these values of the nitrate and the iodide of

## Summary

TABLE T.

| Substance | Dynamic Decomposition Voltages in ammonia (A) | in water (B) | difference (A)-(B) | Metal Overvoltages in ammonia (C) | in water (D) | difference (C)-(D) |
|---|---|---|---|---|---|---|
| $AgNO_3$ | 1.09 | 0.87 | 0.22 | 0.29 | 0.02 | 0.027 |
| $AgNO_2$ | 1.02 | 0.32 | 0.70 | 0.28 | 0.06 | 0.22 |
| AgI | 0.85 | | | 0.05 | | |
| $Ni(NO_3)_2$ | 2.19 | 2.36 | −0.17 | 1.25 | 0.89 | 0.36 |
| $Cd(NO_3)_2$ | 1.87 | 2.36 | −0.49 | 0.23 | 0.16 | 0.07 |
| $CdI_2$ | 1.67 | 1.10 | 0.57 | 0.02 | 0.02 | 0.00 |
| $Hg(NO_3)_2$ | 0.79 | 1.37 | −0.58 | 0.07 | 0.03 | 0.04 |
| $HgCl_2$ | 0.85 | | | 0.05 | | |
| $HgI_2$ | 0.82 | | | 0.02 | | |
| $Pb(NO_3)_2$ | 1.61 | 1.84 | −0.23 | 0.15 | 0.03 | 0.12 |
| $Zn(NO_3)_2$ | 2.09 | 2.86 | −0.77 | 0.03 | 0.48 | −0.45 |
| $ZnI_2$ | 2.23 | 1.36 | 0.87 | 0.08 | 0.04 | 0.04 |
| $Cu(NO_3)_2 \cdot xNH_3$ | 0.94 | 1.08 | −0.14 | (0.02) | (0.01) | 0.01 |
| | | 1.25 | | | 0.01 | |
| $Cu(NO_3)_2 \cdot xH_2O$ | 0.88 | 1.80 | −0.92 | (−0.04) | (0.09) | −0.13 |
| | 1.04 | | | 0.05 | | |
| $CuSO_4$ | | 1.63 | | | (0.09) | |
| $CuSO_4$ with $NH_4OH$ | | 1.06 | | | (−0.16) | |
| $Fe(NO_3)_3$ | 1.02 | 1.19 | −0.17 | 0.15 | −0.8 | 0.23 |
| | 2.02 | 1.78 | 0.24 | 1.32 | −0.2 | 0.44 |
| $NH_4I$ | 2.03 | | | | | |
| $NH_4Cl$ at −33.4 | 2.11 | | | | | |
| $NH_4Cl$ at −60 | 2.17 | | | | | |
| $NH_4Br$ | 1.64 | | | | | |
| | 2.05 | | | | | |
| | 1.53 | | | | | |
| $NH_4NO_3$ | 1.65 | | | | | |
| | 1.88 | | | | | |

TABLE T continued

| Substance | Dynamic Decomposition Voltage minus Metal Overvoltage (A)-(C) (E) | (B)-(D) (F) | (E)-(F) |
|---|---|---|---|
| $AgNO_3$ | 0.08 | 0.85 | −0.05 |
| $AgNO_2$ | 0.74 | 0.26 | 0.48 |
| $AgI$ | 0.80 | | |
| $Ni(NO_3)_2$ | 0.94 | 1.47 | −0.53 |
| $Cd(NO_3)_2$ | 1.64 | 2.20 | −0.56 |
| $CdI_2$ | 1.65 | 1.08 | 0.57 |
| $Hg(NO_3)_2$ | 0.72 | 1.34 | −0.62 |
| $HgCl_2$ | 0.80 | | |
| $HgI_2$ | 0.80 | | |
| $Pb(NO_3)_2$ | 1.46 | 1.81 | −0.35 |
| $Zn(NO_3)_2$ | 2.06 | 2.36 | −0.30 |
| $ZnI_2$ | 2.15 | 1.32 | 0.83 |
| $Cu(NO_3)_2 \cdot xNH_3$ | 0.92 | 1.07 | −0.15 |
| | | 1.24 | |
| $Cu(NO_3)_2 \cdot xH_2O$ | 0.92 | 1.71 | −0.79 |
| | 0.99 | | |
| $CuSO_4$ | | 1.54 | |
| $CuSN_4$ with $NH_4OH$ | | (1.22) | |
| $Fe(NO_3)_3$ | 0.87 | 1.99 | −1.12 |
| | 0.70 | 1.98 | −1.28 |

silver is 0; of cadmium 0.01; of mercury 0.08; and of zinc 0.09. The differences being very small. Making the same comparisons for these salts in water (column (F) Table T) we have for cadmium 1.12 and for zinc 1.04, the iodides being the lower here. It is significant to note the constancy of the differences. Unless unexpected values in overvoltage were obtained, as in the case of zinc nitrate, one could predict that the nitrates and iodides of the same metals would have nearly the same decomposition voltages in ammonia while in water there would be a difference of about one volt, the iodides being the lower.

When electrolysing copper nitrate in ammonia the dynamic decomposition voltage is greater when the salt is anhydrous than when it is moist. This difference is entirely caused by the change in the overvoltage. The cathode process is less irreversible when the copper nitrate is moist than when it is dry. This means that the $Cu(H_2O)_x^{++}$ requires a smaller potential for deposition from solution than when the only ions present are $Cu(NH_3)_x^{++}$. Copper is plated out with greater difficulty when the ammonia is anhydrous as is shown by the fact that under the conditions of the experiment no copper was observed on the cathode when the solution was anhydrous but quite readily when moist.

The dynamic decomposition voltage of copper nitrate in water is affected even more by the presence of a trace of ammonia (ammonia of crystallization)

than the presence of a similar amount of water affected the same in ammonia. The effect on the metal overvoltage is neglible. The process at the cathode is not changed by the presence ammonia but the process at the anode must have been. This is evidently due to the formation of complex anions like $NO_3(NH_3)_x^-$. The copper sulphate was affected very much the same.

Two values of metal overvoltages and dynamic decomposition voltage obtained with ferric nitrate were at first thought to be due to the formation of ferrous ions in the one case and the deposition of free iron in the other. It will be noted (see columns (E) and (F) Table T) that the differences in the decomposition voltage is practically equal to the difference in the metal overvoltage. In the first part of the curve there was only a small amount of metallic iron deposited on the cathode and was then in the active state. Later, either due to the increase in potential or to the cathode having become completely covered with iron, (having become a true iron electrode), the cathode became passive and required a greater potential to deposit the iron upon it. The negative sign before the metal overvoltage is simply caused by the reference electrode (being an iron wire) having different potential than the freshly deposited iron.

The ammonium salts all have the same general dynamic decomposition voltage of about 2.1,[1] volts, just as the acids have one static decomposition voltage in water. The ammonium nitrate has lower dynamic decomposition voltage than the others just as some acids in water solution. As in water, temperature has very little effect on decomposition voltage.

Overvoltages of ammonium salts measured between an ammonium-amalgam electrode and the cathode were not reproducible even at a temperature as low as $-60°$ C.

## Summary

In this investigation the direct method for determining the dynamic decomposition voltages and metal overvoltages has been used. By rapidly rotating the electrodes changes in concentration in their immediate vicinity was avoided.

By plotting the current against voltage applied a curve was obtained which had a straight portion which was then extrapolated to the line of zero current. This point on the zero current line we call the "dynamic" decomposition voltage. When the same thing is done with the current and the cathode overvoltage the metal overvoltage at zero current density is obtained.

The dynamic decomposition voltages and the metal overvoltages of about nineteen salts in liquid ammonia and of fourteen salts in water have been determined by the above method.

The dynamic decomposition voltages of nitrates and chlorides are lower in ammonia than in water. The iodides and the nitrites are exceptions.

The metal overvoltages are generally higher in ammonia than in water.

[1] Even ammonium nitrate indicated a decomposition voltage at this point but the plotted points did not fall on a smooth line.

A trace of water in liquid ammonia and a trace of ammonia in water have great effects on the decomposition voltages and overvoltages of copper nitrate.

Ammonium salts have the same general dynamic decomposition voltage of about 2.1 volts in dry liquid ammonia. Ammonium bromide and ammonium nitrate show several breaks in the current-voltage curve evidently caused by different products being formed on the electrodes.

Temperature has a very slight effect on the dynamic decomposition voltage in liquid ammonia.

I wish to acknowledge my indebtness to Dr. H. P. Cady at whose suggestion and under whose guidance and inspiration this investagition has been carried out.

*Chemical Laboratory,*
*University of Kansas,*
*Lawrence, Kansas.*
*June, 1926.*

# THE CATALYTIC MINIMUM POINT[1]

BY M. BERGSTEIN[2] AND MARTIN KILPATRICK, JR.[3]

On the basis of the protion theory of chemical reactivity Rice[4] has predicted that for those reactions catalyzed both by hydrogen and hydroxyl ions in aqueous solutions the point of minimum catalytic activity (maximum stability of the compound) will be practically the same for all reactions and will be on the acid side. In support of this view the work of Karlsson[5] on ethyl and methyl acetates was cited. Karlson working at 85.55° C. found a minimum for methyl acetate at pH 4.70 and for ethyl acetate at pH 5.10. From the work of Dawson and Powis[6] on the autocatalytic reaction between acetone and iodine Rice calculates a minimum at pH 4.7.

More recently Bolin[7] has reported the following points of maximum stability.

TABLE I

| T °C. | | pH |
|---|---|---|
| 20 | Ethyl ester of formic acid | 4.65 |
| 20 | " " " monochloracetic | 4.8 |
| 20 | " " " aminoacetic | 3.8 |
| 80 | Benzamid | 5.8 |
| 40 | Acetanilid | 6.2 |

On the basis of these results Bolin criticises the unhydrated ion theory as applied to hydrolysis. He states that the results for benzamid are not at all in harmony with the theory of Rice. In order to apply the theory one must assume either that the benzamid affects the hydration of the hydrogen and hydroxyl ions differently or that the dissociation constant of water is changed by the benzamid. In view of the small solubility of the benzamid and the pH values these appear improbable.

Karlsson[8] in a more recent study has repeated his work with ethyl and methyl acetates at lower temperatures and extended the experiments to other esters. He endorses the hypothesis of Euler[9] that the esters may be regarded as amphoteric substances.

---

[1] Contribution from the Havemeyer Chemical Laboratory of New York University and the Chemical Laboratory of Johns Hopkins University. Constructed in part from a thesis presented by M. Bergstein in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Graduate School of New York University, June 1925.

[2] University Fellow, New York University, 1924-25.

[3] National Research Fellow.

[4] Rice: J. Am. Chem. Soc., 45, 2808 (1923).

[5] Karlsson: Z. anorg. Chem., 119, 69 (1921).

[6] Dawson and Powis: J. Chem. Soc., 101, 1502 (1912).

[7] Bolin: Z. anorg. Chem. 143, 201 (1925).

[8] Karlsson: Z. anorg. Chem., 145, 1 (1925).

[9] Euler and Lcurin: Sr. Vet. Akad. Arkiv für Kemi, 7, 30 (1920).

In his earlier work Karlsson reported a distinct shift of the minimum point toward the acid side upon the addition of salts. His later results do not show an appreciable displacement of the minimum point. He attributes the discrepancies to experimental errors in the earlier work. Karlsson's experiments were carried out in buffer solutions. The effect of change of the total equivalent salt concentration on the reaction rate in buffer solutions has been discussed in several recent papers.[1] From the protion theory as presented by Rice we would expect the addition of salts to shift the minimum point to the acid side. In addition the effect of temperature would be to shift the minimum point toward the alkaline side. These considerations would not apply in buffer solution but should apply to the autocatalytic reaction between acetone and iodine in aqueous solution. This reaction has been the subject of a number of studies in acid solution. The reaction in acid solution may be represented by the stochiometric equation

$$CH_3COCH_3 + I_2 + H^+ \longrightarrow CH_3COCH_2I + H^+ + I^-$$

Since the rate of the reaction is independent of the concentration of $I_2$, Dawson and Powis gave as the equation expressing the velocity

$$dx/dt = k(a-x)(c+x)$$

where x is the amount of iodine which has disappeared at time t, a is the initial concentration of acetone, and c is the initial hydrogen ion concentration. In the actual experiments the solution was .1 M in acetone and .005 M in iodine, $x$ being negligible in comparison with $a$. They wrote therefore,

$$dx/dt = k\,a(c+x),$$

and integrating, they obtained

$$\ln \frac{c+x}{c} = kat.$$

Extrapolating to zero time they found $c$ to be equal to $2.1 \times 10^{-5}$ (the mean of three observations). When a small quantity of hydrochloric acid was added to the solution and this concentration of hydrogen ion $2 \times 10^{-5}$ N subtracted from the initial value obtained by extrapolation, c was found to equal $1.4 \times 10^{-5}$. They concluded that the catalytic substance whose activity was represented by this initial hydrogen ion concentration was actually alkaline in nature. When sodium hydroxide was added to the reaction mixture extrapolation yielded a value for c of $2 \times 10^{-6}$. On the whole they could present no satisfactory theory to explain the anomalous catalytic activity of pure water.

Their trouble lay in the fact that they neglected the not inappreciable catalytic activity of the hydroxyl ions in pure water. One of us (M. B.) has shown, in an unpublished research, that the rate of the reaction at pH 7 is approximately twice that at pH 2. As has been indicated above, neutral water is catalytically active. Therefore, the iodine-acetone reaction starting in a neutral solution will proceed at a rapid rate, liberating $H^+$ ion and removing $OH^-$ ion until a point is reached where the products of the concentra-

[1] Brönsted and Teeter: J. Phys. Chem., 28, 579 (1924); Brönsted and King: J. Am. Chem. Soc., 47, 2523 (1925); Kilpatrick: 48, 2091 (1926).

tions of each of them by their catalytic activities are equal. This condition is reached practically instantaneously and cannot be measured because only a minute quantity of iodine has disappeared. At this point the reaction has minimum velocity and gradually accelerates because of the liberation of hydrogen ion. We may consider this point to be the initial point of the reaction. It is actually the catalytic minimum point.

Dawson and Powis's reaction velocity equation is subject to the criticism that it does not recognize the existence of two interdependent catalytic substances at the initial point. If we ascribe half of the effect that they observed to hydrogen ion, we may assume that catalytically neutral water as a hydrogen ion concentration of $10^{-5}$, but this statement is, as the following analysis discloses, far from exact.

Consider the reaction

$$CH_3COCH_3 + I_2 + H^+ + OH^- \longrightarrow CH_3COCH_2I + I^- + 2H^+ + OH^-$$

Let

a = initial concentration of acetone,
c = initial concentration of hydrogen ion,
d = concentration of hydroxyl ion at time t,
x = mols of $I_2$ reacted at time t.
$k_h$ = catalytic activity of hydrogen ion.
$k_{oh}$ = catalytic activity of hydroxyl ion.

Then $dx/dt = (a - x)[k_h(c + x) + k_{oh} d]$. It is known that $(c + x) d = 10^{-14}$ and we may therefore write $d = 10^{-14}/(c + x)$. The constants $k_h$ and $k_{oh}$ are also related. We shall not consider the secondary effect: the formation of iodoform which is also catalyzed by hydroxyl ion in alkaline solution. In catalytically neutral water the rate of reaction due to hydrogen ion is equal to the rate due to hydroxyl ion or

$$k_h c = k_{oh}\, 10^{-14}/c$$

or

$$k_{oh} = c^2/10^{-14} k_h$$

The equation then takes the form

$$\frac{dx}{dt} = k(a-x)\left(c + x + \frac{c^2}{c+x}\right)$$

where $k = k_h$. The solution of this equation is

$$kt = \frac{a+c}{(a+c)^2 + c^2} \ln \frac{\sqrt{(c+x)^2 + c^2}}{a - x} - \frac{c}{(a+c)^2 + c^2} \tan^{-1} \frac{c+x}{c} + K$$

On removing negligible quantities the above equation yields

$$kt = \frac{1}{a} \ln \frac{\sqrt{(c+x)^2 + c^2}}{a - x} + K$$

When $t = 0$, $x = 0$. Therefore, $K = -\frac{1}{a} \ln \frac{c\sqrt{2}}{a}$, and

$$k = \frac{1}{at}\left(\ln \frac{\sqrt{(c+x)^2 + c^2}}{a - x} - \ln \frac{c\sqrt{2}}{a}\right)$$

If the initial molar concentration of acetone is about twenty times that of iodine (as is true in the experiments reported), x is negligible in comparison with a and the equation may be simplified to

$$k = \frac{1}{at} \ln \sqrt{\frac{(c+x)^2 + c^2}{2c^2}}$$

In order to make a determination of c the following device is resorted to. For large values of t (and therefore of x), $c^2$ and 2 cx are negligible in comparison with $x^2$. We may write in this case

$$k\,at + \ln c\sqrt{2} = \ln x$$

It is now possible to determine c without knowing either k or a. Plotting ln x as ordinate against t as abscissa the intercept is equal to $\ln c\sqrt{2}$. Thus c may be determined. The experimental details follow.

Solutions were made up containing .2% potassium iodide and approximately .005 M iodine. To this was added a known weight of acetone from a calibrated pipette, the flask was filled to the mark with distilled water and shaken, and the time was noted as zero time for reactions conducted at 25°. Two samples were removed with a calibrated pipette and titrated against standard sodium thiosulphate using a weight burette. The remainder of the solution was transferred through a quick running siphon to glass-stoppered 80 cc. bottles and the bottles were placed in the thermostat. When the experiments were conducted at temperatures of 30° and above, a time 12 minutes after the bottles were placed in the thermostat was noted as zero time. Two 25 cc. samples were taken from each bottle at regular intervals and the iodine concentrations were determined by titration against sodium thiosulphate. The reactions were stopped by running the solutions into a mixture of acetate buffer of approximately pH 5 and a known weight of thiosulfate. Starch solution was added and the solution titrated to the disappearance of the blue with sodium thiosulphate form a weight burette. When the experiments were run at 25° and 30° the time noted as final for each sample was the time at which the reaction mixture started to run from the pipette into the titrating flask. At higher temperatures the reactions were stoppered by placing the reaction vessels in a freezing mixture. The final time noted in such cases was taken as two minutes after the bottles were placed in the freezing mixture. Check runs were made without any acetone using only the iodine solution and the error due to volatilization of iodine from the glass-stoppered reaction vessels was found to be negligible. Because, as previously stated the hydrogen ion concentration of the water almost immediately came to approximately $10^{-5}$, conductivity water was not required, ordinary distilled water being satisfactory, and any alkalinity due to potassium iodide could be neglected.

The value for the catalytic minimum point in the above experiment was obtained as follows. The drop in titre of the solution in terms of grams of $Na_2S_2O_3$ solution per 24.92 cc. of sample taken was plotted along the logarithmic axis on semi-logarithmic paper against the time plotted along the ordi-

TABLE II

The Autocatalytic Iodine-Acetone Reaction at 25°
2 L of soln. containing 27.54 g. acetone; 2% KI
.005344 M $Na_2S_2O_3$ 24.92 cc. sample

| Time (hours) | Titre | Time | Titre |
|---|---|---|---|
| 0 | 24.66 | 192.7 | 12.25 |
| 26.5 | 24.53 | 196.8 | 11.29 |
| 73.6 | 24.16 | 197.4 | 10.70 |
| 119.9 | 22.77 | 216.1 | 3.10 |
| 142.1 | 21.42 | 220.7 | 1.35 |
| 165.9 | 18.69 | | |

Catalytic minimum point $[H^+]$ $1.57 \times 10^{-5}$; $P_H$ 4.81

nary axis. The points plotted, with the exception of the earlier ones, lay on a straight line which, of course, intersected the logarithmic axis at zero time. The point of intersection represented the apparent drop in titre per 24.92 cc. at zero time. Multiplying this value by the molarity of the sodium thiosulfate and dividing by the volume of the sample taken gives the apparent initial hydrogen ion concentration which is $c\sqrt{2}$. For experiment 103

$$c\sqrt{2} = \frac{.106 \times .005344}{24.92} = 2.274 \times 10^{-5}$$

$$c = 1.57 \times 10^{-5}$$

Table III summarizes a series of experiments carried out in the same manner. In the experiments at 40° C. and 45° C. the concentration of the acetone was .137 M, in the others .237 M. 0.2% KI was present in all experiments.

TABLE III

| Temperature °C. | Minimum point $[H^+] \times 10^{-5}$ | $P_H$ |
|---|---|---|
| 25 | 1.57 | 4.81 |
| 25 | 1.30 | 4.88 |
| 25 | 1.66 | 4.79 |
| 30 | 1.57 | 4.81 |
| 30 | 1.49 | 4.82 |
| 35 | 1.62 | 4.80 |
| 35 | 1.57 | 4.81 |
| 35 | 1.42 | 4.84 |
| 40 | 1.65 | 4.79 |
| 40 | 1.56 | 4.81 |
| 45 | 1.79 | 4.74 |
| 45 | 1.74 | 4.75 |

From Table III it is evident that any variation in the minimum point with temperature is within the experimental error of the measurements. From data on ester hydrolysis the minimum point can be calculated at 20° C. to

be at $P_H$ 5.47 and at 40° C. at $P_H$ 5.35. The mean value determined for the catalytic minimum point in the above experiments ranging from 25° C. to 45° C., is $[H^+] = 1.58 \times 10^{-5}$ or pH 4.8.

Table IV summarizes the results in the presence of neutral salts. All experiments were carried out at 35° C.

TABLE IV

| Salt added Molarity | Minimum point $[H^+] \times 10^{-5}$ | $P_H$ |
|---|---|---|
| 0 | 1.62 | 4.80 |
| 0 | 1.57 | 4.81 |
| .616 KCl | 1.88 | 4.72 |
| 1.267 KCl | 1.94 | 4.72 |
| .830 NaCl | 1.46 | 4.85 |
| 1.635 NaCl | 1.36 | 4.87 |

It is apparent that if there is any neutral salt effect it is within the experimental error of the measurements.

## Other Catalytic Minimum Points

Wijs[1] studying the saponification of methyl acetate in water found a minimum at pH 5.42 at 24.8° C.

Euler and Laurin found pH 5.10 for ethyl acetate at 69.3° C. Hudson[2] studying the mutarotation of glucose, using the data of Osaka[3] and his own calculated the minimum to be at pH 4.64 at 24.7° C. More recently Euler[4] reports the point of minimum catalytic activity for the same reaction at pH 5.0 for 5.2° C.

Bogue[5] in discussing the hydrolysis of collagen noted that the region from pH 4.5 to 6.0 should be avoided as the hydrolysis is very slow at that concentration of hydrogen ions.

The relation of the minimum point to the isoelectric points of proteins has been discussed by Thomas and Kelly.[6]

Many other examples of phenomena which involve consideration of a minimum point in the neighborhood of pH 5 may be found in the fields of industrial and biological chemistry.

One of us (M. B.) wishes to express his thanks to Dr. F. O. Rice of Johns Hopkins University for directing his work in this investigation.

[1] Wijs, Z. physik. Chem., 11, 492 (1893).
[2] Hudson: J. Am. Chem. Soc., 29, 1571 (1907); 31, 1136 (1909).
[3] Osaka, Z. physik. Chem., 35, 702 (1900).
[4] Euler: Z. anorg. Chem., 146, 45 (1925).
[5] Bogue: J. Ind. Eng. Chem., 15, 1154 (1923).
[6] Thomas and Kelly: J. Ind. Eng. Chem., 15, 1148 (1923).

## Summary

1. The catalytic minimum point for the reaction between iodine and acetone has been found to be at pH 4.8.

2. This value is unaffected within the limits of experimental error by either temperature or neutral salts.

3. The results do not support the unhydrated ion theory of catalysis as proposed by Rice.


*New York, N. Y.*
*Baltimore, Md.*

# THE NATURE OF METAL FILMS REDUCED ON THE SURFACES OF SILICA GEL

BY L. H. REYERSON, O. E. HARDER AND L. E. SWEARINGEN

In the chemical laboratory of the University of Minnesota, metallized silica gels are being prepared and used in catalytic studies. It was felt that a study of these metal deposits should be made in order to obtain a better picture of the role of these metals in the catalytic studies. This investigation was begun from that point of view.

The metallized gels which were investigated were usually prepared as described by Latshaw and Reyerson.[1] In this method the reduction to the metallic state is accomplished by the action of adsorbed hydrogen upon the ions of certain metals which lie below it in the electromotive series. Following this reduction the gels were dried at 110° in an atmosphere of hydrogen. In the case of the copper-treated gel it was necessary to complete the reduction in hydrogen at higher temperatures since the first reduction seldom reduced the cupric ion below the cuprous condition. Figs. 1, 2 and 3 are photomicrographs of untreated silica gel granules, platinized gel and copperized gel, respectively. These photographs indicate how completely the metal has impregnated the gel.

The adsorption of hydrogen by silica gel has been measured by Reyerson and Swearingen (to be published later) and found to be less than one cubic centimeter per gram of gel under atmospheric pressure at 0°. On the basis of the value of $6 \times 10^6$ sq. cm. of surface per gram of silica gel as given by Patrick and Grimm,[2] it is evident that the adsorbed hydrogen which reduces the metal ions is of the order of a monomolecular film. An adsorption of hydrogen of this character would not be likely to reduce upon the gel surface a layer of metal atoms which was of any appreciable thickness. Silica gel metallized by this method should have deposited upon its surface metallic films of the order of molecular dimensions. Indeed, microscopic examination failed to identify metal aggregates in the gels impregnated with silver, copper and platinum. In the case of palladium some of the product showed individual aggregates. Fig. 4 shows the spots of palladium in the gel at a magnification of 20 diameters. At this same and higher magnifications the other gels failed to show spots of metal. In the case of palladium this was attributed to the ease of reduction and the possibility of reduction by heat of any of the salt remaining in the gel upon drying.

Metal deposits were also obtained in silica gel by the following methods. The gel was saturated with a concentrated solution of a nickel salt such as the nitrate and the water removed by evaporation. The salt remaining in

[1] J. Am. Chem. Soc., 47, 610 (1925).
[2] J. Am. Chem. Soc., 43, 2144 (1921).

the gel was then reduced by passing a current of hydrogen through the gel heated above 200°. The product was a black appearing gel. A further method consisted in treating the gel with solutions of ammonium chloroplatinate, and evaporation of the water. This impregnated the gel with the solid ammonium chloroplatinate. The gel containing this salt was then heated to about 360° and as a result the salt was decomposed, leaving the metal deposited on the gel surface. Silica gel was also treated in a like manner with chloroplatinic



FIG. 1
Silica Gel (Diameters 6)

acid. The product of the method of treatment was gray to gray-black in color. Microscopic examination of the gels treated by any of these latter methods showed definite metal aggregates in the gel structure. These gels all appeared spotted with sections of clear gel existing around the spots of metal. The appearance is decidedly different from the product obtained by the first method.

It was therefore thought best to examine the various products by means of x-rays. Such an examination might distinguish between the various metal deposits. Accordingly, samples of each of the metallized gels were powdered to pass through standard 200-mesh silk bolting cloth.

The specimen tubes were divided into two compartments by means of a small plug of cotton. The powdered gel sample was introduced into one compartment and pure metal corresponding to the metal on the gel was placed in the other end of the tube as a reference substance. In the case of silica gel itself a sample of powdered sodium chloride was used as a reference substance. Some of the samples were diluted with starch while others were not, and the

results failed to show any difference in the two cases. The silica gel itself was evidently a sufficient diluent. When prepared the tubes were placed in the x-ray diffraction apparatus and exposed to x-rays. The x-ray diffraction apparatus used was a Type V W C Form B, devised by Hull and manufactured by the General Electric Company, Schenectady, New York. The time of exposure for the silica gel itself was ten hours but the usual time for the metallized gels was from fifty to sixty hours. In each case the reference sub-



FIG. 2
Platinum (Diameters 6)

stance gave good patterns on the films. In the case of the silica gel no pattern was obtained. This was also the case for samples of the gel which contained copper, silver and platinum reduced by adsorbed hydrogen. In all cases where the other methods of impregnation were used, definite lines were obtained which corresponded to the lines produced by the reference substance. In the case of the palladium which showed aggregates of metals when examined by the microscope, very fine lines were obtained which corresponded to the lines of the metal palladium.

It is evident from these experiments that reduction by adsorbed hydrogen usually produces metallic deposits upon silica gel which are too thin to give x-ray diffraction patterns or else that the metal is reduced in an amorphous condition. It is more likely that the atoms are arranged in the lattice structure of the metal but that the depth of atoms is too small to give the necessary reinforcement. On the other hand, whenever salts are deposited upon the gel previous to the reduction of these salts to the metallic state, then no



FIG. 3
Copper (Diameters 6)



FIG. 4
Palladium (Diameters 20)

matter how the reduction takes place the metal exists in the crystalline condition in the gel and these metal crystals are of sufficient size to give x-ray diffraction patterns.

In order to decide whether or not the metals deposited by reduction with adsorbed hydrogen were present in too thin a film to give a pattern it was decided to subject the metallized gels successively to the same method of treatment. Accordingly, a sample of platinized gel was retreated by the adsorbed hydrogen method. Then a part of this material was treated a third and fourth time. Samples were kept after each treatment and prepared for x-ray studies. The gels became successively darker on treatment. X-ray examination of these four samples failed to show any lines after fifty hour exposures. Metallic platinum was used as a reference substance in each case. There are two possible explanations of these results. In the first place the successive treatments may deposit metal films on surfaces of the gel which had not received a coating in the previous treatment. In the second place successive treatment may not deepen the atomic layers sufficiently to produce diffraction patterns. The first process is likely to be the predominent one and the darkening of the gel confirms this point of view.

As a final experiment, gels metallized by hydrogen were compared in the same tubes with gels metallized by reducing ammonium chloroplatinate and chloroplatinic acid by heat. In each case lines appeared for the gels having metals reduced by heat while no lines appeared for the gels having metals reduced by adsorbed hydrogen.

## Summary

1. Reduction of the ions of metals by adsorbed hydrogen lays down metallic atoms on silica gel in films too thin to give x-ray diffraction patterns.

2. Impregnation of silica gel by salts of metals or such acids as chloroplatinic acid gives metal aggregates, when the reduction is carried on either by heat or hydrogen, of such size that x-ray diffraction patterns are obtained.

*University of Minnesota*
*Minneapolis, Minnesota,*
*August 1, 1926.*

# ELECTROLYSIS OF DICHROMIC ACID UNDER A MERCURY VAPOR LAMP OF HIGH INTENSITY*

BY GEORGE SHANNON FORBES AND PHILIP ALBERT LEIGHTON

The present research was undertaken to investigate actinic light of high intensity as a possible factor in electrochemical yields, and to test further the alleged activation of chromates by light.

It is impossible to review in this place the hundred or more papers on photovoltaic cells which we have examined. A few of these, however, included electrolysis by an outside source of current. Luggin,[1] for instance, maintained a platinum electrode coated with silver chloride at the potential E by passing the current I in light, and I+i in the dark. The difference he ascribed to light. Schluederberg[2] chlorinated acetic acid, benzene and toluene electrolytically and found little difference in electrochemical yields when diffused daylight alternated with darkness. Bancroft[3] has emphasized the role of depolarizers in initiating or increasing photochemical action, and has demonstrated the analogy between electrochemical and photochemical processes. Baur[4] investigated the depolarization by light of a cathode of gilded silver wire 60 meters long and 0.15 mm thick in acidified uranyl sulfate. Proceeding as did Luggin, he made *i* attain the record value of 0.006 ampere.

Differences of opinion still persist regarding the possibility of activating chromates photochemically. Goldberg,[5] oxidizing quinine with chromic acid, and using light filters, held that such activation occurred. Luther and Forbes,[6] isolating approximately monochromatic light of three wave lengths, and measuring relative intensities and absorptions in all cases, proved that the photochemical activation of chromate must be negligible compared with that of quinine. Plotnikow[7] objected to any findings which belittled the photoactivity of chromates. Winther[8] held that the excited substance in such cases is always the reducing agent even though the oxidizing agent is strongly colored, while Weigert[9] assumed a constellation of electron givers and electron receivers within which exchange occurs. Forbes, Woodhouse and Dean[10] have discussed the data of Luther and Forbes on the hypothesis that activated chromate might be a real, though a minor, factor in the reaction.

* From the Chemical Laboratory of Harvard University and the Jefferson Physical Laboratory.

[1] Luggin: Z. physik. Chem., **23**, 577 (1897).
[2] Schluederberg: J. Phys. Chem., **12**, 574 (1908).
[3] Bancroft: J. Phys. Chem., **12**, 209 (1908).
[4] Baur: Z. Elektrochem., **27**, 72 (1921).
[5] Goldberg: Dissertation, Leipzig (1906).
[6] Luther and Forbes: J. Am. Chem. Soc., **31**, 770 (1909).
[7] Plotnikow: "Allgemeine Photochemie," pp. 215, 416, 583 (1920).
[8] Winther: Z. wiss. Phot. **9**, 229, (1911).
[9] Weigert: Z. physik. Chem., **101**, 414 (1922).
[10] Forbes, Woodhouse and Dean: J. Am. Chem. Soc., **45**, 1891 (1923).

The cathodic reduction of chromic acid to chromic salt in intense actinic light offers several advantages for the purposes of this research. It involves no reducing agent (if one excepts the cathode itself) known to absorb in the visible or long ultraviolet. As chromate is not regenerated at a platinum anode, no diaphragm is required. Numerous studies[1] of the reduction as a "dark" reaction have stressed the accelerating effect of hydrogen ion, which continues to increase up to very high acid concentrations. This effect, usually

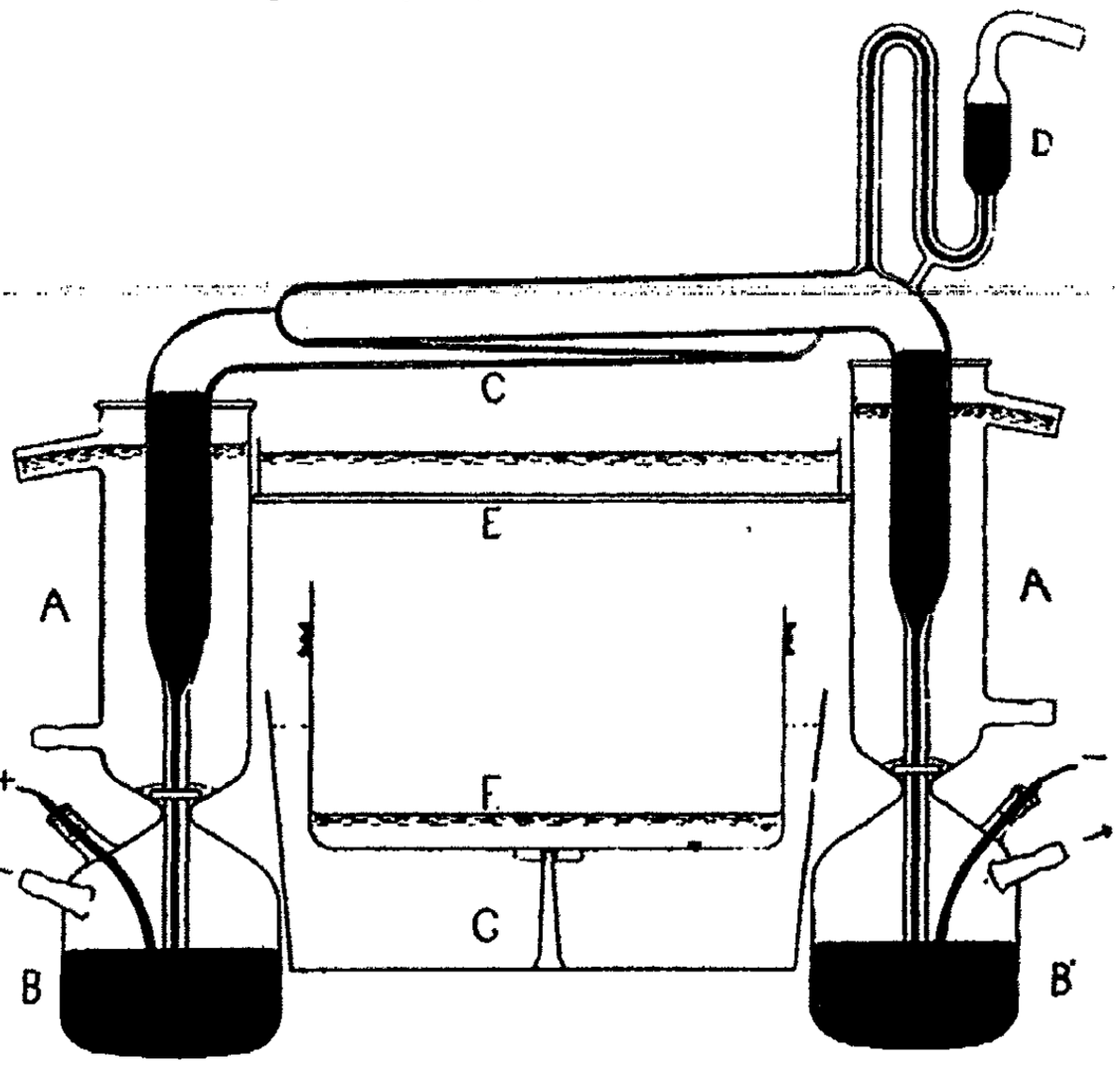



FIG. 1

attributed to formation of chromic acid molecules, indicates that diminished electrochemical yields of chromic salt, with attendant evolution of hydrogen, are not due to depletion, in the stationary film (diffusion layer) adhering to the cathode, of every kind of ion and molecule containing sexavalent chromium. Schluederberg has pointed out the danger of confusion arising from this kind of polarization. We thought that some ion or molecule containing chromate, though unreactive at a cathode while in its normal state, might become reactive electrochemically after being activated by light, and so increase the electrochemical yield.

Apparatus and Method. We evolved a special quartz mercury lamp. Fig. 1, from one previously described elsewhere.[2] Its special feature was a quartz tube, C, 50 cm long and 8 mm in diameter bent into the shape of the

[1] See especially Reese: Am. Chem. J., 22, 162 (1899); Carveth and Curry: J. Phys. Chem., 9, 353 (1905); Askenasy and Revai: Z. Elektrochem, 19, 344 (1913). Vincent (J. Phys. Chem., 29, 875 (1925)) has recently verified much of the above work.

[2] Harrison and Forbes: J. Optical Soc. America, 10, 1 (1925).

letter Z, nearly horizontal, but sloping gradually up to D. Otherwise the construction and mode of operation was much the same. The lamp voltage was ordinarily 460 and the current 3.3 amperes. We could have very considerably increased the intensity, had a line voltage of 1000 volts been available, by operating at 1½ to 2 atmospheres. Some 90% of the total power input of 1500 watts was concentrated into a rectangle about 7 × 12 cm, 15 cm above the reaction mixture. Between these, at E, we interposed a water cell 1 cm in depth, with a bottom of transparent quartz to absorb thermal radiations. Glass vessels have been used in most previous photovoltaic investigations.

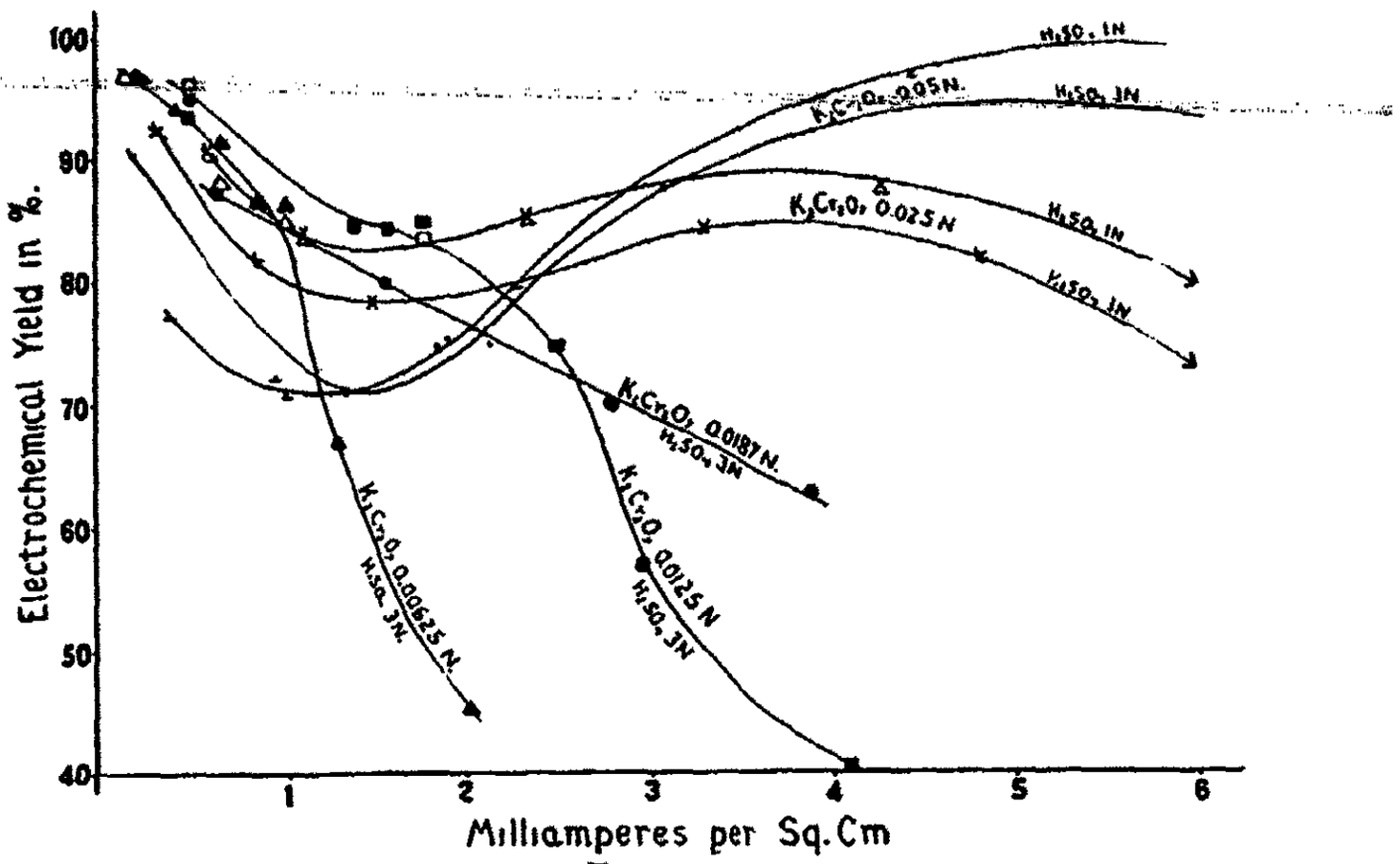



FIG. 2

The reaction mixture 4 mm (sometimes 7 mm deep), was contained in an abbreviated beaker F mounted on a central pivot, rotating at 125 R. P. M. A baffle helped to do away with concentration gradients. The beaker stood in a cooler G, containing ice, and a salt solution of variable concentration by which the mixture could be held at zero within a few tenths of a degree. A device was provided to ensure complete immersion of the thermometer bulb during readings. The illuminated cathode was of bright platinum foil, 5 cm square, mounted on a vertical glass tube containing mercury, and not rotating with the beaker. The anode was a spiral of platinum wire, 5 cm across. A duplicate vessel, having electrodes identical in dimensions, was connected in series and kept in the dark at the same temperature. The rotation of the two beakers was synchronized. As Weigert[1] has demonstrated the marked effect of previous cathodic polarization, both cathodes were before each run polarized for a long time with equal currents. Individual differences in electrodes

[1] Weigert: Z. physik. Chem., 60, 522 (190;)

not so eliminated were cancelled out by exchanging them in successive runs, or in the middle of a single run. In the latter case the adhering solution was washed off and preserved for titration. Such precautions were found to be altogether indispensable. The current was kept constant with the help of a milliammeter, but measured by an iodine coulometer resembling that of Kreider.[1] The iodine liberated was titrated against thiosulfate standardized against resublimed iodine. The residual dichromate in the cells was titrated against carefully standardized ferrous ammonium sulfate, using an outside ferricyanide indicator.

Results. Figure 2 indicates the range of concentrations of reactants and of current densities. A few runs have been entered so that squares and triangles in outline represent electrochemical yields in illuminated solutions, and solid squares and triangles such yields in the dark. In most cases, however, the two were averaged. In nearly all cases duplicate runs agreed within one per cent. The briefest summary of our lengthy investigation must suffice. (Table I).

TABLE I

Average Electrochemical Yields
with lamp described above

| No. of Experiments | Anode | Acid | Illuminated | Not Illuminated | Difference |
|---|---|---|---|---|---|
| 6 | small | 3 n. | 89.91% | 89.13% | 0.78% |
| 1 | " | 1 n. | 82. 5% | 84. 9% | —2.4% |
| 2 | " | 0.1 n. | 75.50% | 74.75% | 0.75% |

Using a small horizontal quartz mercury vapor lamp on a 110 volt circuit and with the same experimental technique, the following results were obtained.

| No. of Experiments | Anode | Acid | Illuminated | Not Illuminated | Difference |
|---|---|---|---|---|---|
| 31 | Small | 3 n | 77.85% | 76.95% | 0.90% |
| 11 | Small | 1 n | 85.25% | 84.93% | 0.32% |
| 11 | Larger | 3 n | 90.30% | 89.56% | 0.74% |

It will be noted that the differences, though within the probable limit of error of our procedure, are uniformly in favor of the illuminated solutions. This outcome might be ascribed wholly to local heating in the "diffusion layer" on the illuminated cathode, which was necessarily overlooked in measuring the average temperature of the stirred portion of the solution. The possibility that part of the difference is due to activation of chromate is not excluded.

Absorption of Light. Table II gives the fraction of incident light reaching the cathode in the case of our two most dilute solutions. The calculations are based upon the extinction measurements of Hantzsch and Clark,[2] with necessary but conservative extrapolations. Unit concentration is 1/6 $K_2Cr_2O_7$ per liter; $d$ is the thickness of the layer in cm.

[1] Kreider: Am. J. Sci (4) 20, 1 (1905).
[2] Hantzsch and Clark; Z. physik. Chem., 63, 367 (1908).

TABLE II

| | c | d | λ = 486 | λ = 436 | λ = 406 | λ = 366 |
|---|---|---|---|---|---|---|
| (1) | 0.0125 | 0.7 | 0.16 | 0.003 | 0.001 | 0.001 |
| (2) | 0.0125 | 0.4 | 0.35 | 0.035 | 0.018 | 0.016 |
| (3) | 0.00625 | 0.7 | 0.41 | 0.056 | 0.035 | 0.028 |
| (4) | 0.00625 | 0.4 | 0.60 | 0.19 | 0.15 | 0.13 |

Presumably the absorption is still greater for shorter wave lengths.

Assuming the lamp to be a point source at an average distance of 15 cm (an assumption less favorable than reality) and that one third of the radiation is of wave-length 436 mμ or less, each $cm^2$ of surface received per second 0.2 watt or $4 \times 10^{17}$ quanta of average wave-length 366 mμ. of which perhaps one tenth reached the cathode in the most favorable case (Case 4, Table II). The typical current density, 0.0004 ampere $cm^{-2}$ furnished $2.5 \times 10^{15}$ electrons per second over the same area. Therefore 160 quanta entered the solution for each electron liberated by the cathode, sixteen of which at most reached the cathode. To carry the calculation further it would be necessary to know the average life period of excited chromate (or dichromate) ion or molecule, if such exist, the thickness of the layer within which electrochemical action occurs, and the speed of diffusion of excited ions or molecules into it.[1] Swensson[2] and also Schlivitch,[3] in their studies of photovoltaic cells, have noted the persistence, in the dark, of the activity of dichromate solutions previously illuminated. If their observations are correctly interpreted, a greater fraction of all the ions or molecules excited in the solution ought to traverse the cathodic diffusion layer while still excited, than would be the case if their life were as brief as that of the average excited atom or molecule.

If we assume (1) that the half per cent increase in electrochemical yield noted is wholly due to activation by light, (2) that the light used excites only forms of chromate not active electrochemically while in a normal state; (3) and that all excited units reach the cathode and react there, it appears that 160 × 1/200 or $3 \times 10^4$ quanta excite but one chromate unit. This large number would be increased by any correction for heating in the diffusion layer, but lowered according to the degree of error in the second and third assumptions. If it were assumed that only one in excited chromate unit in 30,000 passed the diffusion layer, we could even argue that every quantum absorbed produced an excited chromate ion or molecule, but this is highly improbable.

The curves in Fig. 2 are instructive, although all but three of the possible variables are kept constant. The electrochemical yield appears to approach 100% in all cases at minimal current densities. With the least dilute dichromate solutions it passes through a minimum, rises to a maximum, and falls off again. These maxima may be attributed to hydrogen peroxide[4] whose speed

[1] Compare Goldmann: Ann. Physik, 27, 449 (1908).

[2] Swensson: Arkiv. Kemi Mineral: Geol., 6, 21 (1917).

[3] Schlivitch: Compt. rend., 182, 891 (1926).

[4] The controversies regarding hydrogen peroxide formation during electrolysis of dilute sulfuric acid are summarized in Mellor's "Inorganic and Theoretical Chemistry," 1, pp. 923-4.

of formation increases with current density, and whose speed of reaction with dichromate to form chromic salt increases with increasing dichromate concentration. When current density is still further increased, the resultant of these effects cannot keep pace with the increased wastage of current through hydrogen formation. As dichromate concentration decreases, hydrogen ions capture an increasing percentage of electrons liberated by the cathode, so that no second maximum is observed with 0.0187 N dichromate. At high current densities the excess of hydrogen production is 3 N acid as compared with that in 1 N acid is obvious, but the complicated relations at lower current densities would be hard to explain without further data.

We are indebted to the Cyrus M. Warren Fund for a grant covering a part of the cost of the lamp used.

## Summary

A quartz mercury lamp consuming 1500 watts and designed to illuminate very intensely a horizontal surface is described. A quartz water cell intercepted thermal radiation.

Chromate 0.006 to 0.05 N in sulfuric acid 1 N and 3 N was electrolyzed between platinum electrodes at many current densities. Electrochemical yields in light and in darkness were compared in cells otherwise identical in construction, previous polarization, concentrations, stirring, current density, and average temperature.

The plots of electrochemical yields against current density show interesting maxima and minima for the most part explicable in terms of formation of hydrogen and of hydrogen peroxide.

The average of over fifty experiments showed but one half per cent greater efficiency at the illuminated cathode. Part or all of this could be attributed to local heating in the thin diffusion layer above the cathode. Such local heating could not be detected by measuring average temperatures.

Absence of any increase in photochemical yield in light is compatible with light-sensitive chromate if the latter is equally reactive electrochemically before and after excitation.

Granting that the slightly greater electrochemical efficiency in light is in part due to excited chromate, any estimate of the quantum yield requires several assumptions, especially one concerning the life of the excited individual, upon which its chance of reaching the cathode depends.

*Cambridge,*
*Massachusetts.*

# SYNTHETIC FORMALDEHYDE FROM CO + $H_2$
# MECHANISM OF THE SENSITIZED PHOTOCHEMICAL REACTION

Contribution from the Laboratory of Physical Chemistry,
Princeton University.

BY ABRAHAM LINCOLN MARSHALL

This paper deals with a study of the kinetics of the photochemical reaction between hydrogen and carbon monoxide when sensitized by mercury vapor to light of wave length 2536.7 Å from a water-cooled mercury arc. In all the experiments made a circulatory system was used similar to that described in a previous paper[1] and the gases were saturated with mercury at 50°C., the reaction chamber being kept at 80°C..

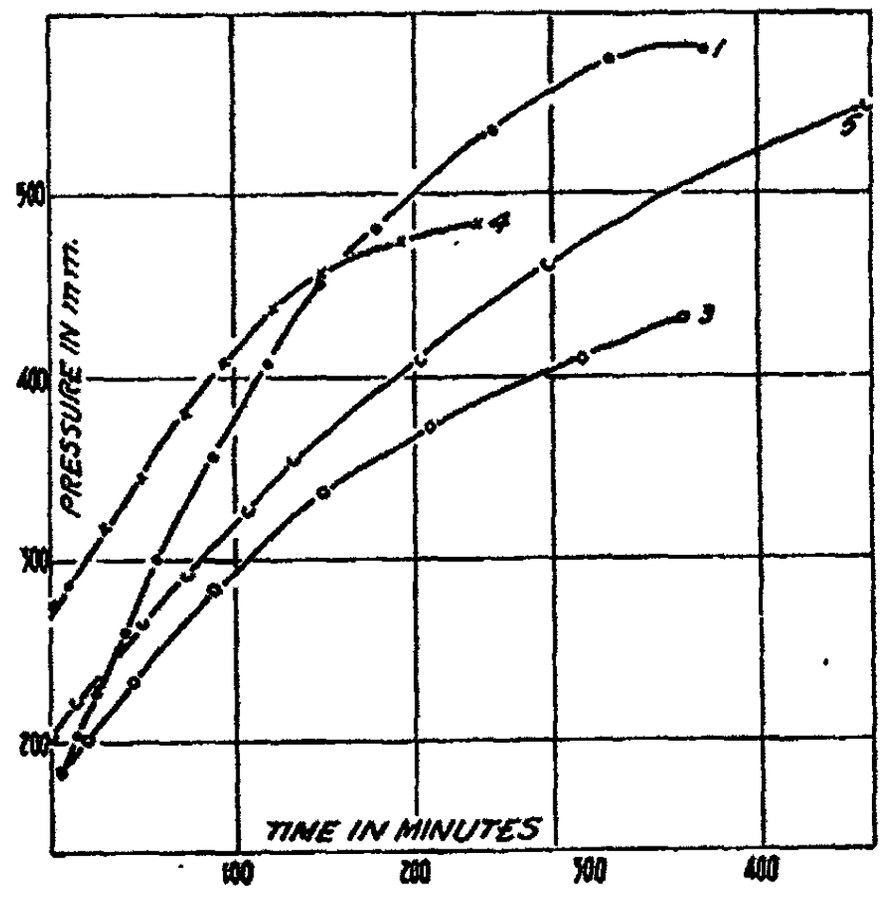



FIG. 1

On account of the variations observed in previous work in the light emitted from a mercury arc completely immersed in water, the lamp in this investigation was only cooled for a distance of 2 cm. above the level of the mercury cathode. Measurements were made of the amount of energy absorbed while the reaction was proceeding in order to be certain that conditions did not change during a given experiment and to be able to calculate the rate for a given energy absorption.

From the data so obtained it is possible to make a number of new calculations of the quantum yield to supplement those already given in a previous

[1] J. Phys. Chem., 30, 1078 (1926).

publication. The volume of the apparatus in all these experiments was 890 c.c. The experimental arrangement and technique were the same as already described.

Table I gives the data for two experiments at slightly varying composition.

TABLE I

| Composition 491 mm. CO, 202 mm. $H_2$ | | | Composition 433 mm. CO, 167 mm. $H_2$ | | |
|---|---|---|---|---|---|
| time | pressure | Δp | time | pressure | Δp |
| 0 | 679 | 6 | 0 | 601 | |
| 5 | 673 | 12 | 5 | 592 | 9 |
| 10 | 661 | 12 | 10 | 583 | 9 |
| 15 | 649 | 12 | 15 | 574 | 9 |
| 20 | 637 | 11 | 30 | 544 | 30 |
| 25 | 626 | 12 | 45 | 515 | 29 |
| 30 | 614 | 21 | 70 | 490 | 25 |
| 41 | 593 | 40 | 85 | 465 | 45 |
| 60 | 553 | 29 | 115 | 420 | 31 |
| 75 | 524 | 28 | 130 | 399 | 18 |
| 90 | 496 | 26 | 145 | 381 | 19 |
| 105 | 469 | 24 | 160 | 362 | 17 |
| 120 | 445 | 43 | 175 | 345 | |
| 150 | 402 | 30 | | | |
| 180 | 372 | 56 | LIGHT ABSORPTION | | |
| 250 | 316 | 37 | cell free from mercury | | 269 |
| 316 | 279 | | reaction proceeding | | 160 |
| 371 | 273 | | absorption | | 109 |
| 416 | 276 | | | | |

| LIGHT ABSORPTION | |
|---|---|
| cell free from mercury | 259 |
| reaction proceeding | 161 |
| absorption | 98 |

The calibration of the thermopile gave 235 scale divisions for an energy density of 47.9 $(10)^{-6}$ watt cm.$^{-2}$. In these experiments the thermopile was 30 cm. from the arc. The average absorption in the two experiments was 1.68 $(10)^{19}$ quanta per minute. In the first experiment 3.76 $(10)^{19}$ molecules of formaldehyde were produced per minute and in the second 2.82 $(10)^{19}$. These values correspond to a quantum yield of respectively 2.24 and 1.68.

A series of ten experiments was made starting with mixtures of varying compositions. The results are plotted graphically in Fig. 1 and are tabulated in Table III. The numbers on the curves refer to the number of the experiment which is given in the first column of the table. The second and third columns give respectively the initial partial pressures of the hydrogen and carbon monoxide and the fourth column the initial rate of reaction in mm. per minute. The remaining columns give reaction velocity constants for various

kinetic equations. The experiments listed in this table took about a week to perform and it can be clearly seen from a reference to the rate in (1) and (10) that the amount of energy absorbed had decreased to about half value in this period. The velocity constants for all four kinetic equations lie within this range and it is impossible to reach a decision from these data.

The results for the final experiment performed are given in Table II.

TABLE II

Composition 510 mm. CO, 279 mm. $H_2$

Thermopile readings: calibration 185 scale divisions for $47.9(10)^{-6}$ watt

| | | | |
|---|---|---|---|
| no mercury present | 253 | " | " cm.$^{-2}$. |
| reaction proceeding | 188 | " | " |
| absorbed | 65 | " | " |

| time | pressure | $\Delta p$ |
|---|---|---|
| 0 | 788 | 8 |
| 5 | 780 | 18 |
| 15 | 762 | 36 |
| 32 | 726 | 26 |
| 44 | 700 | 188 |
| 150 | 512 | 22 |
| 165 | 490 | |

The absorption is at the rate of 1.35 $(10)^{19}$ quanta per minute. The maximum rate of reaction is 2.1 mm. per minute corresponding to 3.3 $(10)^{19}$ molecules of formaldehyde formed or quantum yield of 2.44.

At this point it might be well to point out that the reaction product obtained in the liquid air trap is largely formaldehyde or a polymer which readily yields this gas on heating. In experiment (3) the maximum yield of formaldehyde obtainable was 149 c.c. and 115 c.c. were actually obtained giving a yield of 77 percent. In experiment (5) the theoretical amount was 200 c.c. and 138 c.c. were obtained. Much weight however cannot be placed on the yield of formaldehyde but the results suffice to show that it is the major product of the reaction.

In order to attempt to differentiate between the various possible kinetic equations it was necessary to obtain more reproducible results. It was decided to study only the initial rates of reaction and not to attempt to calculate from point to point along a curve as it is still uncertain that the gases disappear in exactly the ratio of 1 : 1 and for this reason such a method would be indecisive. Two series of experiments were made which are listed in Tables IV and V. Some of these results are plotted in Fig. 2. It will be observed that for the first hour the reaction velocity is practically constant. On inspecting the reaction velocity constants in these tables it is soon seen that those depending on proportionality to $(\sqrt{p_{H_2}})(p_\infty)$ give a much steadier value than those depending on $(p_{H_2})(p_\infty)$. In Table IV the former vary between 25-34 $(10)^5$ and the latter over the range 13-34 $(10)^{-6}$. In Table V the variation is 19-25 $(10)^{-5}$ and 8-29 $(10)^{-6}$ respectively. It would thus seem

TABLE III

| | $p_{H_2}$ | $p_{CO}$ | rate in mm. min.$^{-1}$ | $\sqrt{p_{H_2}}$ | $\frac{\text{rate}}{(p_{H_2})(p_{CO})} \times (10)^7$ | $\frac{\text{rate}}{(p_{H_2})(p_{CO})/(p_{H_2}+p_{CO})} \times (10)^4$ | $\frac{\text{rate}}{(\sqrt{p_{H_2}})(p_{CO})} \times (10)^6$ | $\frac{\text{rate}}{(\sqrt{p_{H_2}})(p_{CO})/(p_{H_2}+p_{CO})} \times (10)^3$ |
|---|---|---|---|---|---|---|---|---|
| (1) | 202 | 491 | 2.37 | 14.2 | 239 | 166 | 339 | 235 |
| (2) | 167 | 433 | 1.90 | 12.9 | 263 | 158 | 339 | 203 |
| (3) | 483 | 194 | 1.27 | 21.9 | 136 | 92 | 298 | 202 |
| (4) | 101 | 673 | 1.47 | 10.0 | 217 | 168 | 217 | 168 |
| (5) | 328 | 319 | 1.27 | 18.1 | 121 | 78 | 219 | 142 |
| (6) | 39 | 674 | 0.60 | 6.2 | 228 | 163 | 141 | 101 |
| (7) | 670 | 43 | 0.42 | 25.9 | 146 | 104 | 378 | 270 |
| (8) | 165 | 168 | 0.46 | 12.8 | 166 | 55 | 213 | 71 |
| (9) | 334 | 316 | 1.25 | 18.3 | 118 | 77 | 215 | 140 |
| (10) | 200 | 500 | 1.19 | 14.1 | 119 | 83 | 168 | 118 |

TABLE IV

| | $p_{H_2}$ | $p_{CO}$ | rate in mm./min. | $\sqrt{p_{H_2}}$ | $\frac{\text{rate}}{(p_{H_2})(p_{CO})} \times (10)^7$ | $\frac{\text{rate}}{\frac{(p_{H_2})(p_{CO})}{[p_{H_2}+p_{CO}]}} \times (10)^4$ | $\frac{\text{rate}}{(\sqrt{p_{H_2}})(p_{CO})} \times (10)^6$ | $\frac{\text{rate}}{\frac{(\sqrt{p_{H_2}})(p_{CO})}{\sqrt{[p_{H_2}+p_{CO}]}}} \times (10)^4$ |
|---|---|---|---|---|---|---|---|---|
| (11) | 124 | 668 | 2.34 | 11.1 | 283 | 225 | 314 | 88 |
| (12) | 639 | 128 | 1.0 | 25.6 | 119 | 94 | 304 | 85 |
| (13) | 243 | 488 | 2.60 | 15.6 | 219 | 160 | 342 | 93 |
| (14) | 503 | 278 | 1.79 | 22.4 | 128 | 100 | 287 | 80 |
| (15) | 355 | 345 | 1.74 | 18.8 | 142 | 100 | 267 | 71 |
| (16) | 54 | 672 | 1.24 | 7.3 | 341 | 247 | 249 | 67 |
| (17) | 327 | 327 | 1.6 | 18.1 | 150 | 98 | 271 | 74 |

TABLE V

| | $p_{H_2}$ | $p_{CO}$ | rate in mm. $min.^{-1}$ | $\sqrt{p_{H_2}}$ | $\frac{\text{rate}}{(p_{H_2})(p_{CO})} \times (10)^7$ | $\frac{\text{rate}}{\frac{(p_{H_2})(p_{CO})}{[p_{H_2}+p_{CO}]}} \times (10)^4$ | $\frac{\text{rate}}{(\sqrt{p_{H_2}})(p_{CO})} \times (10)^6$ | $\frac{\text{rate}}{\frac{(\sqrt{p_{H_2}})(p_{CO})}{\sqrt{[p_{H_2}+p_{CO}]}}} \times (10)^4$ |
|---|---|---|---|---|---|---|---|---|
| (18) | 669 | 51 | 0.27 | 25.8 | 79 | 57 | 204 | 55 |
| (19) | 130 | 631 | 1.81 | 11.4 | 221 | 168 | 252 | 69 |
| (20) | 535 | 224 | 1.11 | 23.1 | 93 | 71 | 214 | 59 |
| (21) | 121 | 656 | 1.76 | 11.0 | 222 | 172 | 244 | 68 |
| (22) | 583 | 148 | 0.82 | 24.1 | 95 | 69 | 229 | 62 |
| (23) | 550 | 175 | 0.81 | 23.4 | 84 | 61 | 197 | 53 |
| (24) | 179 | 608 | 1.57 | 13.4 | 144 | 113 | 194 | 54 |
| (25) | 64 | 158 | 0.293 | 8.0 | 290 | 64 | 232 | 35 |
| (26) | 36 | 82 | 0.075 | 6.0 | 254 | 30 | 152 | 16 |
| (27) | 279 | 510 | 2.15 | 16.7 | 151 | 119 | 252 | 71 |

that the velocity depended in some way on the one-half power of the hydrogen and the first power of the carbon monoxide concentration. This would seem to mean that the velocity depended on the concentration of atomic hydrogen. The mechanism which has previously been postulated for this reaction leads to a kinetic equation of this type,

$$Hg' + H_2 = {}_2H + Hg \qquad (1)\ k_1$$
$$H + CO = HCO \qquad (2)\ k_2$$
$$HCO + H_2 = HCHO + H \qquad (3)\ k_3$$
$$H + H = H_2 \qquad (4)\ k_4$$
$$+ d/dt\,(H) = k_1 I \left(\frac{H_2}{H_2 + CO}\right) + k_3 (HCO)(H_2) \qquad (5)$$
$$- d/dt\,(H) = k_2 (H)\,(CO) + k_4 (H)^2 \qquad (6)$$
$$+ d/dt\,(HCO) = k_2 (H)\,(CO) \qquad (7)$$
$$- d/dt\,(HCO) = k_3 (HCO)\,(H_2) \qquad (8)$$

In the steady state (5) = (6) and (7) = (8). From this it is easy to show that the rate of reaction (3) is governed by the equation

$$d/dt\,(HCOH) = \left(K\sqrt{I\frac{H_2}{H_2 + CO}}\right)(CO) \qquad (9)$$

$$= K(\sqrt{H_2})\,(CO)\sqrt{\frac{I}{H_2 + CO}} \qquad (10)$$

It was not possible to determine the dependence of the reaction velocity on light intensity with the experimental arrangement employed but by varying the total pressure a test could be made on the variation with pressure. Experiments (8), (25) and (26) were made to test this point. With the slow velocities observed in these cases the results are somewhat uncertain but seem to indicate that the rate for a given composition is not inversely proportional to the square root of the total pressure as deduced in (10) but is given by the equation

$$d/dt\,(HCHO) = k(\sqrt{p_{H_2}})\,(p_{CO})$$

If this is the correct equation for the rate the velocity with a given gas mixture should depend on $p^{3/2}$. It therefore becomes important to investigate this reaction at high pressures.

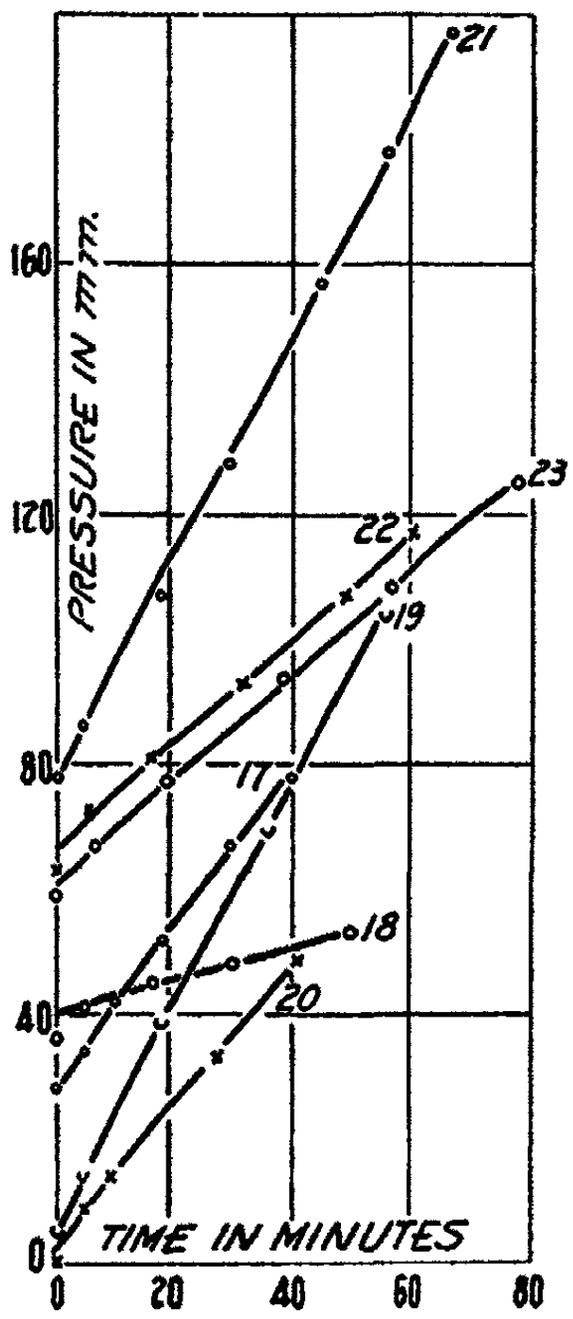


FIG. 2.

Boehm and Bonhoeffer[1] have studied the reactions between atomic hydrogen produced by Wood's method and carbon monoxide or dioxide. Their total pressure was

[1] Z. physik. Chem., 119, 385 (1926).

about 0.4 mm. and they obtain a yield of about a milligram of formaldehyde in 10 minutes. in the two cases. The apparent discrepancy between their results and those of Taylor and Marshall[1] who observed no reaction with carbon dioxide and a relatively rapid reaction with carbon monoxide at 50-60 cm. pressure is easily understood. Since the latter reaction depends on $p^{3/2}$ one would expect that at a fraction of a millimetre the rate would be negligible.

The reaction between carbon dioxide and hydrogen has been reinvestigated with the present set up and it has been found that reaction proceeds at a relatively slow rate. Pressure changes of the order of 2-4 mm. per hour have been observed with a total volume of 1950 c.c.

## Summary

1. A study has been made of the dependence of the rate of formation of formaldehyde on the concentrations of hydrogen and carbon monoxide in the photochemical reaction sensitized by mercury.

2. A theoretical equation has been deduced of the form

$$d/dt\ (HCHO) = K(\sqrt{p_{H_2}})\ (p_{CO})\sqrt{\frac{1}{p\ total}}$$

3. The results obtained indicate that the velocity is determined by the equation

$$d/dt\ (HCHO) = K(\sqrt{p_{H_2}})\ (p_{CO}).$$

4. Such a kinetic equation points clearly to the fact that atomic hydrogen is one of the constituents taking part in the reaction.

In conclusion we would like to acknowledge our indebtedness to the Hanovia Chemical and Manufacturing Company and the General Electric Company for much of the quartz apparatus which has made this and previous investigations possible.

[1] J. Phys. Chem., 29, 1140 (1925).

# THE METHANE EQUILIBRIUM. I

BY R. C. CANTELO

In a series of four papers, the writer proposes to discuss (1) the methane equilibrium with methane as the initial system; (2) and (3) the same equilibrium with ethylene as the initial system; (4) the free energy of formation of methane. The present paper deals with the methane equilibrium when methane is used as the initial system.

Three previous investigations have been carried out on the methane equilibrium at temperatures below 1000° C. Mayer and Altmayer[1] studied it from 300° to 600°C. They derived an equation based on the integration of the van't Hoff Isochore and used their determined equilibrium constants to calculate the constant of integration. Then making use of this equation, viz:

$$21.1 + \frac{18,507}{T} - 5.9934 \ln T - 0.002936\, T = R\ln K_p$$

they derived values for $K_p$ for temperatures from 250° to 850°C. and from these constants calculated the equilibrium concentrations of methane and hydrogen for the given temperatures.

These concentration values are reproduced in part in Table I.

TABLE I

| Temp. °C. | % $CH_4$ | % $H_2$ | Temp. °C. | % $CH_4$ | % $H_2$ |
|---|---|---|---|---|---|
| 250 | 98.79 | 1.21 | 650 | 19.03 | 80.97 |
| 350 | 93.12 | 6.88 | 750 | 6.08 | 93.92 |
| 450 | 76.80 | 23.20 | 850 | 1.59 | 98.41 |
| 550 | 46.69 | 53.31 | | | |

They attack the observation of Bone and Jerdan[2] that in their experiments upon the synthesis of methane at 1200°C, they obtained 1 to 2% methane.

Fonda and van Aernem[3] repeated Mayer and Altmayer's work at 440° and 550°C. using as the initial system a mixture of methane and nitrogen analyzing 2% methane. It is significant that the application of Mayer and Altmayer's equation to their results gave somewhat different constants of integration.

On the other hand, Coward and Wilson[4] studied the equilibrium from 850° to 1100°C. with and without a nickel catalyst; and were able to obtain constants for these temperatures. They claim that below the lower temperature 850°C., "equilibrium cannot be attained within any reasonable period of time." They say: "It is not concluded that it is impossible to prepare carbon in a sufficiently active state to attain equilibrium at this temperature (650°C)

[1] Ber., 40, 2134 (1907).
[2] J. Chem. Soc., 71, 42 (1897).
[3] J. Ind. Eng. Chem., 14, 539 (1922).
[4] J. Chem. Soc., 115, 1380 (1919).

but the claim of Mayer and Altmayer to have succeeded at still lower temperatures is much weakened by the fact that they record no attempt to discover whether their gaseous products contained carbon monoxide.

"If, as it seems fair to assume, therefore, they overlooked carbon monoxide, much of their so-called methane may have had no acutal existence. That there must have been carbon monoxide present in their products can scarcely be doubted in view of, first, the presence of large amounts of nitrogen, and second, their use of somewhat large amounts of nickel, which as is known, is difficult to obtain free from nickel oxide by the reduction of the latter at a low temperature."

This apparent total disagreement admits of a simple explanation. Mayer and Altmayer in the equation derived by them used the value 18,507, which is the heat of formation of methane from graphitic carbon, whereas both they and Coward and Wilson were using amorphous carbon. The heat of formation of methane from amorphous carbon and hydrogen is 21,730 calories, calculated from the mean of Thomsen's and Berthelot's values. If this value for the heat of formation of methane be used, the calculated equilibrium concentrations of methane and hydrogen are in agreement with the work of all the various investigators, as will be shown below.

Saunders,[1] by the application of the Nernst Heat Theorem, developed the following equation for the methane equilibrium and showed that it gave results in agreement with Mayer and Altmayer's determined values:

$$\log K_p = \frac{4,583}{T} - 1.75 \log T + 0.000630\, T - 0.7$$

The extent of the agreement of this equation with Mayer and Altmayer's values is shown in Table II.

TABLE II

| T° K | log $K_p$ calcd. | log $K_p$ exptl. | T° K | log $K_p$ calcd. | log $K_p$ exptl. |
|---|---|---|---|---|---|
| 600 | 2.45 | 2.5 | 900 | −0.21 | −0.37 |
| 800 | 0.45 | 0.40 | 1000 | −0.74 | −1.0 |

The writer has used Saunders' Equation to calculate values for $K_p$ between 500 and 1100°C. for

$$C + 2\,H_2 \rightleftarrows CH_4 + 21,730$$

These are given in Table III.

TABLE III

| T° C | T° K | $K_p$ calcd. | T° C | T° K | $K_p$ calcd. |
|---|---|---|---|---|---|
| 500 | 773 | 4.6 | 850 | 1123 | 0.053 |
| 600 | 873 | 0.93 | 900 | 1173 | 0.036 |
| 700 | 973 | 0.23 | 1000 | 1273 | 0.018 |
| 750 | 1023 | 0.17 | 1100 | 1373 | 0.010 |
| 800 | 1073 | 0.086 | | | |

Table IV contains the equilibrium concentrations of $CH_4$ and $H_2$ calculated by the writer, using the values for $K_p$ given in Table III.

[1] J. Phys. Chem., 28, 1151 (1924).

TABLE IV

| T° C | % $CH_4$ | % $H_2$ | T° C | % $CH_4$ | % $H_2$ |
|---|---|---|---|---|---|
| 500 | 63.9 | 36.1 | 850 | 4.5 | 95.5 |
| 600 | 37.9 | 62.1 | 900 | 3.6 | 96.4 |
| 700 | 16.3 | 83.7 | 1000 | 2.0 | 98.0 |
| 750 | 13.0 | 87.0 | 1100 | 0.8 | 99.2 |
| 800 | 7.5 | 92.5 | | | |

The above table reconciles the results of Mayer and Altmayer, Bone and Coward, Bone and Jerdan, and of Coward and Wilson. It is evident, however, from Coward and Wilson's work, that Mayer and Altmayer were particularly fortunate in obtaining very active catalysts. That such active catalysts are necessary in the study of the methane equilibrium, and that it is quite possible to obtain them has been shown by the writer in two previous papers.[1]

## Experimental

(1) *The Materials Used.*

Methane—The methane used in these experiments was prepared from ethylene. The ethylene itself was prepared by the dehydration of ethyl alcohol by phosphoric acid. The gas so prepared after being purified in the usual manner analyzed 96-98% $C_2H_4$. The methane was prepared from this by passing the ethylene back and forth several times over the nickel catalyst in a fused silica tube kept at about 550°C.

The Nickel Catalyst—The nickel catalyst was prepared from 10 grams of nickel nitrate. This was converted to the oxide, which was dissolved in nitric acid. The solution was evaporated to dryness, the residue taken up in water and again evaporated to dryness. This residue was dissolved in water, asbestos fibres were added, and the dried material was ignited to the oxide. This material was reduced ½ to ¾ hours with hydrogen and was then used as a catalyst.

(2) *Apparatus.*

The heating unit was a cylindrical electric resistance furnace with a lamp-bank in circuit for regulating the current to give any desired temperature. The reaction tube of fused silica fitted fairly tightly into the furnace; and the ends of the furnace were packed with asbestos fibre about the reaction tube. By this means it was possible to obtain a uniform temperature for about 6 inches of the reaction tube. The temperature in the reaction zone was determined in each case by a calibrated iron-constantin thermocouple with millivoltmeter.

The gasometer containing the methane was connected by means of two large calcium chloride tubes with the reaction tube of fused silica. The gas, accordingly, passed from the gasometer thru the U-tubes and then thru the reaction tube, after which it passed thru another pair of calcium chloride tubes into a second gasometer. These gasometers were large calibrated glass bottles fitted with large separatory funnels and drains whereby the pressure

[1] J. Phys. Chem., 28, 1036 (1924); 30, 899 (1926).

was regulated. The admission of liquid thru the funnel of the first bottle increased the pressure on the contained gas, and the opening of the drain of the second bottle removed water and lowered the pressure. By proper regulation gas could be transferred from one to the other at any desired rate. The calcium chloride tubes were provided to keep the gases in the reaction chamber free from water.

(3) *Experimental Method.*

The furnace was heated to the desired temperature and the required resistance for the given temperature was then inserted, and the furnace was allowed to remain untouched for 2 hours to be certain that it was in temperature equilibrium. Hydrogen was then passed at a rapid rate through the whole system except the two gasometers. Following this, the two gasometers were connected in their proper positions, and the methane passed thru the reaction tube over the catalyst. The *same* nickel catalyst was used throughout the present series of experiments.

The gaseous reaction products were passed backwards and forwards over the catalyst (itself placed between two asbestos plugs in the zone of uniform temperature) until there was no further increase in volume, indicating the approach to equilibrium. The products were then circulated in the same way another half-dozen times. The gaseous products were collected in all cases over a 1:1 mixture of glycerol and water.

(4) *Method of Analysis.*

The gas was analyzed for $CO_2$, unsaturated hydrocarbons, $O_2$ and CO by the usual absorption methods. The percentages of $CH_4$ and $H_2$ were determined by combustion at a bright red-heat, by means of granular copper oxide contained in a quartz tube of about 3 c.c. capacity. From the reactions

$$4\,CuO + CH_4\,(g) \longrightarrow CO_2\,(g) + 2\,H_2O\,(l) + Cu\,(s)$$
$$CuO + H_2\,(g) \longrightarrow H_2O\,(l) + Cu\,(s)$$

it is evident that the contraction after combustion is equal to the c.c. of hydrogen; and that the contraction after treatment with KOH is equal to the c.c. of methane.

(5) *Experimental Results.*

The values for $K_p$ given in Table VIII are probably too high for the folllowing reasons. The same catalyst was used throughout the experiments and the gas used in each case contained some carbon monoxide. Subsequent experiments in which the carbon monoxide content was increased to 12% proved that this gas poisoned the nickel catalyst for the methane equilibrium. It is significant to note that Chakravarty and Ghosh[1] found that in the synthesis of methane from carbon monoxide and hydrogen, in the presence of a nickel catalyst, very little carbon was deposited.

In view of the above, therefore, it appeared advisable to repeat the equilibrium experiments, using fresh catalyst each time. It was felt, too, that if it were possible to produce the methane in direct contact with the catalyst, the

[1] Quart. J. Indian Chem. Soc., 2, 150 (1925).

chances of actually reaching equilibrium would be increased greatly. These conditions were produced successfully with ethylene as the initial system. These experiments will be discussed in the third paper of this series, and the equilibrium values obtained by the writer will be compared with the calculated values and with those obtained experimentally by Mayer and Altmayer.

TABLE V

Original Gas

| $CO_2$ | $C_2H_4$ | $O_2$ | CO | $CH_4$ | $H_2$ | $N_2$ |
|---|---|---|---|---|---|---|
| 0.0[1] | 6.3 | 0.0 | 1.2 | 25.8 | 58.4 | 8.3 |
| 0.0[2] | 0.0 | 0.0 | 2.6 | 50.4 | 38.5 | 8.5 |
| 0.9[3] | 0.0 | 0.0 | 1.8 | 36.1 | 57.7 | 3.5 |
| 1.0[4] | 0.0 | 0.0 | 2.1 | 55.8 | 34.6 | 6.5 |
| 0.0[5] | 0.0 | 0.0 | 1.5 | 22.6 | 72.2 | 3.7 |

Final Gas

| $CO_2$ | $C_2H_4$ | $O_2$ | CO | $CH_4$ | $H_2$ | $N_2$ | $K_p$ |
|---|---|---|---|---|---|---|---|
| 0.4[1] | 0.0 | 0.0 | 1.6 | 24.4 | 64.4 | 9.2 | ——— |
| 0.5[2] | 0.0 | 0.0 | 1.4 | 32.7 | 58.9 | 6.5 | 0.95 |
| 0.5[3] | 0.0 | 0.0 | 1.9 | 24.4 | 68.8 | 5.3 | 0.51 |
| 0.0[4] | 0.0 | 0.0 | 2.7 | 20.4 | 69.0 | 7.9 | 0.43 |
| 0.0[5] | 0.0 | 0.0 | 1.2 | 9.2 | 85.9 | 3.7 | 0.12 |

[1] 565°, no catalyst. [2] 565°, nickel. [3] 670°, nickel. [4] 670°, nickel. [5] 770°, nickel.


## Summary

By the use of Saunders' Equation for the equilibrium between methane and amorphous carbon and hydrogen, equilibrium constants have been calculated for this reaction, for temperatures from 500° to 1100° C. From these constants the equilibrium concentrations of methane and hydrogen have been calculated for the same series of temperatures, and it is shown that these values reconcile the apparent disagreement of previous investigators. Experiments are described in which the equilibrium constants for three temperatures were determined by the use of methane as the initial system and a specially prepared nickel as the contact agent.



*Department of Chemistry,*
*University of Cincinnati,*
*Cincinnati, Ohio.*


## Errata

In the article, "Thermal Decomposition of Methane. II," which appeared in this JOURNAL for July, 1926 the following correction should be made:

The expression $\frac{(1.92 - y)^2}{(.04 + y)} = K_p = 55.5$ (for 1000°C) middle of page 900 should read $\frac{(1.92 - y)^2}{(.04 + y/2)} = K = 55.5$, y by trial is found to be between 0.04 and 0.05.


R. C. CANTELO

*University of Cincinnati*

1-80

# VISCOSITY MEASUREMENTS OF CERTAIN SOLS IN PRESENCE OF ELECTROLYTES

BY D. N. CHAKRAVARTI AND N. R. DHAR

In previous papers[1] we have shown that the influence of electrolytes on the viscosities of sols can be satisfactorily explained from the following assumptions:—

(1) Other things being identical, the uncharged substance is more hydrated than the sol.

(2) The greater the hydration of a substance, the greater is the viscosity.

(3) When a sol adsorbs an ion carrying the same charge as the sol because of chemical affinity, the charge on the sol is increased and consequently according to our view the viscosity of the sol should decrease.

TABLE I

$Cr(OH)_3$ sol and $Al(NO_3)_3$. Concentration of the sol = 3.92 grms. per litre
Viscosity of water = 0.00937. Temperature 23.1°C

| Mixtures of sol (*Chromium hydroxide*) and KCl | Time of rise in the capillary tube in minutes | Time of fall in the capillary tube in minutes | Viscosity |
|---|---|---|---|
| 20 c.c. sol and 5 c.c. water | 7/17 | 13/38 | 0.01079 |
| 20 c.c. sol and 5 c.c. N/2000 $Al(NO_3)_3$ | 7/8 | 14/7 | 0.01077 |
| 20 c.c. sol and 5 c.c. N/1000 $Al(NO_3)_3$ | 6/55 | 13/58 | 0.01048 |
| 20 c.c. sol and 5 c.c. N/500 $(Al(NO_3)_3$ | 6/59.5 | 14/00 | 0.01060 |
| 20 c.c. sol and 5 c.c. N/200 $Al(NO_3)_3$ | 7/1 | 13/44 | 0.01056 |
| 20 c.c. sol and 5 c.c. N/100 $Al(NO_3)_3$ | 7/9 | 13/44 | 0.01069 |
| 20 c.c. sol and 5 c.c. N/50 $Al(NO_3)_3$ | 8/48 | 13/59 | 0.01227 |
| 20 c.c. sol and 5 c.c. N/25 $Al(NO_3)_3$ | 9/1 | 14/6 | 0.01256 |

It will thus be seen that we have completely given up the orthodox view that the viscosity is greater in the charged condition than in the uncharged one. Our view is specially applicable to hydrophobe colloids.

In a recent paper[2] we have presented the results obtained on the measurements of viscosity carried on with sols of vanadium pentoxide, antimony

[1] Z. Elektrochem., 31, 261; J. Phys. Chem., 29, 1556 (1925).
[2] Z. anorg. Chem., 152, 393 (1926).

TABLE II

Gum dammar sol and HCl.
Concentration = 0.89 gram per litre. Temp. 23.1°C
Viscosity of water = 0.00937

| Mixtures of sol and HCl | Time of rise in the capillary tube in minutes | Time of rise in the capillary tube in minutes | Viscosity |
|---|---|---|---|
| 20 c.c. sol and 5 c.c. water | 7/51 | 15/34 | 0.01186 |
| 20 c.c. sol and 5 c.c. N/2000 HCl | 7/40 | 15/24 | 0.01163 |
| 20 c.c. sol and 5 c.c. N/1000 HCl | 8/4 | 16/45 | 0.01239 |
| 20 c.c. sol and 5 c.c. N/500 HCl | 8/8 | 17/11 | 0.01254 |
| 20 c.c. sol and 5 c.c. N/200 HCl | 8/12 | 17/28 | 0.01268 |

TABLE III

Gum dammar sol and $K_4Fe(CN)_6$
Concentration of the sol = 0.81 grm. per litre. Temp. 23.1°C
Viscosity of water = 0.00937

| Mixtures of sol and $K_4FC(CN)_6$ | Time of rise in the capillary tube in minutes | Time of fall in the capillary tube in minutes | Viscosity |
|---|---|---|---|
| 20 c.c. sol and 5 c.c. water | 7/34 | 15/53 | 0.01165 |
| 20 c.c. sol and 5 c.c. M/2000 $K_4Fe(CN)_6$ | 7/57 | 16/52 | 0.01231 |
| 20 c.c. sol and 5 c.c. M/1000 $K_4Fe(CN)_6$ | 7/48 | 16/49 | 0.01182 |
| 20 c.c. sol and 5 c.c. M/500 $K_4Fe(CN)_6$ | 7/26 | 15/47 | 0.01145 |
| 20 c.c. sol and 5 c.c. M/200 $K_4Fe(CN)_6$ | 7/20 | 15/23 | 0.01115 |
| 20 c.c. sol and 5 c.c. M/100 $K_4Fe(CN)_6$ | 7/20 | 15/34 | 0.01130 |
| 20 c.c. sol and 5 c.c. M/50 $K_4Fe(CN)_6$ | 7/25 | 15/54 | c.01146 |
| 20 c.c. sol and 5 c.c. M/25 $K_4Fe(CN)_6$ | 7/32.5 | 15/59.5 | 0.01166 |
| 20 c.c. sol and 5 c.c. M/10 $K_4Fe(CN)_6$ | 7/41 | 16/7 | 0.01182 |

sulphide, mastic, and gum dammar in presence of potassium chloride of different concentrations. The experimental results show that there is a fall in viscosity when small quantities of KCl are added to the sol. When larger quantities are added the viscosity rises. Hence in all cases in all the above sols it has been observed that the viscosity of the sols passes through a minimum when the concentration of the electrolyte is increased. The experimental results have been explained on the view that the uncharged substance is more hydrated than the sol, the greater the hydration the greater the viscosity and that when the charge on the sol is increased the viscosity decreases by the adsorption of ions carying the same charge as the sol.

In the present communication we are submitting the results obtained in the viscosities of sols of (1) $Cr(OH)_3$, (2), gum dammar, (3) gamboge, (4) ferric arsenate, (5) stannic hydroxide (prepared in the cold and in the boiling condition), (6) Congo-red (dialysed and undialysed.) (7) Nile blue, (dialysed and undialysed) and (8) thioflavin in presence of different electrolytes.

TABLE IV

Gamboge sol and KCl

Concentration of the sol = 1 grm. per litre. Temp. 23.1°C

Viscosity of water 0.00937

| Mixtures of sol and KCl | Time of rise in the capillary tube in minutes | Time of fall in the capillary tube in minutes | Viscosity |
|---|---|---|---|
| 20 c.c. sol and 5 c.c. water | 7/46 | 16/36 | 0.01202 |
| 20 c.c. sol and 5 c.c. N/1000 KCl | 7/40 | 16/25 | 0.01187 |
| 20 c.c. sol and 5 c.c. N/500 KCl | 7/40 | 16/19 | 0.01185 |
| 20 c.c. sol and 5 c.c. N/200 KCl | 7/41 | 16/26 | 0.01189 |
| 20 c.c. sol and 5 c.c. N/100 KCl | 7/51 | 16/19 | 0.01206 |
| 20 c.c. sol and 5 c.c. N/50 KCl | 7/51 | 16/27 | 0.01209 |
| 20 c.c. sol and 5 c.c. N/20 KCl | 7/52 | 16/30 | 0.01210 |
| 20 c.c. sol and 5 c.c. N/10 KCl | 7/53 | 16/36 | 0.01215 |

TABLE V

Gamboge sol and HCl.
Concentration of the sol = 0.83 grm. per litre. Temp. 23.1°C
Viscosity of water 0.00937

| Mixtures of sol and HCl | Time of rise in the capillary tube in minutes | Time of fall in the capillary tube in minutes | Viscosity |
|---|---|---|---|
| 20 c.c. sol and 5 c.c. water | 7/34 | 16/13 | 0.01169 |
| 20 c.c. sol and 5 c.c. N/4000 HCl | 7/30 | 16/25 | 0.01170 |
| 20 c.c. sol and 5 c.c. N/2000 HCl | 7/34 | 16/35 | 0.01180 |
| 20 c.c. sol and 5 c.c. N/500 HCl | 7/48 | 16/42 | 0.01188 |
| 20 c.c. sol and 5 c.c. N/200 HCl | 7/42 | 16/57 | 0.01194 |
| 20 c.c. sol and 5 c.c. N/100 HCl | Coagulated. | | |

N. B. In this case no decrease in viscosity is observed even with 5 c.c. N/400 HCl. This is probably due to the fact that HCl being a very good coagulant the influence of ions carrying the same charge as the sol ($Cl'$) is not observable.

TABLE VI

Gamboge sol and $K_4Fe(CN)_6$
Concentration of the sol 0.83 grm per litre. Temp. 23.1°C
Viscosity of water 0.00937

| Mixtures of sol and $K_4Fe(CN)_6$ | Time of rise in the capillary tube in minutes | Time of fall in the capillary tube in minutes | Viscosity |
|---|---|---|---|
| 20 c.c. sol and 5 c.c. water | 7/24 | 16/13 | 0.01169 |
| 20 c.c. sol and 5 c.c. M/1000 $K_4FeCN()_6$ | 7/38 | 16/5 | 0.01176 |
| 20 c.c. sol and 5 c.c. M/500 $K_4Fe(CN)_6$ | 7/8 | 15/30 | 0.01111 |
| 20 c.c. sol and 5 c.c. M/200 $K_4Fe(CN)_6$ | 7/33 | 15/44 | 0.01159 |
| 20 c.c. sol and 5 c.c. M/100 $K_4Fe(CN)_6$ | 7/41 | 15/58 | 0.01178 |
| 20 c.c. sol and 5 c.c. M/50 $K_4Fe(CN)_6$ | 7/43 | 15/57 | 0.01181 |
| 20 c.c. sol and 5 c.c. M/25 $K_4Fe(CN)_6$ | 7/44 | 15/58 | 0.01184 |
| 20 c.c. sol and 5 c.c. M/10 $K_4Fe(CN)_6$ | 7/48 | 16/1 | 0.01192 |

TABLE VII

Ferric arsenate sol and $Al(NO_3)_3$
Concentration of the sol 7.6 grms. per litre. Temp. 23.1°C
Viscosity of water 0.00937

| Mixtures of sol and $Al(NO_3)_3$ | Time of rise in the capillary tube in minutes | Time of fall in the capillary tube in minutes | Viscosity |
|---|---|---|---|
| 20 c.c. sol and 5 c.c. water | 7/13 | 14/43 | 0.01101 |
| 20 c.c. sol and 5 c.c. M/1000 $Al(NO_3)_3$ | 7/9 | 14/10 | 0.01080 |
| 20 c.c. sol and 5 c.c. M/500 $Al(NO_3)_3$ | 7/11.5 | 14/48 | 0.01099 |
| 20 c.c. sol and 5 c.c. M/250 $Al(NO_3)_3$ | 7/12.5 | 14/53 | 0.01103 |
| 20 c.c. sol and 5 c.c. M/100 $Al(NO_3)_3$ | 7/12 | 14/55 | 0.01104 |
| 20 c.c. sol and 5 c.c. M/50 $Al(NO_3)_3$ | 7/22 | 14/57 | 0.01121 |
| 20 c.c. sol and 5 c.c. M/25 $Al(NO_3)_3$ | 7/27 | 15/1 | 0.01131 |

TABLE VIII

Stannic hydroxide sol and KCl
(The sol was prepared by boiling a well-washed precipitated hydroxide with $NH_4OH$ till no smell of ammonia.)
Concentration of the sol 6.89 grms of $SnO_2$ per litre. Temp. 25°C

| Mixtures of sol and KCl | Time of rise in the capillary tube in minutes | Time of fall in the capillary tube in minutes | Viscosity |
|---|---|---|---|
| Water | | | 0.00894 |
| 20 c.c. sol and 5 c.c. water | 6/41 | 14/55 | 0.00949 |
| 20 c.c. sol and 5 c.c. N/1000 KCl | 6/43 | 14/52 | 0.00951 |
| 20 c.c. sol and 5 c.c. N/500 KCl | 6/33 | 14/43 | 0.00933 |
| 20 c.c. sol and 5 c.c. N/200 KCl | 6/33 | 14/58 | 0.00937 |
| 20 c.c. sol and 5 c.c. N/50 KCl | 6/44 | 15/13 | 0.00960 |
| 20 c.c. sol and 5 c.c. N/20 KCl | | Coagulated. | |

TABLE IX

Stannic hydroxide sol (heated) and $K_4Fe(CN)_6$

(Different viscosity tube used in the following experiments.)

Concentration of the sol 6.89 grms of $SnO_2$ per litre. Temp. 25°C

| Mixtures of sol and $K_4Fe(CN)_6$ | Time of rise in the capillary tube in minutes | Time of fall in the capillary tube in minutes | Viscosity |
|---|---|---|---|
| Water | | | 0.00894 |
| 20 c.c. sol and 5 c.c. water | 5/4 | 10/50 | 0.00971 |
| 20 c.c. sol and 5 c.c. M/1000 $K_4Fe(CN)_6$ | 5/0 | 10/39 | 0.00957 |
| 20 c.c. sol and 5 c.c. M/500 $K_4Fe(CN)_6$ | 4/57.5 | 10/47 | 0.00934 |
| 20 c.c. sol and 5 c.c. M/200 $K_4Fe(CN)_6$ | 5/5 | 10/49 | 0.00972 |
| 20 c.c. sol and 5 c.c. M/100 $K_4Fe(CN)_6$ | 5/51 | 11/26 | 0.01068 |

TABLE X

Stannic hydroxide[1] sol and KCl

(The sol was prepared by the action of KOH and $SnCl_4$ solutions and then dialysed for about 7 days till alkali and chloride are free in the outside water.)

Concentration of the sol 0.89 grm $SnO_2$ per litre. Temp. 25°C

| Mixtures of sol and KCl | Time of rise in the capillary tube in minutes | Time of fall in the capillary tube in minutes | Viscosity |
|---|---|---|---|
| Water | | | 0.00894 |
| 20 c.c. sol and 5 c.c. water | 4/56.3 | 9/48.5 | 0.00924 |
| 20 c.c. sol and 5 c.c. N/1000 KCl | 4/55 | 9/56 | 0.00927 |
| 20 c.c. sol and 5 c.c. N/500 KCl | 4/55 | 9/47 | 0.00920 |
| 20 c.c. sol and 5 c.c. N/200 KCl | 4/57.5 | 9/56 | 0.00930 |
| 20 c.c. sol and 5 c.c. N/100 KCl | 5/1.5 | 10/6 | 0.00943 |
| 20 c.c. sol and 5 c.c. N/50 KCl | 5/6.6 | 10/6.3 | 0.00946 |
| 20 c.c. sol and 5 c.c. N/25 KCl | 5/13 | 10/11 | 0.00970 |
| 20 c.c. sol and 5 c.c. N/10 KCl | 5/17 | 10/16 | 0.00978 |

[1] Graham: Pogg. Ann., 123, 538 (1864).

TABLE XI

Congo red and KCl

(Congo red was dialysed for about 10 days till the sol was free from chloride)

Concentration of the sol 10.2 grms per litre. Temp. 25°C

| Mixtures of sol and KCl | Time of rise in the capillary tube in minutes | Time of fall in the capillary tube in minutes | Viscosity |
|---|---|---|---|
| Water | | | 0.00894 |
| 20 c.c. sol and 5 c.c. water | 5/17 | 10/28 | 0.00988 |
| 20 c.c. sol and 5 c.c. N/2000 KCl | 5/20 | 10/20 | 0.00081 |
| 20 c.c. sol and 5 c.c. N/500 KCl | 5/26 | 10/24 | 0.01004 |
| 20 c.c. sol and 5 c.c. N/100 KCl | 5/28 | 10/30 | 0.01011 |

TABLE XII

Congo red and KCl

Concentration of the sol 8.95 grms per litre. Temp. 25°C

| Mixtures of sol and KCl | Time of rise in the capillary tube in minutes | Time of fall in the capillary tube in minutes | Viscosity |
|---|---|---|---|
| Water | | | 0.00894 |
| 20 c.c. sol and 5 c.c. water | 4/58.5 | 9/53 | 0.00930 |
| 20 c.c. sol and 5 c.c. N/1000 KCl | 4/55.3 | 9/54.5 | 0.00925 |
| 20 c.c. sol and 5 c.c. N/200 KCl | 4/56.3 | 9/51.3 | 0.00926 |
| 20 c.c. sol and 5 c.c. N/100 KCl | 4/56 | 9/55 | 0.00927 |
| 20 c.c. sol and 5 c.c. N/50 KCl | 5/3 | 9/54 | 0.00939 |
| 20 c.c. sol and 5 c.c. N/25 KCl | 5/3.5 | 9/54.3 | 0.00941 |
| 20 c.c. sol and 5 c.c. N/10 KCl | 5/4 | 9/54.3 | 0.00943 |

TABLE XIII

Nile blue and KCl

Concentration of the sol 6.56 grms per litre. Temp. 25°C

| Mixtures of sol and KCl | Time of rise in the capillary tube in minutes | Time of fall in the capillary tube in minutes | Viscosity |
|---|---|---|---|
| Water | | | 0.00894 |
| 20 c.c. sol and 5 c.c. water | 4/56 | 9/54.5 | 0.00905 |
| 20 c.c. sol and 5 c.c. N/500 KCl | 4/53.6 | 9/52 | 0.00899 |
| 20 c.c. sol and 5 c.c. N/200 KCl | 4/54 | 9/54 | 0.00902 |
| 20 c.c. sol and 5 c.c. N/100 KCl | 4/57 | 9/55 | 0.00907 |
| 20 c.c. sol and 5 c.c. N/50 KCl | 4/59 | 9/57 | 0.00913 |
| 20 c.c. sol and 5 c.c. N/10 KCl | 5/3 | 10/1 | 0.00923 |

TABLE XIV

Nile blue and KCl

(The sol was dialysed for about 10 days till it was free from chloride.)

Concentration of the sol 7.18 grms per litre. Temp. 25°C

| Mixtures of sol and KCl | Time of rise in the capillary tube in minutes | Time of fall in the capillary tube in minutes | Viscosity |
|---|---|---|---|
| Water | | | 0.00894 |
| 20 c.c. sol and 5 c.c. water | 5/3 | 9/40.5 | 0.00911 |
| 20 c.c. sol and 5 c.c. N/1000 KCl | 4/56.5 | 9/41 | 0.00899 |
| 20 c.c. sol and 5 cc. N/200 KCl | 4/58 | 9/47 | 0.00906 |
| 20 c.c. sol and 5 c.c. N/100 KCl | 5/12 | 9/51 | 0.00920 |
| 20 c.c. sol and 5 c.c. N/40 KCl | 5/13.5 | 9/52.5 | 0.00940 |
| 20 c.c. sol and 5 c.c. N/20 KCl | 5/15 | 9/56 | 0.00949 |

TABLE XV

Thioflavin and KCl

Concentration of the sol 4.04 grms per litre. Temp. 25°C

| Mixtures of sol and KCl | Time of rise in the capillary tube in minutes | Time of fall in the capillary tube in minutes | Viscosity |
|---|---|---|---|
| Water | | | 0.00894 |
| 20 c.c. sol and 5 c.c. water | 5/11 | 10/13 | 0.00945 |
| 20 c.c. sol and 5 c.c. N/2000 KCl | 4/55 | 9/57.5 | 0.00905 |
| 20 c.c. sol and 5 c.c. N/1000 KCl | 4/57.5 | 10/5 | 0.00915 |
| 20 c.c. sol and 5 c.c. N/200 KCl | 5/3 | 10/8 | 0.00926 |
| 20 c.c. sol and 5 c.c. N/100 KCl | 5/4.5 | 10/8.5 | 0.00932 |
| 20 c.c. sol and 5 c.c. N/40 KCl | 5/7 | 10/10 | 0.00936 |
| 20 c.c. sol and 5 c.c. N/40 KCl | 5/12 | 10/14 | 0.00948 |

The viscosity measurements were carried on at 23.1°C. and 25°C and the experimental arrangement was the same as that of Farrow[1] with certain modifications.

## Observations

From the foregoing results it will be seen that when small quantities of electrolytes are added to a sol, in every case there is an appreciable fall in the viscosity. We are of the opinion that this is due to the increase in the charge on the particles of the sol, by the adsorption of ions carrying the same charge as the sol. It has definitely been proved in publications[2] from this laboratory that usually when small quantities of electrolytes are added to a sol the adsorption of ions carrying the same charge as the sol is more prominent than the adsorption of ions carrying the opposite charge. The increase in the charge of the sol is associated with the decrease in the viscosity of the sol in presence of electrolytes.

On the other hand, when greater quantities of electrolytes are added, the adsorption of ions carrying the opposite charge is more prominent than that of the ions carrying the same charge. Consequently the charge on the sol is decreased and hence the viscosity of the sol goes on increasing with the increase in concentration of the electrolyte until the coagulation point is reached.

[1] J. Chem. Soc., 101, 347. (1912).
[2] J. Phys. Chem., 29, 435, 659 (1925).

One remarkable fact is however observed when gum dammar and gamboge sols are treated with $K_4Fe(CN)_6$. We find that there is always first a very slight increase and then a decrease in the viscosity of the sols. This is probably due to the fact that tetravalent ferrocyanide ions, which possess greater number of unit charges than univalent chloride ions are not adsorbed by the colloid particles because of great electrical repulsion. Consequently the potassium ions are first adsorbed by the sol, and, when the charge on the negatively charged colloid particles has slightly decreased, the adsorption of highly charged ferrocyanide ions become possible with the result that the charge on the colloid particles rise rapidly and hence a marked decrease is now observed in the viscosity.

It is well known that the hydrophobe colloids have only a very slight effect on the viscosity of water; on the other hand the hydrophile colloids are much more viscous than water. Moreover, the hydrophobe colloids like ferric hydroxide, arsenious sulphide, etc., do not appreciably effect the surface tension of water while some of the gelatinous colloids and emulsions have a marked effect. The addition of soap or gelatine in small quantities to water markedly decreases the surface tension of water. The experiments of Morgan and Woodward[1] have shown that the surface tension of serum obtained from the blood of hounds, dogs, men, sheep, horses, etc., at 37°C varies from 45.4 to 46.3 dynes/cm. whilst that of water at that temperature is 70 dynes/cm. Moreover Rothlin[2] has shown that the viscosity of serum obtained from sheep, pig, deer, etc., at 37°C varies from 1.8 to 2.08 times that of water at the same temperature.

In the case of inorganic electrolytes we also find that the greater the viscosity of a solution the less is its surface tension. Thus it will be seen that solutions of lithium salts in general are more viscous than water or solutions of potassium chloride of the same concentrations. Moreover lithium salts increase the surface tension of water only to a much smaller extent than potassium salts. The viscosity of solutions of acids like sulphuric, hydrochloric, nitric, is appreciably greater than that of water but their surface tensions are much less than that of water. Moreover similar relations are observable with other salts.

It is well known that lithium salts are more hydrated than potassium salts and it seems likely also that acids will be more hydrated than the salts. Consequently it seems that measurement of surface tension and viscosity would supplement each other in ascertaining the degree of hydration on the substance.

In a previous paper an explanation of the viscosity results of hydrophile colloids in presence of electrolytes has been advanced, based on the natural disintegration tendency of such substances. It must be emphasized that the changes in a colloidal system need not always consist in the diminution of the dispersion. Occasionally we find that the particles become smaller with the

[1] J. Am. Chem. Soc., 35, 1294 (1913).
[2] Pflüger's Archiv, 179, 195 (1920).

lapse of time and this has hitherto been obtained only in the case of hydrophile colloids. In the case of hydrophobe colloids the particles of the sol have small affinity for the dispersion media; let us take the case of water and arsenious sulphide. The particles of arsenious sulphide have only a low affinity for water and consequently the particles do not combine appreciably with water and form larger aggregates and consequently the viscosity is practically the same as that of water. Moreover as the particles of arsenious sulphide have only slight tendency to take up the particles of water, hence the presence of arsenious sulphide particles does not appreciably alter the surface forces between the water particles. On the other hand the case is different when the particles of gelatine or any other hydrophile colloid are brought in contact with water. The water particles have an appreciable affinity for the particles of gelatine and they attract each other and form bigger groups containing water and gelatine, and the viscosity of the medium is much greater. Moreover, because of the chemical affinity of water particles for gelatine, the surface forces between the individual water particles is greatly disturbed by the presence of gelatine particles, which have a great affinity for water particles, and consequently the surface tension of water is greatly decreased. In a previous paper it has been assumed that particles of a sol of gelatine or albumin have a natural tendency to disintegrate. In the case of these substances, according to this point of view, the suspended particles are becoming smaller and smaller because of their natural tendency for disintegration and consequently these smaller particles will adsorb more water and consequently the viscosity of the system will increase. This is the probable explanation of the fact that the viscosity of a 5% solution of isoelectric gelatine increases rapidly at the temperature of 20°C or below as observed by Pauli, Loeb and others. It seems pretty certain from the view advanced in this paper that the surface tension of the same isoelectric gelatine should decrease with time. In this connection it will be interesting to note that recently Johnston and Peard[1] and Card[2] have shown that the surface tension of gelatine passes through a maximum practically at the isoelectric point.

When an acid like hydrochloric is added to isoelectric gelatine, the gelatine becomes positively charged by adsorption of $H^{\cdot}$ ions and the particles of gelatine containing more charge than the particles of isoelectric gelatine have a greater tendency for disintegration than the particles of the isoelectric gelatine itself. Consequently in presence of HCl the degree of dispersion of gelatine or albumin and along with it the hydration and viscosity will also increase. Now in presence of larger quantities of HCl the adsorption of negatively charged $Cl'$ ions by the positively charged gelatine will become appreciable and consequently the charge on the gelatine will not rise proportionately with the increase in concentration of HCl. And after a time the charge will have a tendency to decrease due to the adsorption of $Cl'$ ions. As

[1] Biochem. J., 19, 281, (1925).
[2] Atti R. Accad. Lincei, (6), 1, 729 (1925).

soon as the charge on the gelatine is decreased the degree of dispersion will also decrease and along with it the hydration and viscosity will also decrease. Exactly similar results have been obtained with substances like gelatine, albumin, etc., in presence of alkalies. Hence we can explain the viscosity of gelatine, albumin, etc., curves with a definite maximum when varying quantities of acids or alkalies are added. From the foregoing pages it will be at once clear that the surface tension of gelatine or albumin in presence of increasing quantities of acids or alkalies should show a minimum at those points where the viscosity curve shows a maximum. Hence it is clear that a maximum of viscosity and a minimum of surface tension are closely associated and depend on the amount of hydration of gelatine or albumin.

It has been repeatedly asserted that many sols become more viscous with the progress of dialysis when the originally prepared sol is subjected to dialysis, and it sometimes happens as the dialysis goes on that the sol sets to a clear jelly. Thus we have observed that when a sol of vanadium pentoxide prepared according to the method of Biltz,[1] by the action of hydrochloric acid on ammonium vanadate, is allowed to dialyse, the sol becomes more and more viscous and when the dialysis is complete the sol sets to a clear jelly. Moreover, when a sol of ceric hydroxide is obtained by the hydrolysis of a solution of cerium ammonium nitrate and is allowed to dialyse, the viscosity of the sol goes on increasing as the dialysis progresses and finally it may set to a stiff jelly. All these results can be satisfactorily explained from our view that the less the charge on the sol the greater is its viscosity. When a sol is dialysed, the adsorbed electrolyte goes out and consequently the electrical charge on the sol decreases and along with it the viscosity increases. It seems very probable that the surface tension should also decrease with the progress of dialysis of such sols. From the experimental evidence as advanced in this paper, as well as those obtained by other workers, we have been able to prove that the viscosity of a sol decreases appreciably when small quantities of electrolytes are added to it. We are of the opinion that this behaviour is due to the increase in the charge of the sol and consequent decrease in the amount of hydration. We are trying to prove experimentally whether addition of small quantities of electrolytes to a sol especially of the hydrophobe type causes an increase in the surface tension of such sols.

In a recent paper Kruyt and Tendeloo[2] have obtained some interesting results on the viscosity of gelatine in presence of electrolytes. These results can be explained from the point of view advanced in the foregoing pages. Their results are as follows:—

The relative viscosity of 1% gelatine with a pH value of 4.65 varies from 1.435 to 1.421, and the following values were obtained with different pH values of the same gelatine.

| | | | |
|---|---|---|---|
| pH | 3.65 | 3.72 | 3.74 |
| Relative viscosity | 2.079 | 1.848 | 1.834 |

[1] Ber., 37, 1095 (1904).
[2] J. Phys. Chem., 29, 1303 (1925).

These results are similar to those obtained by Loeb. Kruyt and Tenderloo have observed that when KCl, $K_2SO_4$, $K_3Fe(CN)_6$ are added to gelatine containing acid, the viscosity decreases with increasing concentration of the salt solution. The depression is greatest with $K_4Fe(CN)_6$, then comes $K_2SO_4$ and finally KCl. When KCl is added to isoelectric gelatine, the gelatine becomes positively charged by the adsorption of hydrogen ions for which gelatine has a great chemical affinity and along with the charge, the disintegration tendency and the hydration and the viscosity will decrease. The trivalent ferricyanide ion will produce the maximum effect.

Exactly similar results have been obtained by Kruyt and Tendeloo with 0.5% gelatine with a pH value = 4.4 in presence of the above electrolytes.

From the experiments of Kruyt and Tenderloo it will be seen that with 0.5% gelatine of pH value = 4.65 the addition of small quantities of $K_3Fe(CN)_6$ produces a slight lowering of viscosity, whilst the addition $CO(NH_3)_6\ Cl_3$, $BaCl_2$ and $MgSO_4$ produces a slight increase in the viscosity. By the addition of $K_3Fe(CN)_6$ the positive charge becomes less due to the adsorption of polyvalent $Fe(CN)'''_6$ ions and consequently, the disintegration tendency, the degree of hydration, and the viscosity become less. Further addition of $K_3Fe(CN)_6$ causes an increase in viscosity. It seems very probable that the charge on the gelatine sol becomes negative by the preferential adsorption of $Fe(CN)'''_6$ ion. On the addition of $Co(NH_3)_6Cl_3$, $BaCl_2$, $MgMO_4$, there is an increase in the positive charge on the gelatine and hence the disintegration tendency, hydration, and viscosity of gelatin are increased.

With gelatine pH value = 4.73, which is practically neutral, the addition of both $K_3Fe(CN)_6$ and $Co(NH_3)_6\ Cl_3$ causes an increase in viscosity due to the increase in the charge, negative in the case of $K_3Fe(CN)_6$ and positive in the case of $Co(NH_3)_6\ Cl_3$.

With gelatine pH value = 4.9, which is negatively charged, addition of $K_3Fe(CN)_6$ causes an increase in viscosity due to increase in negative charge caused by preferential adsorption of $Fe(CN)'''_6$ ions. When $Co(NH_3)_6Cl_3$ is added to a negatively charged gelatine, there is at first a drop and then an increase in the viscosity. This is due to the fact that the addition of small quantities of $Co(NH_3)_6\ Cl_3$ causes a decrease in the negative charge and therefore at first there is a fall in viscosity, but when greater quantities of $Co(NH_3)_6\ Cl_3$ are added to a negatively charged gelatine, charge reversal takes place and gelatine now becomes positively charged. The amount of charge, the amount of disintegration tendency and the amount of hydration goes on increasing up to a limiting value as the concentration of $Co(NH_3)_6Cl_3$ is gradually increased.

From the researches of Loeb, Pauli and others it seems pretty certain that the influence of $H^{\cdot}$ ions is most prominent on these substances, then comes the influence of OH ions and then come other neutral salts like KCl, $BaCl_2$, $K_3Fe(CN)_6$, etc. This is certainly due to the fact that substances like gelatine, albumin, etc., possess a great affinity for $H^{\cdot}$ ions and adsorb them markedly. From the viscosity measurements of isoelectric gelatin it will be observed that

the presence of small quantities of HCl produces a much larger increase in viscosity than that produced by an equivalent amount of a neutral salt. Having done a lot of very good experimental work on the influence of $H^{\cdot}$ ions which no doubt play the most important role amongst all the other ions, on several physical properties of the sol, Loeb was led to overemphasise the influence of $H^{\cdot}$ ions, but this should be overlooked because of his important investigations on this line.

## Summary and Conclusion

(1) Viscosities of sols of (a) $Cr(OH)_3$, (b) gum dammar, (c) gamboge, (d) ferric arsenate, (e) stannic hydroxide (prepared both in the cold and boiling conditions), (f) Congo red (dialysed and undialysed), (g) Nile blue (dialysed and undialysed), (h) Thioflavin, in presence and absence of electrolytes have been determined. In every case we have observed that there is first a decrease in the viscosity, when small quantities of electrolytes are added to the sol and finally it increases with increasing concentration of electrolytes. The decrease in viscosity is most likely due to the increase in the charge and consequent decrease in hydration of the sol due to the adsorption of ions carrying the same charge as the sol, and after a time the adsorption of ions carrying the opposite charge become prominent.

(2) With sols of gelatine, albumin, etc., we find that the greater the viscosity the less is its surface tension, and consequently it seems quite probable that measurements of surface tension, and viscosity would supplement each other in ascertaining the hydration of a colloid.

(3) With the progress of dialysis sols of vanadium pentoxide, ceric hydroxide etc. become more and more viscous and finally set to a jelly. This can be explained from our view that the less the charge on the sol the greater is its viscosity. When a sol is dialysed, the adsorbed electrolytes goes out and consequently the electric charge on the sol decreases and along with it the viscosity increases. It seems very probable that surface tension should also decrease with the progress of dialysis.

(4) We expect that the surface tension of hydrophobe colloids should increase when small quantities of electrolytes are added.

*Chemical Laboratory,*
*Allahabad University,*
*Allahabad, India*
*April 22, 1926.*

# EQUILIBRIUM IN COLLOID SYSTEMS. II. COAGULATION

BY OSCAR KNEFLER RICE

Recently I have applied equilibrium principles to a study of colloids[1]. A few pages of this paper were devoted to a consideration of the coagulation of colloids, but in this part of the work it was assumed that ions were adsorbed at the surface of the particles and that the electrical forces were the only ones affecting the surface tension of the particles, assumptions which equation (7) of the article[2] entitled "The Surface Tension of Charged Surfaces," now shows to be inconsistent, unless it is possible to neglect the term $RTQ_1/\epsilon$. But calculation in an actual case (as we shall see) shows this to be inadmissible. We also assumed, for purposes of approximation, that the ions formed a condenser of constant capacity. In the present paper we intend to improve, extend, and generalize the part of the former one which deals with coagulation, and to show to what extent and in what cases the former considerations hold.

As we shall have to refer to the previous paper frequently, we shall designate it as "Eq. Coll. Sys. I," and we shall refer to equations in that paper simply by number, with the Roman numeral I before it.

## General Criterion for Coagulation

In the earlier paper an expression was derived for the total change in free energy when all the colloid particles in a given system, assumed to be of the same size, were changed to another size, with consequent change in the number of particles (the total amount of material in the system being assumed not to change). This was done by considering the amount of work done by the particles due to their surface tension when they were all removed simultaneously without change of composition to a standard phase of the same composition but with a flat surface; and then the work done in building up a different number of particles in a similar manner, to such a size as would be necessary to have the same total amount of material in the system. The particles as finally built up in this manner would have the same composition as the original particles; they might not then be in equilibrium with the solution, and a transfer of material from the solution into the particles, or *vice-versa*, might still be necessary, but it was shown that the energy changes in this final step to equilibrium were negligible. By this means the free energy change was found to be given by

$$\frac{\partial(\Sigma F_1)}{\partial m_1} = \frac{\partial F_1/\partial m_1}{m_1} - \frac{F_1}{m_1^2} \qquad (1)$$

where $\Sigma F_1$ is the total free energy of the whole system, $F_1$ is the free energy of one particle, due to the work done against surface tension in generating it from an infinitesmal size and $m_1$ is the mass of one particle.

[1] Rice: J. Phys. Chem., **30**, 189 (1926).
[2] Rice: J. Phys. Chem., **30**, 1348 (1926).

By definition $F_1 = \int_0^{v_1} pdv$, where $p$ is the excess of pressure in the particle due to surface tension, and $v$ is its volume. (We have here written the subscript 1 to distinguish the particular values of the variables at the upper limit. The addition of this subscript throughout should be noted in comparing this article with the earlier one.) $p = 2\gamma/a$ where $\gamma$ is the surface tension and $a$ the radius of the particles. Now if the particles are large enough the surface tension should be independent of the size, that is, it should asymptotically approach a limiting value as the particles grow large. This is because of the disappearance of the effect of curvature on the surface tension, which may act either directly, or indirectly, through changes caused in the composition of the particle; because the surface of the particles will be relatively so small that any surface adsorption will not be able to change the composition of the solution; and because the number of particles will be so few that they will not appreciably affect the properties of the solution. Now we will write $\gamma = \gamma_1 f(a)$, the subscript having the same meaning as before and we will take $v_1$ as large, so that $\gamma_1$ will be essentially the limiting surface tension of large particles. This gives us

$\int_0^{v_1} pdv = 8\pi\gamma_1 \int_0^{a_1} f(a)ada$. Now $f(a)$ is equal to 1 when $a_1$ is large, so the upper limit of $\int_0^{a_1} f(a)ada$ will not differ from that of $\int_0^{a_1} ada$, while the lower limit is fixed within the range of our considerations. We therefore have

$$\int_0^{a_1} f(a)ada = \int_0^{a_1} ada + C = \frac{a_1^2}{2} + C$$

where C is a constant.

Hence

$$\int_0^{v_1} pdv = 4\pi\gamma_1 a_1^2 + 8\pi C\gamma_1$$

$$\frac{d}{dv_1}\int_0^{v_1} pdv = \frac{2\gamma_1}{a_1} = p_1$$

and[1]

$$\frac{\partial F}{\partial m_1} = p_1 \frac{dv_1}{dm_1}$$

[1] $\frac{\partial F_1}{\partial m_1} = \left(\frac{d}{dv_1}\int_0^{v_1} pdv\right)\frac{dv_1}{dm_1} = \left\{\int_0^{v_1}\frac{\partial p}{\partial v_1}dv + p_1\right\}\frac{dv_1}{dm_1}$. $\left(\int_0^{v_1}\frac{\partial p}{\partial v_1}dv\right)\frac{dv_1}{dm_1}$ corresponds to what we have previously called $\left(\frac{\partial F_1}{\partial m_1}\right)_1$ (Eq. Coll. Sys, I. p. 197) while $p_1\frac{dv_1}{dm_1}$ is $\left(\frac{\partial F_1}{\partial m_1}\right)_2$. Since $\frac{\partial F_1}{\partial m_1} = p_1\frac{dv_1}{dm_1}$, $\left(\frac{\partial F_1}{\partial m}\right)_1$ is evidently zero. This is true for large particles, and the assumptions are the same as are used in the footnote, Eq. Coll. Sys. I, p. 203. (In this footnote we inadvertently wrote $\left(\frac{\partial F_1}{\partial m_1}\right)_1 = \int_0^{v_1}\frac{\partial p}{\partial v_1}dv$.) It was shown, loc. cit., p. 197, that $\left(\frac{\partial F_1}{\partial m_1}\right)_1$ is also zero for any dilute colloidal solution, whether the particles are large or not. (In comparing the expressions, again note the use of the subscripts for values of the variables at the upper limit of the integrals, which was not done in the previous article.)

Putting the values of $\partial F_1/\partial m_1$ and $F_1$ into (1) we get

$$\frac{\partial(\Sigma F_1)}{\partial m_1} = \frac{p_1 \quad dv_1}{m_1 \quad dm_1} - \frac{\int_o^{v_1} p dv}{m_1^2} \tag{2}$$

If we can assume $dv_1/dm_1$ to be constant and equal to $v_1/m_1$ for large particles this becomes

$$\frac{\partial(\Sigma F_1)}{\partial m_1} = \frac{p_1 v_1}{m_1^2} - \frac{\int_o^{v_1} p dv}{m_1^2} \tag{2a}$$

Now if the colloid is to be stable when coagulated we must have the total free energy becoming less as the particle size increases. So the criterion for a stable coagulate is that for large particles

$$p_1 - \frac{\int_o^{v_1} p dv}{v_1} < 0 \tag{3}$$

This depends only on certain assumptions regarding the properties of large particles[1].

Using the values already found for $\int_o^{v_1} p dv$ and $p_1$ we get

$$p_1 - \frac{\int_o^{v_1} p dv}{v} = \frac{2\gamma_1}{a_1} - \frac{4\pi\gamma_1 a_1^2 + 8\pi C\gamma_1}{4/3\ \pi a_1^3} = -\frac{\gamma_1}{a} - \frac{6C\gamma_1}{a^3} \tag{3a}$$

As $a$ is very large we may neglect the term $8\pi C\gamma_1$ getting finally $-\gamma_1/a < 0$ or

$$\gamma > 0 \tag{4}$$

which we had previously obtained in a less general way[2], and which Tolman[3] also used, though without a rigorous derivation. Stated in words, coagulation is stable if the tension of large particles is positive, dispersion if it is negative.

We may now prove in a more general way than previously[4] that if coagulation is stable large particles are not temporarily stable. For the condition for the coagulated mass to be stable may be written $p_1 v_1 - \int_o^{v_1} p dv < o$. But it is seen by putting in the values of $p_1$, $v_1$, and $\int_o^{v_1} p dv$ in terms of $\gamma_1$ and $a_1$, that this becomes negatively infinite when $v_1$ or $a_1$ increases indefinitely, because $\gamma_1 < 0$. Therefore $\frac{d}{dv_1}(p_1 v_1 - \int_o^{v_1} p dv) = dp_1/dv_1 < o$, which is contrary to the condition of temporary stability[5]. On the other hand, if dispersion is stable, the condition of temporary stability holds for large particles. The conclusions which were drawn from these facts now have a more general basis.

---

[1] Compare with the assumptions on which expression I (15), was based. (The assumption of mutual insolubility of phases was not actually used in deriving I (15)).

[2] Eq. Coll. Sys. I, p. 202. On the fourth line, p. 202 $\gamma = \gamma_o^{\alpha} + k^2 h/4\pi K$ should read $\gamma = \gamma_o^{\alpha} - k^2 h/4\pi K$.

[3] Tolman: J. Am. Chem. Soc., **35**, 307-333 (1913).

[4] Eq. Coll. Sys. I, p. 201.

[5] Eq. Coll. Sys. I, p. 249, equation I (6).

## Coagulation of Electrically Charged Colloids

We may now apply the results of the article,[1] "The Surface Tension of Charged Surfaces", to a determination of $\gamma_1$. In that article we considered the possibility of having two diffuse layers of ions, one on either side of the surface, or of having certain ions adsorbed as a monomolecular layer on the surface, with a diffuse layer of ions on one side. Now in the case of colloids we might conceive of having either of these situations occurring. We could have ions both inside and outside the particle, with no charge at the surface, or we could have the interior of the particle entirely neutral, with a surface charge and a diffuse layer outside[2]. In the article above-mentioned we considered cases in which equilibrium was not established between ions on the two sides of the boundary, or between ions in the monomolecular layer and ions in the solution, as the case might be; although equilibrium was always established between all the ions on any one side of the boundary. In the case of colloids the situation is different in that the charge of the particles is a result of the establishment of equilibrium between the particles and the solution. Yet this is really only a special case of the former. We can start with a neutral colloid particle, and effect certain transfers of ions keeping the particle completely polarized, just as we did in the case of any other surface, but we must make the proper transfers of material to get the particle into the condition it would *assume* if it were left to itself[3]. We will let $\gamma_0$ then be the surface tension of the neutral colloid with a pure surface, in the given solution. If there are no forces which act on ions in the neighborhood of the boundary, except the electrical forces due to the ions which have crossed the boundary, then we have shown that $\gamma_0$ is the same for all solutions[4]. We have then for the case of a monomolecular layer and one diffuse layer

$$\gamma_1 = \gamma_0 - \int_0^{\phi_1} Q d\Phi - \sum_{i=1}^{n} \int_0^{\phi_1} \frac{Q_i}{\epsilon_i} \frac{d\mu_i}{d\phi} d\phi \qquad (5)$$

where $\phi$ is the potential of the particle over that of the solution, Q is the charge per unit area on the colloid surface, $Q_i$ being caused by the $i$th ion, $\epsilon_i$ being the charge per unit mass of the $i$th ion, and $\mu_i$ its excess of chemical potential in the monomolecular layer at the surface over its chemical in the solution[5]. We assume that $\gamma = \gamma_0$ when $\phi = \phi_0$. $\gamma_1$ is the surface tension when $\phi = \phi_1$.

For any given solution (5) (theoretically, at least) determines the value of $\phi_1$ in terms of $\gamma_1$. But suppose we have a colloid dispersed in a salt solution; we may then vary the concentration of salt until $\gamma_1$ is zero. This condition

---

[1] Rice: J. Phys. Chem., 30, 1348 (1926).

[2] We could also conceive of an intermediate case, but we will treat only the two extremes.

[3] It is to be remarked, however, that the same relation holds if the particle is not brought to equilibrium, and as equilibrium is often slow to be established, it might at times be useful to remember this fact.

[4] See paragraph immediately following equation (4a) in the article, "The Surface Tension of Charged Surfaces".

[5] See equations (3a) and (4) in the article, "The Surface Tension of Charged Surfaces".

holding for *large* particles may be taken as the equation determining a critical value of $\phi_1$, corresponding to a critical value of the concentration of salt, which will be the border value between coagulation and dispersion.

Let us consider the case where only one ion is involved in the adsorption and charging processes. Then if the adsorbed substance is ideal we have shown[1] that we may write (5) in the form

$$\gamma_1 - \gamma_0 = -\int_0^{\phi_1} Q d\phi - \frac{RTQ_1}{\epsilon} \qquad (6)$$

(The subscript of $Q_1$ does not refer to the particular ion, but $Q = Q_1$ when $\phi = \phi_1$). This could occur, for example, if the colloid particle were itself completely uncharged, but could adsorb some ion in the solution[2]. In this case both terms in the equation will be positive, and increasing with the magnitude of $\phi_1$. There will therefore be a value of $\phi_1$ below whose absolute magnitude coagulation will occur, and above dispersion.

If there were no adsorption at the surface, but two diffuse layers instead, then the term $\int_0^{\phi_1} Q d\phi$ would alone be left on the right hand side of (6), whether only one ion or several were effective in producing the charge. In this case we would expect two limiting potentials, one positive, one negative, as is frequently observed[3].

Since by equation (3) in the article on the Electrocapillary Curve, $Q_1$ is proportional to $\phi_1$ when $\phi_1$ is small, for such values the electric layer acts as if it were a condenser of constant capacity, even though the ions are under no forces except those due to other ions. In this case and if there are two diffuse layers and no adsorption at the surface the considerations of the former article[4] hold good. In fact, all the considerations of that article hold for the case of two diffuse layers if only we write $\int_0^{\phi_1} Q d\phi$ for the decrease of surface tension due to the electrical effects instead of $k^2h/2\pi K$, it being understood that these expressions are for large particles. In particular equations I(21) and I(22) hold, with this substitution, if the assumptions about $c_1$ and $c_2$ are true[5].

## Application to Coagulation of Arsenious Sulfide

A discussion of coagulation experiments has already been given[6]. We desire, however, to discuss one particular case further. Powis[7] has measured the

[1] Article, "The Surface Tension of Charged Surfaces".

[2] See e.g., Svedberg: "Colloid Chemistry", Am. Chem. Soc. Monograph, p. 26, on the peptization of mercury by potassium nitrate.

[3] See, e.g., Ellis: Z. physik. Chem., 80, 597 (1912); Powis: 89, 186-212 (1915).

[4] Eq. Coll. Sys. I., pp. 199-202.

[5] It may be thought that I (21) is not consistent with (3a). The explanation lies in the fact that C of equation (3a) is not necessarily independent of the salt concentration, while $c_1$ and $c_2$ of I (21) are. In fact C increases indefinitely when $\gamma_1$ approaches zero, unless $c_1 = c_2$, as is seen by comparing (3a) and I (21) (noting that for large particles $\gamma_0^\infty - k^2h/4\pi K$ of I (21) is equal to $\gamma_1$ of (3a) ). The derivation of I (22) breaks down if $c_1 = c_2$. The fact that C becomes, or may become, very large for small values of $\gamma_1$ does not invalidate the deductions made by neglecting C. For C may always be neglected when $\gamma_1$ has any appreciable value, positive or negative, and the critical value of $\gamma_1$ will lie somewhere between these.

[6] Eq. Coll. Sys. I, p. 202.

[7] Powis: J. Chem. Soc., 109, II, 734 (1916).

critical concentrations and potentials for coagulation of arsenious sulfide in several solutions. Now the potentials were measured by cataphoresis experiments and therefore include only the drop of potential on the outside of the particle, and give us no information about what is happening inside the particle at all. This does not alter the fact of a critical potential, but means that the potential measured is not the whole one.

There is a negative charge on arsenious sulfide particles in a solution in which the salt concentration is zero. This can be accounted for either by assuming that the particles adsorb some of the sulfide ions which would necessarily be present in equilibrium (this is effectively the same thing as negative adsorption of arsenious ions) or that they adsorb hydroxyl ions. This charge is partially neutralized in the salt solutions. It is possible to calculate $Q_1$, the charge per unit surface, in the solutions at coagulation, from the data of Powis, using equation (3) of the preceding article on the Electrocapillary Curve[1], then if we assume all the adsorption to take place in a monomolecular layer at the surface, to calculate $\int_0^{\phi_1} Q d\phi$. This and $RTQ_1/\epsilon$ are related to $\gamma_0$ (see equations (5), (6)), which is an invariant, and though we cannot use (5) as more than one kind of ion is effective in producing the surface charge, and though we are at a loss to estimate the terms in (6) because we do not know just which and how many of each kind of ions produce the charge, still $\int_0^{\phi_1} Q d\phi$ and $RTQ_1/\epsilon$ should, if the assumption of surface adsorption in a monomolecular layer is correct, give an idea of the order of magnitude of $\gamma_0$. These quantities have been calculated and are given in Table. I

TABLE I

Calculations based on Powis's data on the coagulation of arsenious sulfide by electrolytes, assuming T = 18°C

| Salt | Conc. at coagulation (millimols per liter) | $\phi_1$ (volts) | $\int_0^{\phi_1} Q dp$ | $\frac{RTQ_1}{\epsilon}$* | $\int_0^{\phi_1} Q dp$ | $\frac{RTQ_1}{\epsilon}$ |
|---|---|---|---|---|---|---|
| KCl | 40.0 | .044 | .49 | .59 | .49 | .59 |
| $BaCl_2$ | .5 | .023 | .029 | .066 | .019 | .044 |
| $AlCl_3$ | .05 | .025 | .019 | .042 | .009 | .019 |
| $Th(NO_3)_4$ | .07 | .026 | .038 | .09 | .013 | .027 |

They should be of the same order of magnitude for all the solutions, and this is the case, except for the potassium chloride solution. We will show that this discrepancy can be accounted for if there are two diffuse layers, and no surface adsorption.

[1] J. Phys. Chem., 30, 1501 (1926).

* $\epsilon$ in this column is given its value for uniunivalent ions throughout. However in calculating $Q_1$ for this column, and $\int_0^{\phi_1} Q d\phi$ in the preceding column allowance is made for the valence of the ions in the solution, assuming them to be those of the first column. In the last two columns it is assumed that there is an equivalent amount of univalent ions in solution.

Except where otherwise noted electrostatic and C. G. S. units are used.

First we must consider some experiments of Whitney and Ober[1] who found that when arsenious sulfide was precipitated with barium chloride about one atom of barium to ninety molecules of arsenious sulfide was carried down in the precipitate; and that equivalent amounts of other salts were carried down if the precipitation was carried out with them. This salt does not wash out of the arsenious sulfide, and the ratio of metal ion to arsenious sulfide in the precipitate seems to be independent, according to Whitney and Ober, of the concentrations of salt and arsenious sulfide. The adsorption was always accompanied by the release of an equivalent amount of hydrogen ion into the solution, the metal ion taking hydroxyl ion with it, or possibly displacing the hydrogen in adsorbed hydrogen sulfide which is present in the particles. Unless this adsorption were a surface effect, which does not seem likely, it would not affect our consideration of the surface tension appreciably, except that if all the salt, or a large proportion of it were thus adsorbed it would leave us with a solution of the acid, a uniunivalent electrolyte, instead of the polyunivalent salt. The values we would thus get for $\int_0^{\phi_1} Q d\phi$, and $RTQ_1/\epsilon$ are given in the last two columns of the table. As a matter of fact, judging from the concentration of Powis's solutions and Whitney and Ober's data, not all of the salt, but quite an appreciable part of it, was adsorbed in Powis's experiments. The actual values for $\int_0^{\phi_1} Q d\phi$ and $RTQ_1/\epsilon$ will be something intermediate to those given in the table[2].

Now the high values of $\int_0^{\phi_1} Q d\phi$ and $RTQ_1/\epsilon$ for potassium chloride can be simply explained by the assumption that there is a diffuse layer in the particle, instead of an adsorption at the surface, and that the adsorbed potassium hydroxide (or sulfide) is much more strongly ionized than the other hydroxides (or sulfides) are. Suppose that there is a certain concentration of ions in the particles when they are coagulated with barium, aluminum, or thorium salts, the concentration not differing in each of these cases. Then there is a contribution to the lowering of the surface tension due to the inside diffuse layer in each of these cases, which is not exactly the same, but at least the same order of magnitude in each of them. The inside layer in these cases might even be dominated by arsenious and sulfide ions. Now a glance at equation (3) of the preceding article on the Electrocapillary Curve[3] will show that a large

---

[1] Whitney and Ober: J. Am. Chem. Soc., 23, 852 (1901); see also Linder and Picton: J. Chem. Soc., 67, 63 (1895); Mukhopadhyaya: J. Am. Chem. Soc., 37, 2031 (1915); Duclaux: J. Chim. phys., 6, 592 (1908).

[2] The people who have investigated adsorption by arsenious sulfide do not agree in all the details. Duclaux (loc. cit.) found evidence that the adsorption is a more complicated phenomenon than was believed by Whitney and Ober. Duclaux found a considerable amount of arsenic in the solution after the sol is precipitated. He did not believe that this was present in the solution outside the particles before precipitation, but his evidence on this point is not entirely convincing. As Whitney and Ober apparently accounted for all the metal ion, anion, and hydrogen ion, and as arsenious sulfide, ionized or unionized, would not exist in any quantities outside the particles, it would seem that if arsenic were present outside the particles it must exist as arsenious acid, or as some other weak acid, which was not even detected as contributing to the hydrogen ion concentration by Whitney and Ober. In the absence of any more definite data as to the number of ions contributed by this arsenic compound we have neglected its presence.

[3] J. Phys. Chem., 30, 1501 (1926).

concentration of ions in the particle will cause a smaller $\phi_i$ to correspond to a given $Q_i$, as far as the layer inside the particle is concerned. This would mean, in effect, that the contribution of the inside diffuse layer to the lowering of the surface tension would be partially destroyed, thus accounting for the larger contribution of the outer layer (which, it is to be remembered, is what is estimated from cataphoresis experiments, and tabulated in the table). This is understood when we remember that $Q_i$ always has the same value for the two sides of the boundary, so that for any given lowering of the surface tension contributed by the outer layer, the lowering due to the inner layer is smaller the greater the number of ions on that side of the boundary. In this connection it is interesting to note that Linder and Picton[1] find that the presence of potassium chloride lowers the coagulating power of strontium chloride.

It must, of course, be admitted, as we have stated before, that in a case of this kind an equilibrium theory can give only the general character of the results, and calculations made will be good to the order of magnitude only. There is one piece of evidence, which has recently come to my notice, which might be construed as being contradictory to an equilibrium theory. Börjeson[2] finds that the size of the particles in arsenious sulfide solutions depends on the concentration of the arsenious oxide from which the solution is made by passing in hydrogen sulfide. As excess hydrogen sulfide is passed in, the solution should come finally to be the same in all cases except for the concentration of arsenious itself. Unless this makes an appreciable difference it seems as if equilibrium could not have been completely established in these cases, but that the size of the particle depends on the rapidity of formation. At any rate it is evident from Powis's description[3] of the coagulation of arsenious sulfide that equilibrium cannot be established rapidly, for the coagulating concentration was not very definitely defined, and when the concentration was near the critical one coagulation was very slow. We have already expressed our opinion that the observations of some investigators, who found the concentration of salt necessary to coagulate the colloid depended on the concentration of the colloid, were to be explained on the grounds that they were observing rate of reaction rather than equilibrium effects.

## Summary

On the assumption that the surface tension and other properties of colloid particles do not vary with the size of the particles as long as the particles are large (i.e., that they asymptotically approach a limiting value with increasing particle size) we have shown that dispersion is a stable state if the surface tension of the large particles is negative, and coagulation is a stable state if the surface tension is positive. Then, by applying the laws for the surface tension of electrically charged surfaces (see the summary[4] of the preceding article) we have considered the stability of charged colloids, in salt solutions. These considerations show us that a dispersed system will coagulate at certain

[1] Linder and Picton: J. Chem. Soc., 67, 63 (1895).
[2] Börjeson: Kolloid-Z., 27, 25 (1920).
[3] Powis: J. Chem. Soc., 109, II, 735 (1916).
[4] J. Phys. Chem., 30, 1501 (1926).

definite concentrations and potentials of the particles, which are such that the surface tension is zero. We consider the possibility (1) that the interior of the colloid particle may be neutral, the surface being charged, with a diffuse layer of ions in the surrounding solution, or (2) that there may be no charge at the surface of the particles but two diffuse layers of ions, one in the solution surrounding the particle and one in the particle. The various considerations mentioned are discussed in connection with the precipitation of arsenious sulfide sols.

*Department of Chemistry,*
*The University of California,*
*Berkeley, California.*

# THE VAPOR PRESSURES OF POTASSIUM NITRATE SOLUTIONS AT 20°C*

BY J. C. W. FRAZER, B. F. LOVELACE, AND R. K. TAYLOR.

The apparatus and methods used in this research were largely those employed by previous workers at this University on the vapor pressure of aqueous solutions; and as descriptions have been published in the Journal of the American Chemical Society, only the modifications of the apparatus and technique will be given here. The articles referred to are:
Frazer and Lovelace; J. Am. Chem. Soc., **36**, 2439 (1914); Frazer Lovelace, and Miller: **38**, 515 (1916.) (Potassium chloride); Frazer, Lovelace, and and Rogers: J. **41**, 1793 (1920.) (Mannite); Frazer, Lovelace, and Sease, **43**, 102 (1921.) (Potassium chloride at 20°C).

From the position of the potassium and nitrate ions in the lyotropic series, it was anticipated that inasmuch as hydration and salt effect are less in evidence than in the case of the solutes previously used, potassium nitrate solutions would approximately obey the laws of dilute solutions to higher concentrations, or in other words potassium nitrate would be more nearly an ideal solute, than the other electrolytes with which results have been obtained. The data secured indicate that such is the case.

## Preparation of Material

The starting material was a commercial C. P. potassium nitrate containing as the impurity present in the largest amount, a trace of sodium. This salt was twice recrystallized from hot water, and dried in a desiccator over sulphuric acid. Solutions were prepared by weighing out appropriate amounts of the dry crystals and dissolving in distilled water.

A sample of the recrystallized salts was submitted to the Bureau of Standards for spectrographic analysis; this analysis indicated the complete absence of sodium and other probable impurities.

It is not likely that any impurity would have influenced the vapor pressure lowering to a greater extent than its concentration with reference to potassium nitrate; and as the percentage of impurities reported in the *original* material was hardly as great as the experimental error of the measurements, the amount of impurities in the *recrystallized* salt was certainly not large enough to have an appreciable effect on the readings.

## Method of Analysis

The solutions, after removal from the thermostat, were analyzed by evaporating weighed samples (delivered from a weight burette) to dryness in Pyrex evaporating dishes over a steam bath, and then heating in an oven

*Extract from Dissertation submitted to the Board of University Studies of the Johns Hopkins University in conformity with the requirements for the degree of Doctor of Philosophy.

between 150° and 200° C. till constant weight was attained. Duplicate analyses of each solution were made; the normalities so found differed on an average by about one in the fourth decimal place, the maximum difference being three in the fourth place. The normalities reported are for mols of $KNO_3$ per 1000 g. of water, weighings in vacuo; to correct for air displacement, the normalities found from weighings in air were multipled by a constant factor, 0.99938.

### Temperature and Temperature Control

The temperature of the solutions at which the measurements were taken was 20°C., as nearly as could be read with a magnifying glass on a thermometer divided into tenths of degrees. The probable error of reading is not greater than five thousandths of a degree. At the conclusion of the series of readings, the thermometer was sent to the Bureau of Standards for calibration at the 20° and 25° points. The repert from the Bureau of Standards stated that at each of these points, the indicated temperature was five hundredths of a degree above the actual temperature. An additional correction of one hundredth of a degree, for exposed stem, makes the temperature 19.94°. The data of Scheel and Heuse as given in the latest edition of Landolt-Börnstein's Tabellen, give the vapor pressure of water at this temperature as 17.4736 mm of Hg(0°), and this value was employed in the calculations.

The temperature was controlled by a sensitive toluene thermoregulator; and a Beckmann thermometer, calibrated in hundredths of a degree, was used to insure that the variation remained less than the readable difference on the standard thermometer. As a matter of fact, the temperature was ordinarily constant on the Beckmann thermometer as well; and the variation over the entire series of measurements is probably not as great as four or five thousandths of a degree.

### Manometer and Readings

The apparatus was in general the same as when used by the previous workers on this problem. However, the metal screw used to keep the mirror of the Rayleigh manometer in place was removed, and it was found that as a result the zero readings of the manometer remained much more nearly constant, not being affected, as formerly, by change in length of the screw from slight fluctuations of the room temperature. The illuminating system of the manometer was also slightly modified to decrease the illuminated area and consequently the eye-fatigue involved in making settings of the manometer.

The number of readings taken for each "deflection" is in general not so great as the number taken by previous workers. As a certain amount of fatigue to the eyes is inevitable, which militates against accuracy, the smallest number consistent with reliability of results was desirable. When it was found that the zero reading was ordinarily constant over the time occupied by a set of readings, the practice of taking three or more readings of the zero before and after the readings on each solution was abandoned in favor of fewer settings of the manometer. Furthermore, as the readings usually checked at once within the limits of accuracy of the apparatus, fewer readings

on the solution for each "deflection" were also taken. The result was that on account of the greater speed possible, a larger number of deflections could be taken without tiring the eyes too greatly. For the fifteen solutions, a hundred and sixty-five deflections in all, or an average of eleven for each solution, were taken. The readings on each solution usually covered a period of three or four days.

On an average, four settings of the manometer were made for each of the "deflections," six hundred and sixty altogether. An idea of the accuracy of the observations can be obtained from the following statements: One millimeter, scale divison, corresponds to about five thousandths of a millimeter difference in the mecury levels of the manometer. Readings were taken to tenths, and usually to twentieths, of a scale divison; and it is estimated that the error of reading is ordinarily less than one tenth of a millimeter. There is justification for this belief in the fact that fifty percent of the readings are within five hundredths mm. or less of the average; thirty percent deviate between five hundredths and one tenth mm. from the mean; ten percent, between one tenth and fifteen one hundredths mm.; and the remaining ten percent deviate from the mean by more tham fifteen hundredths mm. Furthermore, most of the greater deviations occur in the case of the more concentrated solutions, so that the effect on percentage error is not very large. Accordingly the error of reading is not over one percent with a 0.1 N solution, and is roughly inversely proportional to concentration; though when solutions were so concentrated that they had to be measured against more dilute solutions instead of water, there is of course to that extent a summation of errors.

## Changes in Technique

Although the methods employed were in general those worked out and improved by previous workers ( as given in the respective publications), several modifications were made which, though possibly without effect on the accuracy of the results, considerably facilitated and shortened the operations. The innovations are as follows:

Preparation and introduction of solutions. The bulb in which the solutions were freed of air was of about 265 cc. capacity, and had a tube leading into it from both top and bottom. The lower tube was connected by about a foot and a half of rubber tubing to a leveling bulb of mercury; the upper tube, containing a 90° bend and a stopcock, was connected to a condenser in such a way that the water distilled from the solution in the bulb could be collected in a graduated cylinder. An amount of potassium nitrate to give a solution of the desired concentration in a volume of 225 cc. was weighed out and dissolved, and the solution was made up to a volume of 250 cc. and placed in the bulb. The mercury in the lower tube was brought just to the bottom of the bulb. The solution was then heated and kept at the boiling point for about an hour, and then boiled, slowly at first and increasingly rapidly, till 25 cc. had been collected. The flame was then turned out, and the mercury reservoir raised till the solution was forced past the stopcock, thus displacing

all vapor above the solution; and the stopcock was closed. An introducing tube, of the same type as used by former workers, was immediately substituted for the condenser, and all the tubing down to the stopcock was filled with mercury. When the solution was cold, the end of the introducing tube was dipped into the cup of mercury below the solution bulb in the thermostat; the stopcock was opened, and after ten or fifteen cc. of the solution had escaped into the cup, thus rinsing out the tubing, the end of the introducing tube was placed beneath the tube leading to the bulb in the thermostat (which had, of course, been previously completely pumped out) and the remainder of the solution was run in.

Removal of air: The solutions thus prepared were ordinarily by no means sufficiently air-free to take readings on directly; but a process worked out for the removal of the last traces of air, though requiring frequent attention, made it possible to take readings comparatively soon after introduction—regularly within twenty-four hours of the last readings on previous solution. The plan used by the first workers on the problem, depending chiefly on diffusion of the air into the large expansion bulbs, which were periodically pumped out, through several meters of 7-mm tubing, was quite slow, as it usually required a week or more before readings could be taken. Parker and Bahlke introduced a decided improvement by devising what they termed the "rapid expansion" method of air removal, in which, while being continually stirred, the solutions were opened up directly at intervals of about four hours, for one minute to the vacuum pump, so that all the air then in the vapor phase was effectively swept out of the apparatus. By repetitions of this process the solutions were usually made ready for readings in two or three days.

We suspected that most of the air was carried out in the first second or so of the minute the solutions were opened to the pump; and this suspicion was confirmed by suitable tests. The comparative efficacy of the "rapid expansion" method was largely due to the continual stirring of the solutions, thus hastening equilibrium as to air content between the solutions and the vapor space directly above them. We found it was not necessary to open the solutions to the pump at all; if the manometer, McLeod gauge, and connecting tube were pumped out, shut off from the pump, and then opened for a moment to a solution, practically all the air then in the vapor phase would be contained in this volume; for upon repeating the process a minute or so later, the vapor would be found to all intents and purposes air-free. It was discovered, furthermore, that up to about thirty minutes the concentration of air in the vapor space above a given solution is nearly proportional to the time since the vapor was last pumped off; beyond that time the concentration of course increases, but not so rapidly. These observations refer to solutions being continually stirred.

Accordingly, the plan adopted as most efficient for air removal was as follows: the solutions were stirred constantly, and each half hour the manometer, gauge, and connecting tubing were pumped out, closed off from the pump, and the vapor from a solution was allowed to expand into this volume

by opening the trap to it for a few seconds; this process was repeated till on standing for six hours or so with the stirrers going, the vapor drawn off in this way showed a partial pressure of air less than two or three ten-thousandths of a millimeter of air—the probable error of reading the manometer is greater than this.

After readings have been taken on a solution, if enough air should later come out of the solution into the vapor phase to cause trouble, it is naturally undesirable to change the concentration of the solution by pumping off the vapor in the ordinary way. A scheme was devised, however, to get around this difficulty. The expansion bulbs were filled with air-free water vapor (from a special solution bulb for this purpose) at the same pressure as the vapor above the solutions, and the bulbs were left standing open to the solutions. The air eventually distributes itself uniformly throughout the vapor space, and as the bulbs represent by far the largest volume, by trapping off these bulbs of vapor and pumping out, most of the air in the vapor phase was gotten rid of. The bulbs could again be filled with air-free vapor, and again left open to the solutions. It was found that when only a little air remains, it comes out of solution extremely slowly, so that though the vapor might be sufficiently air-free to take the readings at one time, in the course of days enough air might get into the vapor phase to cause inaccurate readings. Accordingly a uniform practice was made of leaving the solutions open at all times to bulbs full of vapor; each day these bulbs were trapped off and tested for air, and fresh vapor was substituted. In this way we were sure that when readings were taken the vapor was air-free, and we had a continual check on this point, instead of relying on one reading for each solution for the air-freeness of its vapor, which might well have been deceptive.

Air in the solutions is probably the greatest single source of trouble in this problem, and may account for some of the anomalous results which have been obtained, as at its best the method should be capable of high accuracy. Testing for Air. The method previously used for testing for air in the water vapor consisted in opening a bulb of the vapor to phosphorus pentoxide, and after twenty minutes determining the residual pressure by means of a McLeod gauge. However, on account of the immense surface of the pentoxide, considerable quantities of air are adsorbed by it; and to secure reliable results with its use it must be practically air-free, for when it takes up water a large amount of heat is evolved and a certain portion of the surface is destroyed, both of which effects would tend to liberate adsorbed air and vitiate the reading. A fresh lot of pentoxide was heated to 90-100° and pumped with a Langmuir high-vacuum pump at intervals for three weeks, and even at the end of that time readings obtained by its use could not be relied upon. A simple and more rapid method was devised for testing for air without the use of any absorbent for the water. The McLeod gauge in the system was so modified that the mercury in the outside tube could be raised considerably above the tip of the gauge. When a sample of vapor is trapped in the gauge and compressed into the tip, liquid water is formed; and if there is no air present in the vapor, the

difference of the mercury levels inside and outside the gauge is independent of the distance from the tip, as long as liquid water is present. That is, inside the gauge there is the vapor pressure of water at the particular room temperature, and outside is the pressure prevailing in the system, whatever that may be; and the difference is constant. However, when air is present, the difference becomes greater, the smaller the volume the air occupies; and from the constants of the gauge a relation was determined between the partial pressure of air, and the change in the difference of the mercury levels upon bringing the level within the gauge from one standard mark to another. A test for air in this way could be completed in about two minutes.

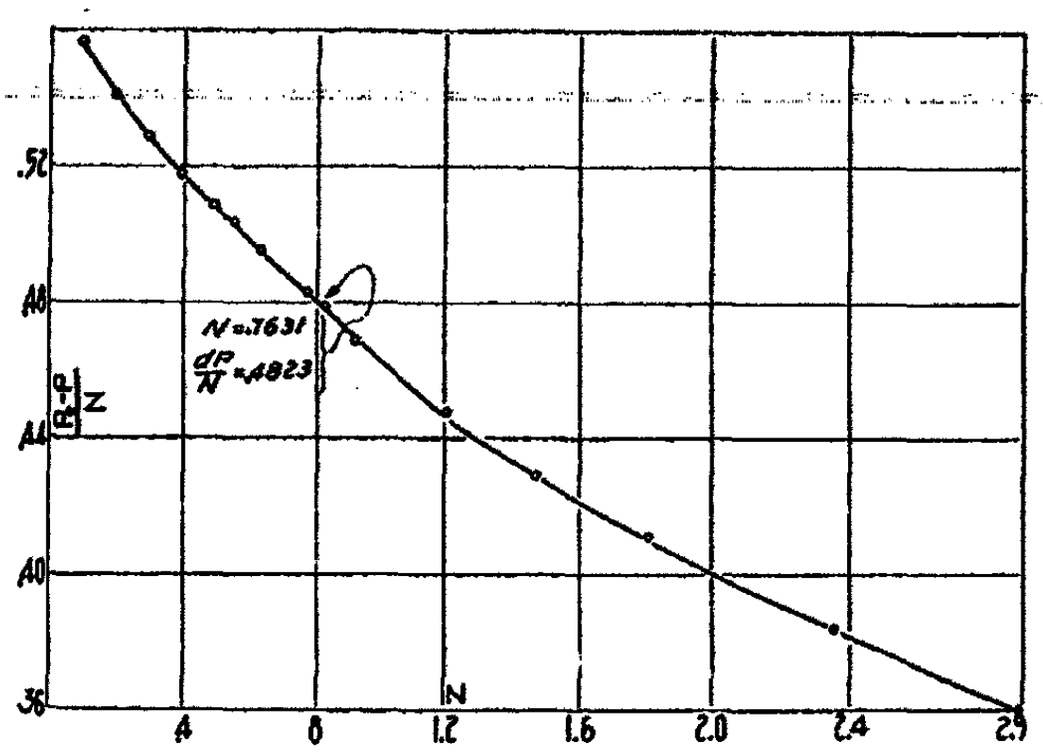



FIG. 1

## Explanation and Calculation of Results

"Deflection" is the average scale reading, in millimeters.

"Average Deviation" is the average deviation of the readings, in millimeters on the scale, from the mean.

"dP" is the lowering of the vapor pressure, in millimeters of mercury at its density at 0° C. It is calculated from the scale reading as follows.

If $a$ is the angle through which the manometer is turned and D the distance from the mirror to the scale, reading/D = tan 2 a. If $d$ is the distance between the manometer points, the difference in the mercury levels on the two sides of the manometer is d sin a. The ratio of the density of mercury at the average room temperature to that at 0° C. is 0.99569. D = 3793.6 mm., and d = 37.810 mm.; accordingly the vapor pressure lowering is

$$0.99569 \times 37.810 \sin \tfrac{1}{2}[\tan^{-1}(\text{reading}/3793.6)]$$

This formula was used throughout, though when $a$ is less than 1°, sin a is not widely different from (tan 2 a)/2, and the simpler formula dP = reading $\times$ 0.99569 $\times$ d/2D may be employed without significant error.

"N" is the concentration of the solution, in mols of $KNO_3$ per 1000 g. of water, calculated to weighings in vacuo.

"i", van't Hoff's factor, was calculated by the formula $i = dP(N + M)/P_oN$; M is 55.51, the number of mols of water in 1000 g. and $P_o$ is the vapor pressure of pure water, 17.4736 mm. Hg (0°) at 19.94°C. It is easily seen that $i = dP/N$, the "molecular lowering," $\times (N+M)/P_o$, and accordingly the i:N graph would have the same general characteristics as the dP/N:N curve; only the latter is given, Fig. 1.

| Number of solution | Number of readings | Average deviation from mean (mm., on scale) | Scale reading | $P_o-P$ | N | $P_o-P/N$ | "i" | $Ln(P_o/P)$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 12 | .04 | 10.98 | .05448 | .0979 | .5565 | 1.771 | .003124 |
| 2 | 9 | .04 | 21.21 | .10524 | .1947 | .5405 | 1.723 | .006039 |
| 3 | 14 | .05 | 31.03 | .15396 | .2913 | .5285 | 1.688 | .008852 |
| 4 | 9 | .06 | 40.39 | .20040 | .3875 | .5172 | 1.654 | .011535 |
| 5 | 12 | .08 | 49.52 | .24570 | .4837 | .5080 | 1.628 | .014161 |
| 6 | 9 | .04 | 54.90 | .27238 | .5415 | .5030 | 1.614 | .015712 |
| 7 | 14 | .06 | 62.43 | .30979 | .6261 | .4947 | 1.589 | .017889 |
| 8 | 10 | .06 | 74.18 | .36902 | .7631 | .4823 | 1.553 | .021285 |
| 9 | 6 | .02 | 79.07 | .39318 | .8205 | .4781 | 1.545 | .022759 |
| 10 | 14 | .11 | 86.07 | .42690 | .9114 | .4684 | 1.512 | .024734 |
| 11(vs. 12) | 12 | .10 | 18.92 | .53795 | 1.2029 | .4472 | 1.451 | .031274 |
| 12 | 8 | .03 | 127.39 | .63183 | 1.4652 | .4283 | 1.406 | .036828 |
| 13(vs. 14) | 10 | .13 | 31.86 | .74267 | 1.8098 | .4104 | 1.346 | .043434 |
| 14(vs. 12) | 13 | .08 | 54.20 | .90075 | 2.3504 | .3832 | 1.269 | .052928 |
| 15(vs. 14) | 13 | .11 | 27.84 | 1.03889 | 2.8873 | .3598 | 1.202 | .061296 |

In the following calculation of $\ln(P_o/P)$ from freezing and boiling point data, where $P_o$ and P are the vapor pressures of pure solvent and solution, respectively, at the freezing or boiling point of the solution, the approximate formula $\ln(P_o/P) = Q\triangle T/RT_oT$ was employed, Q being the latent heat of fusion or vaporization, $T_o$ and T the freezing or boiling point of solvent and solution, and R the gas constant. The accuracy of a more rigorous formula was approached by taking into account the change of Q with T, and employing in each case the mean value of Q, at $\frac{1}{2}(T_o + T)$.

Freezing point data:

(1) W. A. Roth: Z. physik. Chem., **79**, 605 (1912).
(2) Jones, Barnes, and Hyde: Am. Chem. J., **27**, 29 (1902).
(3) Le Blanc and Noyes: Z. physik. Chem., 6, 386 (1890).

Boiling point data:

Kahlenberg: J. Phys. Chem., **5**, 368 (1901).

| N | dT | ln(P$_o$/P) | N | dT | P | ln(P$_o$/P) |
|---|---|---|---|---|---|---|
| 0.0691 | 0.2349 | 0.00228 (1) | 0.2758 | 0.248 | 741.1 | 0.00870 |
| 0.1088 | 0.3603 | 0.00349 (1) | 0.4239 | 0.378 | 744.5 | 0.01325 |
| 0.1516 | 0.4893 | 0.00475 (1) | 0.5992 | 0.518 | 741.1 | 0.01816 |
| 0.2069 | 0.6507 | 0.00631 (1) | 0.8341 | 0.725 | 744.6 | 0.02537 |
| 0.2404 | 0.7469 | 0.00724 (1) | 0.9620 | 0.822 | 741.1 | 0.02879 |
| 0.2525 | 0.771 | 0.00731 (2) | 1.2925 | 1.101 | 744.6 | 0.03849 |
| 0.2709 | 0.8839 | 0.00809 (1) | 1.4636 | 1.207 | 741.1 | 0.04221 |
| 0.3299 | 0.9949 | 0.00965 (1) | 1.9522 | 1.603 | 744.6 | 0.05594 |
| 0.5019 | 1.500 | 0.01455 (3) | 2.1099 | 1.706 | 741.2 | 0.05956 |
| 0.5102 | 1.470 | 0.01427 (2) | 2.6799 | 2.123 | 741.2 | 0.07399 |
| 0.7735 | 2.107 | 0.02046 (2) | | | | |
| 1.0385 | 2.570 | 0.02491 (3) | | | | |
| 1.043 | 2.656 | 0.02579 (2) | | | | |

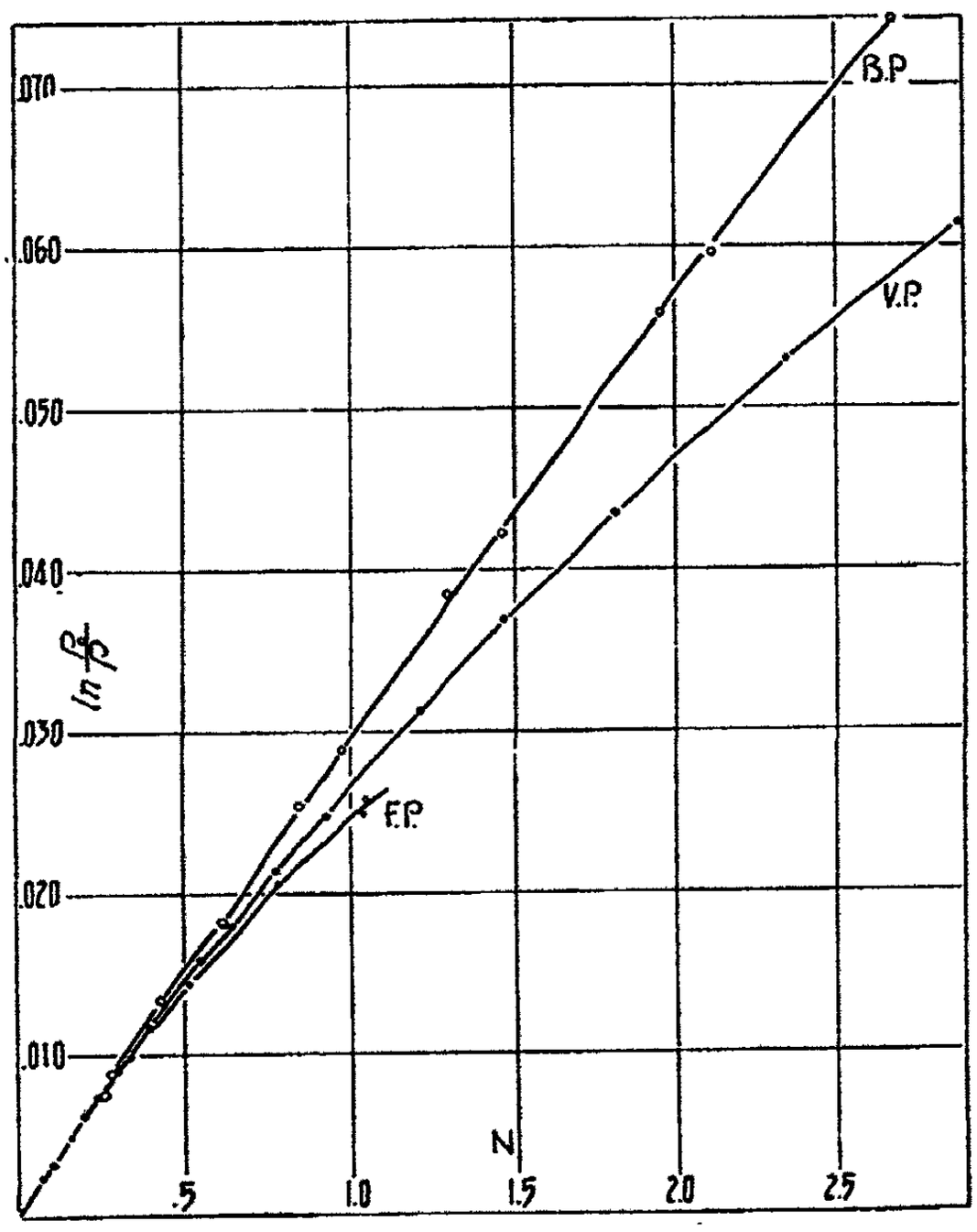



FIG. 2

A comparison of the N:ln($P_o$/P) graphs, Fig. 2, for the freezing point, 20°, and boiling-point data shows, as was anticipated, that von Babo's law is not even approximately obeyed, except in the case of very dilute solutions, whose heat of dilution is small. The curve for the vapor pressure measurements naturally lies between those for the freezing and boiling points.

## Summary

1. The vapor pressures of $KNO_3$ solutions at 19.94°C, from 0.1 to 2.9 N, have been measured.

2. A comparison of these results with freezing point and boiling point data is offered.

*Baltimore, Md.*
*July, 1926*

B-916

# A SENSITIVE ELECTRICAL PRECISION APPARATUS FOR THE DETERMINATION OF THE BOILING POINT ELEVATION

J. N. PEARCE AND MILDRED M. HICKS

Among the experimental methods which have been employed for determining free energy data in aqueous and non-aqueous solutions those involving the lowering of the freezing point and of the vapor pressure of the solvent, and the electromotive forces of concentration cells have been most frequently used. These methods are all capable of high accuracy and precision, but each is limited by the experimental conditions. The freezing point method is conveniently applicable to only a relatively few solvents. While the vapor pressure and electromotive force methods may be employed at any temperature, the former is limited to the study of a few solvents and volatile solutes, because of the difficulty in finding suitable absorbents for the vapor; the latter can only be employed for solutions of electrolytes in any solvent when perfectly reversible electrodes are obtainable.

From the standpoint of thermodynamics the principle of the boiling point elevation ranks equally with that of the freezing point method as a means of measuring the activity and free energy relations of dissolved substances. It has the one decided advantage that it can be applied to solutions in all solvents. Except as a means of determining molecular weights of dissolved substances, the use of the boiling point method has been neglected for many reasons. Among these are (1) the unavoidable superheating of the liquid and vapor; (2) uncontrollable fluctuations in the barometric pressure during a series of determinations; (3) imperfections in the Beckmann thermometer, which involve uncertainty in the correction for the emergent mercury thread, the friction in the capillary, the mechanical and thermal hysteresis of the thermometer bulb, and the effect of change of pressure on the bulb; (4) radiation of heat to and from the bulb; (5) introduction of impurities from the air or stopper and changes in concentration due to the presence of the solvent in the vapor phase and to the pure liquid returning from the condenser.

Until recent years all boiling point elevation determinations have been made with the thermometer bulb immersed in the solvent or solution. The same equilibrium temperature is obtained for the pure solvent when the thermometer is immersed in the boiling liquid as when immersed in the vapor. This is due to the fact that the condensing vapor covers the thermometer bulb with a film of the solvent which in contact with the vapor insures ideal conditions for temperature equilibrium. This is not true, however, when the thermometer bulb is immersed in the vapor above a boiling solution.

It was Cottrell[1] who first conceived the ingenious idea of actually pumping up the boiling liquid and allowing it to flow over the thermometer bulb which

[1] Cottrell: J. Am. Chem. Soc., 41, 721 (1919).

was suspended in the vapor phase. In principle, the pump consisted of a small inverted glass funnel with a long stem extending to above the bulb. The vapor forming below the funnel carries with it through the bulb the boiling liquid and pours it in a thin film over the bulb. During transit superheating is removed and the solution film on the bulb is in temperature equilibrium with the vapor.

The principle involved in the Cottrell apparatus has since been employed by Washburn and Read.[1] Their apparatus and the technique employed were designed to eliminate as completely as possible all sources of error. They avoided the necessity of making corrections for changes in barometric pressure by using two similar boiling flasks, one of which contained the boiling solution under investigation and the other the pure boiling solvent. They attempted to avoid superheating and to insure quiet boiling by placing in each boiling flask a small quantity of fragments of porcelain. Both they and Cottrell employed small gas flames for heating.

In this paper we have attempted to develop an apparatus capable of even greater precision and yet one in which the former objectionable features are entirely eliminated. To this end we have further modified the apparatus of Washburn and Read in such a way as not only to employ electrical heating, but also to substitute for the Beckmann thermometer a delicate thermocouple. The potentials thus read give values which are proportional to the differences between the boiling points of the solution and solvent.

The apparatus devised is shown in Fig. 1. The boiling flask C is provided with a ground-glass stopper L into which is sealed a test tube of sufficient diameter to admit one of the arms of the thermocouple N. A glass tube J sealed into the flask at W supports the heating coil of platinum wire V. B is a removable vapor pump by means of which the boiling liquid is sprayed through the openings S and over the test tube M. The openings H and I permit both the circulation of the boiling liquid over the heating coil V and the exit of vapor bubbles which insures a rapid mixing throughout the boiling liquid. A glass sheath E sealed in at F prevents the cooling of the boiling liquid flowing through the vents S by the cool liquid returning from the condenser K. The capillary tube D is used for withdrawing samples for analysis. The wires P are the leads which connect the whole or a part of the thermoelement with the potentiometer circuit. To insure rapid adjustment of the temperature between the element C and the boiling liquid the tube N is not only charged with naphthalene vapor, but it is also surrounded with mercury in M to a depth of two or three inches. J is a small glass tube carrying one lead of the heating coil V which is wound about J, the second lead enters the flask at W and is completely insulated from the first by a narrow glass tube. Since twin boiling vessels are used in this differential method of determining the boiling point elevation, it is necessary that the two heating coils shall have the same resistance. For this reason each coil was made of exactly 30 cms. of uniform No. 26 platinum wire.

[1] Washburn and Read: J. Am. Chem. Soc., 41, 729 (1919).

In the experimental procedure duplicate pieces of apparatus are mounted side by side and one arm of the thermocouple is placed in each. The projecting parts of the element are wrapped in flannel. The condenser tubes are protected from moisture by drying trains containing soda lime and fused calcium chloride. Small tubes filled with pure mercury and mounted on movable blocks are used to close the capilary tubes D. Effects due to radiation are eliminated by surrounding each boiling vessel with an asbestos sheath; both boiling vessels, including condensers, are inclosed in a large asbestos box. The copper wires leading from the heating coils are connected in series through a suitable resistance with the 110-volt A. C. lighting circuit. In this way exactly the same current is passed through identical resistances, and uniform heating is assured for both vessels.

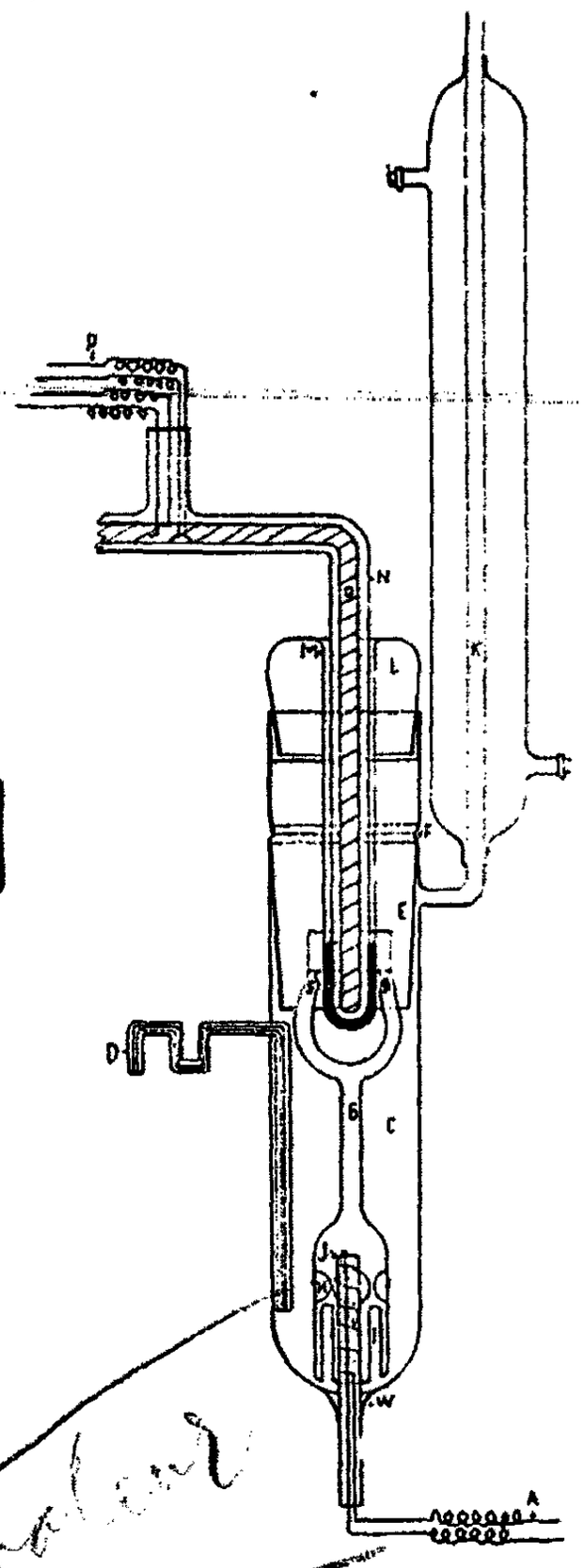



FIG. 1

Pure solvent is introduced intc each vessel and the depth so adjusted that with the proper current a steady flow of boiling liquid can be maintained through the pumps. The solvent in each vessel is allowed to boil until temperature equilibrium is obtained, or until the potential indicated by the thermoelement becomes constant. In no case did the potential thus obtained amount to more than a few microvolts; these potentials are recorded as the zero reading and are used in the subsequent calculations. While both liquids are kept continuously boiling, sufficient solute in the form of pellets is added through the condenser to the solvent in one of the boiling flasks to make a highly concentrated solution. When both solvent and solution have again attained a temperature equilibrium a 50 c.c. sample is withdrawn through the capilary for analysis. This sample is then replaced by an equal volume of pure solvent and the process is repeated *ad libitum*.

In the test that we have made all potentiometer readings were made by means of a Leeds and Northrup "Super K" potentiometer, in conjunction with a high sensitivity galvanometer. These pieces and the boiling apparatus

were mounted on a sheet iron base and earthed. With the apparatus thus described it is possible to detect potential readings to 0.1 microvolt.

The thermocouple was made in strict accord with the specifications laid down by White.[1] In boiling point elevation determinations of this kind it is necessary that the thermocouple be calibrated for a temperature interval close to the boiling point of the liquid to be used as solvent. In this work the procedure consisted in placing one arm of the element in pure boiling benzene and the other in pure boiling alcohol. Each of these boiling liquids was connected

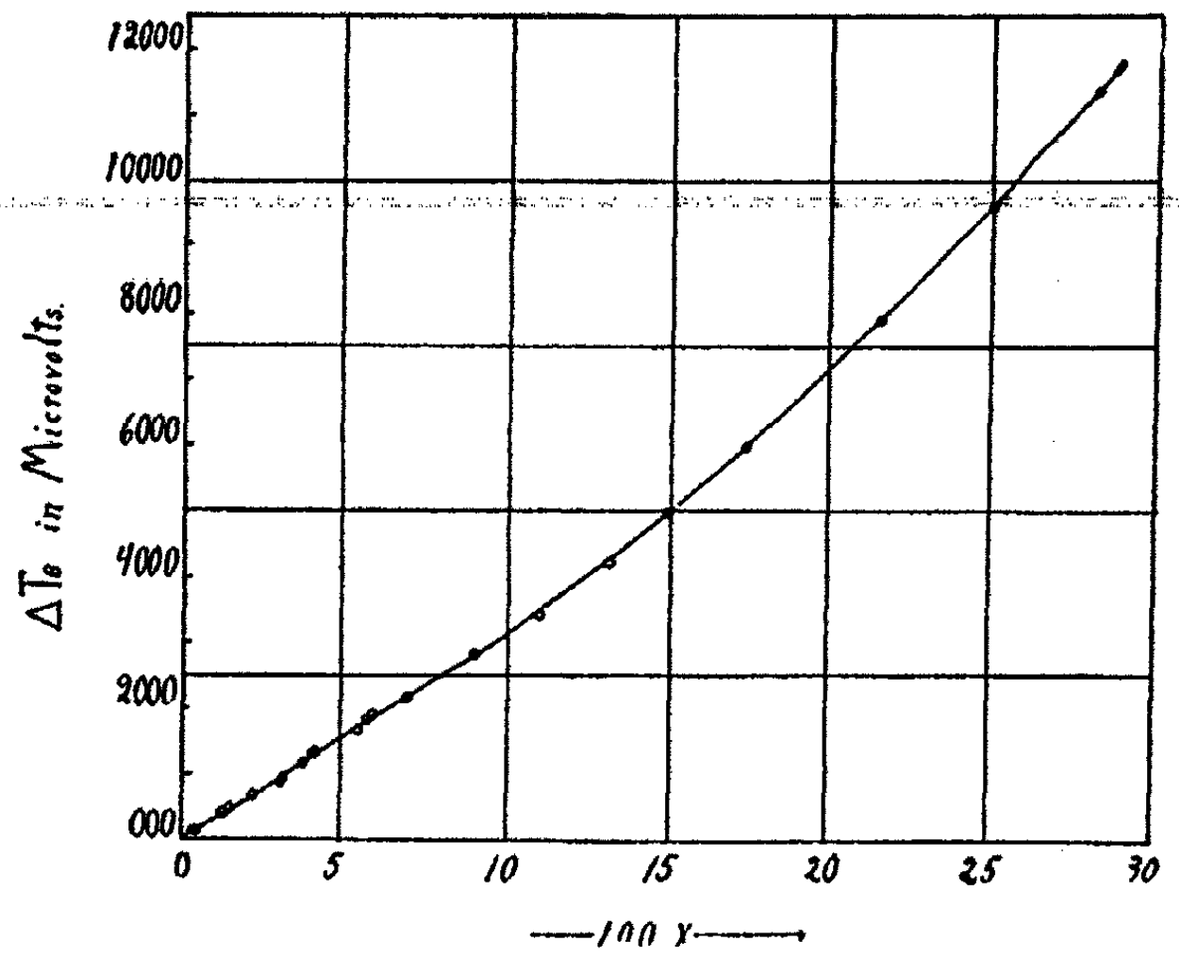



FIG. 2

in turn with a large Dewar flask filled with moist conductivity water ice by one of two reference thermocouples. From the two reference elements we obtained the exact boiling temperatures of the two liquids: from the difference in these boiling points we calculated the change in temperature in degrees per microvolt on the standard thermocouple.

Benzene which had been shaken with concentrated sulphuric acid until thiophene free was further purified by repeated crystalization and fractional distillation. A large mass of naphthalene was repeatedly crystallized by first fusing and allowing to cool slowly: in each step the last 100 c.c. of the liquid was rejected.

A long series of solutions of naphthalene were made up by weight. The angle of refraction of each solution at 25° ±0.01 was then determined for sodium light by means of a large Pulfrich refractometer capable of being read by vernier to 0.1 minute. The refractometer readings were then plotted on a large scale as ordinates against the mol-fractions of naphthalene as abscissae.

[1] White: J. Am. Chem. Soc., 36, 2293, 2313 (1914).

The equilibrium sample was expelled from the boiling vessel into a clean, dry, glass-stoppered flask, quickly cooled to 25° and the angle of refraction determined. The composition of the solution was read directly from the plot. This method of analysis proved to be very rapid; the data obtained were checked by the pycnometer method and have been found to be very accurate.

The data obtained in this test of the apparatus are plotted in Fig. 2. Owing to the fact that one of our reference thermocouples proved to be defective in a later experiment we do not wish to publish the calculated boiling point elevations. The smoothness of the curve and the uniform position of the various points on the curve speaks for the accuracy of the method. In passing we may say that the curve is identical in form with that given by Washburn and Read. We hope that the method suggested may prove of value to others.

*Physical Chemistry Laboratory,*
*The State University of Iowa.*

-887

# DETERMINATION OF THE DISSOCIATION CONSTANTS OF PHENOL AND THE HYDROXYL GROUP OF TYROSINE BY MEANS OF ABSORPTION MEASUREMENTS IN THE ULTRA-VIOLET*

BY WILHELM STENSTRÖM AND NORRIS GOLDSMITH

In the November, 1925 issue of this periodical there was published an article by W. Stenström and M. Reinhard with the title "The influence of pH upon the ultraviolet absorption spectra of certain cyclic compounds." The article stated that the affinity constants with respect to the hydroxyl group could be determined for phenols in aqueous solution by absorption measurements in the ultraviolet. The investigation described below is a test of this method.

A Hilger ultraviolet spectroscope size C and a Hilger sector photometer were used, with an under-water spark between tungsten rods for the light source.

The absorption curves in the ultraviolet for phenol and for tyrosine, for two different values of the hydrogen ion concentration, were published in the article referred to above. The curves for tyrosine at pH < 4 and pH = 12.7 are reproduced in Fig. 1. It was assumed that curve B (pH = 12.7) represents the absorption by tyrosine ions ionized at the hydroxyl group, (complete ionization) and curve A the absorption by other forms of the tyrosine molecule. For a given wavelength there is a certain difference between the extinction coefficients of the two curves. It seems evident that a mixture of the two types of absorbing units will have an extinction coefficient lying between these two values, and that the following relation ought to hold.

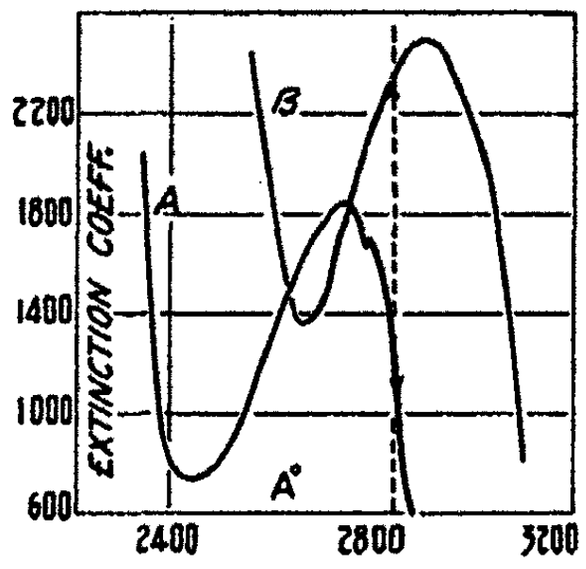



FIG. 1
Tyrosine A, pH < 4. B, pH = 12.7

$$a(1 - X) + bX = \epsilon \quad (1)$$

where

$X$ = the fraction of tyrosine molecules ionized at the hydroxyl group.

$1 - X$ = the fraction of tyrosine molecules not ionized at the hydroxyl group.

$a$ = the extinction coefficient for molecules not ionized at the hydroxyl group.

$b$ = the extinction coefficient for molecules ionized at the hydroxyl group.

*From the State Institute for the Study of Malignant Disease, Buffalo, N. Y., Burton T. Simpson, M.D., Director.

$\epsilon$ = the extinction coefficient for a mixture of ions and molecules.

The law of mass action requires that

$$[H^+]\,[acid^-] = D\,[acid]$$

$$\text{or } [H] \times KX = D \times K\,(1 - X) \quad (2)$$

where K is the original concentration of the acid and D is the dissociation constant.

$$\text{wherefore } X = \frac{D}{[H] + D}$$

combining this expression for X with equation (1)

$$\epsilon = a\left(\frac{[H]}{[H] + D}\right) + b\left(\frac{D}{[H] + D}\right)$$

$$\text{or, } D = \frac{\epsilon - a}{b - \epsilon} \cdot [H] \quad (3)$$

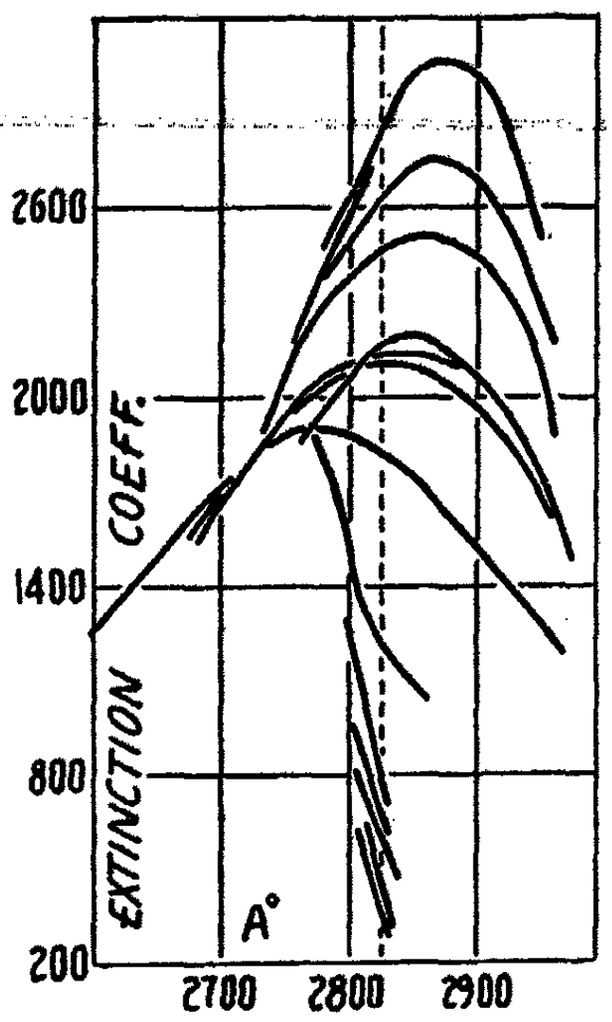



FIG. 2

Curves for phenol, showing how the points are obtained for the curves between the extinction coefficient and pH.

By using equation (3), the dissociation constant can be calculated when a and b are known, and a value of $\epsilon$ lying between a and b has been determined for a certain pH. To obtain a reliable value of D it seemed best to construct the entire curve of the relation between pH and $\epsilon$, $\lambda$ being chosen and constant. Under the same assumptions the method can be used to determine the dissociation constant of other phenols. We first applied it to phenol to compare the value found with older values obtained by other methods.

For each hydrogen ion concentration a curve giving the relation between extinction coefficient and wavelength can be calculated by making a series of exposures with different sector openings and determining the wavelength at which the comparison and absorption spectra show the same blackness on the plate. The desired values of pH were obtained by the addition of sodium hydroxide and were determined colorimetrically. The extinction coefficient for each wavelength

$$\epsilon = \frac{1}{\text{thickness of the absorption cell in cm.}} \times \frac{1}{\text{concentration}} \times \text{log of ratio of sector openings}$$

For each value of pH used, we had to find several points of such a curve in order to determine the extinction coefficient for the wave length chosen (Fig. 2). For phenol the wavelength 2825 Å was selected as the one for which the change in extinction coefficient with wavelength could be most readily followed. An aqueous solution of phenol, N/1570 was used, with the ½ cm.

and 1 cm. absorption cells. The temperature during the exposures varied between 18°C and 24°C. The corresponding values of pH and of the extinction coefficient were obtained as in Fig. 2, where the ordinate through $\lambda = 2825$Å intersects the curves. These values for the first series run with phenol are given in Table I. They were plotted in Fig. 3 and the full curve was drawn as symmetrically as possible with respect to the points.

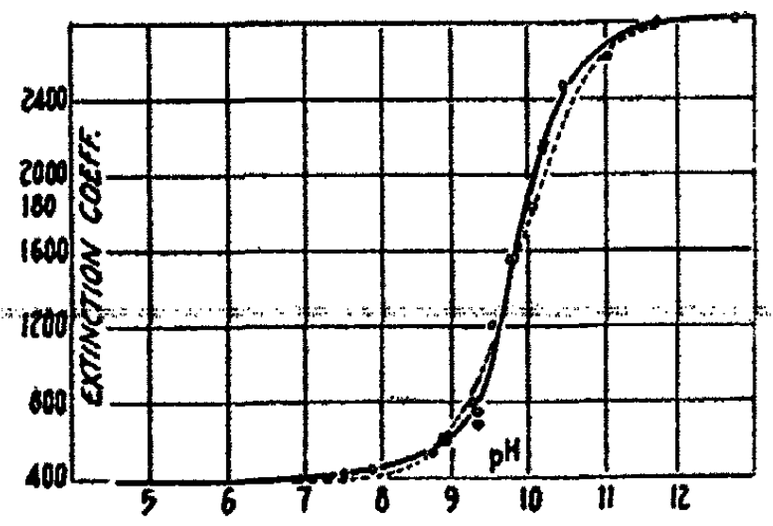



FIG. 3

Phenol, first run. Full curve experimental, broken curve theoretical. $\lambda = 2825$ Å

TABLE I

Phenol: Fig. 3 $\lambda = 2825$Å

| pH | Extinction Coefficient | pH | Extinction coefficient |
|---|---|---|---|
| 4.5 | 380 | 9.95 to 9.8 | 1550 |
| 6 approx. | 380 | 10.0 to 10.1 | 1830 |
| 7.5 | 435 | 10 ± .05 | 2100 approx. |
| 8.75 | 540 | 10.15 to 10.2 | 2125 |
| 8.9 | 610 | 10.2 | 2160 |
| 8.95 ± .05 | 600 | 10.45 | 2465 |
| 9.25 | 790 approx. | 11. | 2630 |
| 9.3 | 690 | 11.7 ± .05 | 2800 |
| 9.3 | 755 | 12.75 | 2822 |
| 9.5 | 1215 | 13 | 2970 |

To calculate the dissociation constant, a point of the curve was used for which $\epsilon$ was approximately the arithmetical mean of the highest value (b) and the lowest value (a) of the extinction coefficient.

$a = 380$, $b = 2822$, $\epsilon = 1600$, pH = 9.86.
Calculated value of $D = 1.38 \times 10^{-10}$

A new solution of phenol was made up and the same procedure repeated, of which the results are plotted in Fig. 4. Thus we found

$a = 380$, $b = 2670$, $\epsilon = 1600$, pH = 9.975
Calculated value of $D = 1.21 \times 10^{-10}$

The values for the dissociation constants of phenol at a temperature between 18 and 25 degrees given in the Landolt-Börnstein tables vary from $.85 \times 10^{-10}$ to $1.3 \times 10^{-10}$. A value of $1.3 \times 10^{-10}$ was obtained by Walker and by Hantzsch. From this value a theoretical curve can be constructed for the relation between extinction coefficient and pH, using equation (3) in another form. The dotted line in Fig. 3 represents this curve.

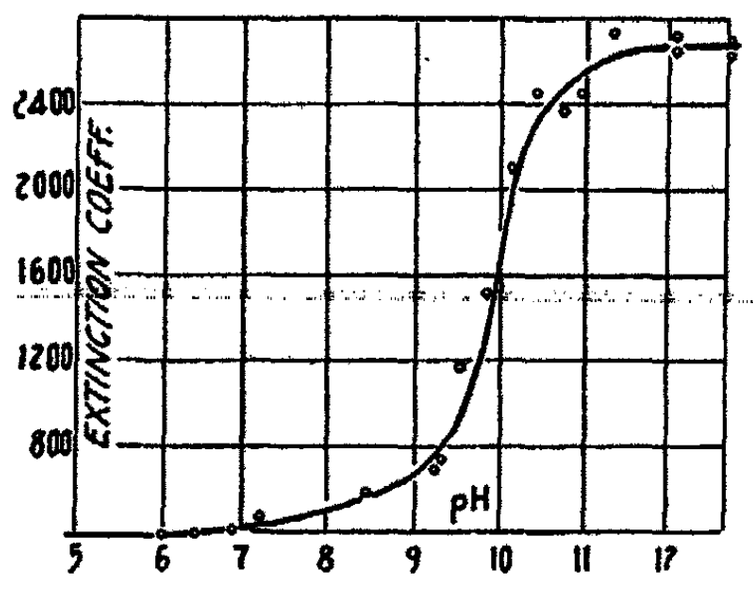



FIG. 4
Phenol, second run. $\lambda = 2825$ Å

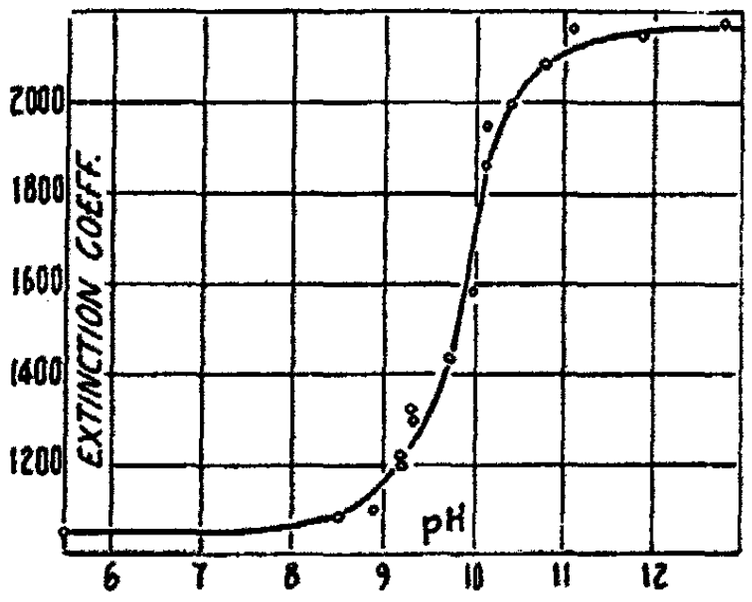



FIG. 5
Tyrosine, first run. $\lambda = 2840$ Å

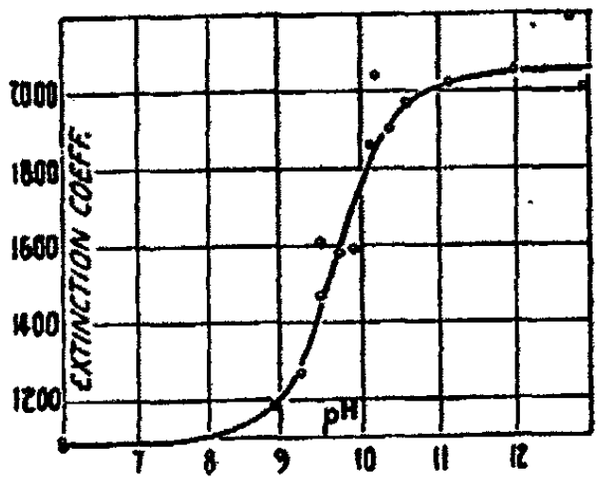



FIG. 6
Tyrosine, second run. $\lambda = 2840$ Å

To find the dissociation constant for tyrosine, the same method was followed, and separate determinations made with two solutions, each of a concentration N/1550, made up independently. The constant wavelength chosen was 2840 Å.

The values of pH, and the corresponding values of the extinction coefficient are given in Table II, and the curves plotted from them are given in Figs. 5 and 6.

TABLE II

Fig. 5. Fig. 6. Tyrosine $\lambda = 2840$Å

| pH | Extinction coeff. | pH | Extinction coeff. |
|---|---|---|---|
| 5.5 approx. | 1050 | 6 approx. | 1085 |
| 8.5 ±.05 | 1085 | 6 approx. | 1095 |
| 8.9 —.05 | 1100 | 8.95 ±.05 | 1185 |
| 9.21 ±.02 | 1200 | 9.29 ±.03 | 1270 |
| 9.2 to 9.25 | 1215 | 9.38 to 9.43 | 1340 |
| 9.32 ±.02 | 1320 | 9.55 ±.08 | 1470 |
| 9.34 ±.02 | 1295 | 9.55 ±.08 | 1610 |
| 9.71 ±.02 | 1435 | 9.74 ±.03 | 1580 |
| 10.15 ±.01 | 1945 | 9.85 to 10. | 1590 |
| 10.15 ±.02 | 1860 | 10.14 ±.02 | 1860 |
| 10.4 to 10.45 | 1990 | 10.2 ±.03 | 2040 |
| 10.8 ±.1 | 2082 | 10.35 to 10.4 | 1900 |
| 11.1 to 11.15 | 2160 | 10.55 to 10.7 | 1970 |
| 11.9 ±.05 | 2145 | 11.15 ±.05 | 2020 |
| 12.8 ±.05 | 2170 | 12.0 ±.01 | 2055 |
| 12.9 approx. | 2360 | 12.77 ±.05 | 2190 |
| 9.95 to 10 | 1580 | 12.95 | 2010 |

From Fig. 5 a = 1050, b = 2160, $\epsilon = 1600$, pH = 9.90.
Calculated value of $D = 1.24 \times 10^{-10}$
From Fig. 6 a = 1090, b = 2055, $\epsilon = 1550$, pH = 9.70.
Calculated value of $D = 1.83 \times 10^{-10}$.

The two values do not agree as well as the two obtained for phenol. A comparison of the four values does not show any marked difference between the dissociation constants of phenol and tyrosine with respect to the hydroxyl group.

It is evident from the curves in Fig. 2 that a large number of exposures must be made to determine D by the method here described. We believe that a greater accuracy than the above results indicate can be attained by using several wavelengths instead of one, a procedure which would involve little extra labor if planned for in the beginning.

# THE ELECTROMETRIC DETERMINATION OF SMALL AMOUNTS OF FERRIC IRON*

BY J. F. KING AND R. N. WASHBURNE

During some work which is in progress in this laboratory, it became necessary to determine quantitatively small amounts of iron in solution in the ferric condition. Gravimetric methods were not used because they are too inaccurate for small amounts of iron. The ordinary volumetric methods could not be used because of the great errors caused by the poor end points when dilute solutions are used. The usual colorimetric methods were tried but were found to be unsatisfactory because of the intrinsic inaccuracy of the colorimetric method, the difficulty of comparing slight differences in colors and of correctly reproducing these colors. Hostetter and Roberts[1] have developed a very exact method for the direct electrometric determination of small quantities of ferrous iron in which they are able to realize an accuracy of one part in a thousand with a total of 0.00056 grams of iron in a volume of solution of from 10 to 35 cc. This method could have been adapted to our use if a satisfactory way could have been worked out for the reduction of a small quantity of ferric iron in a small volume of solution. Hostetter and Roberts have also suggested the use of stannous chloride for electrometrically determining small quantities of ferric iron but we found very dilute solutions of stannous chloride difficult to store and with them reproducible end points hard to obtain. Adam[2] finds that the direct electrometric titration of ferric iron with stannous chloride gives unsatisfactory results. Hendrixson and Verbeck[3] have suggested the use of titanium salts as reducing agents in electrometric titrations and have shown how such solutions may be standardized against potassium permanganate and potassium dichromate directly or through ferric alum solutions. The titanous solutions which they used were approximately 0.1 normal concentration. In some work with titanous salts on the direct electrometric titration of numerous cations and anions singly and in mixtures, Kolthoff and Tomicek[4] have determined ferric iron, working with approximately 0.1 normal solutions.

The value of an accurate method for the direct determination of small quantities of ferric iron is obvious. When iron samples are put into solution for analysis, the iron is usually partly or completely in the ferric state. Ferrous iron is more easily oxidized to ferric iron than is ferric iron reduced to ferrous iron and the excess of the oxidant is more easily removed than the excess of the reductant. Any process for determining small quantities of iron in which

* Contribution from the Thompson Chemical Laboratory, Williams College.

[1] Hostetter and Roberts: J. Am. Chem. Soc., 41, 1337 (1919).

[2] H. R. Adam: J. S. African Chem. Inst., 8, 7 (1925).

[3] W. S. Hendrixson and L. M. Verbeck: J. Am. Chem. Soc., 44, 2382 (1922).

[4] I. M. Kolthoff and O. Tomicek: Rec. Trav. chim., 43, 798 (1924).

the entire process is carried out continuously in one container is desirable because of the elimination of loss by transfer and because of the possibility of keeping down the volume of the solution.

We have worked out the details of a method by which we are able to determine as little as 0.0003 to 0.0005 grams of ferric iron by the direct electrometric titration with titanous sulfate with an error of less than 0.1 percent.

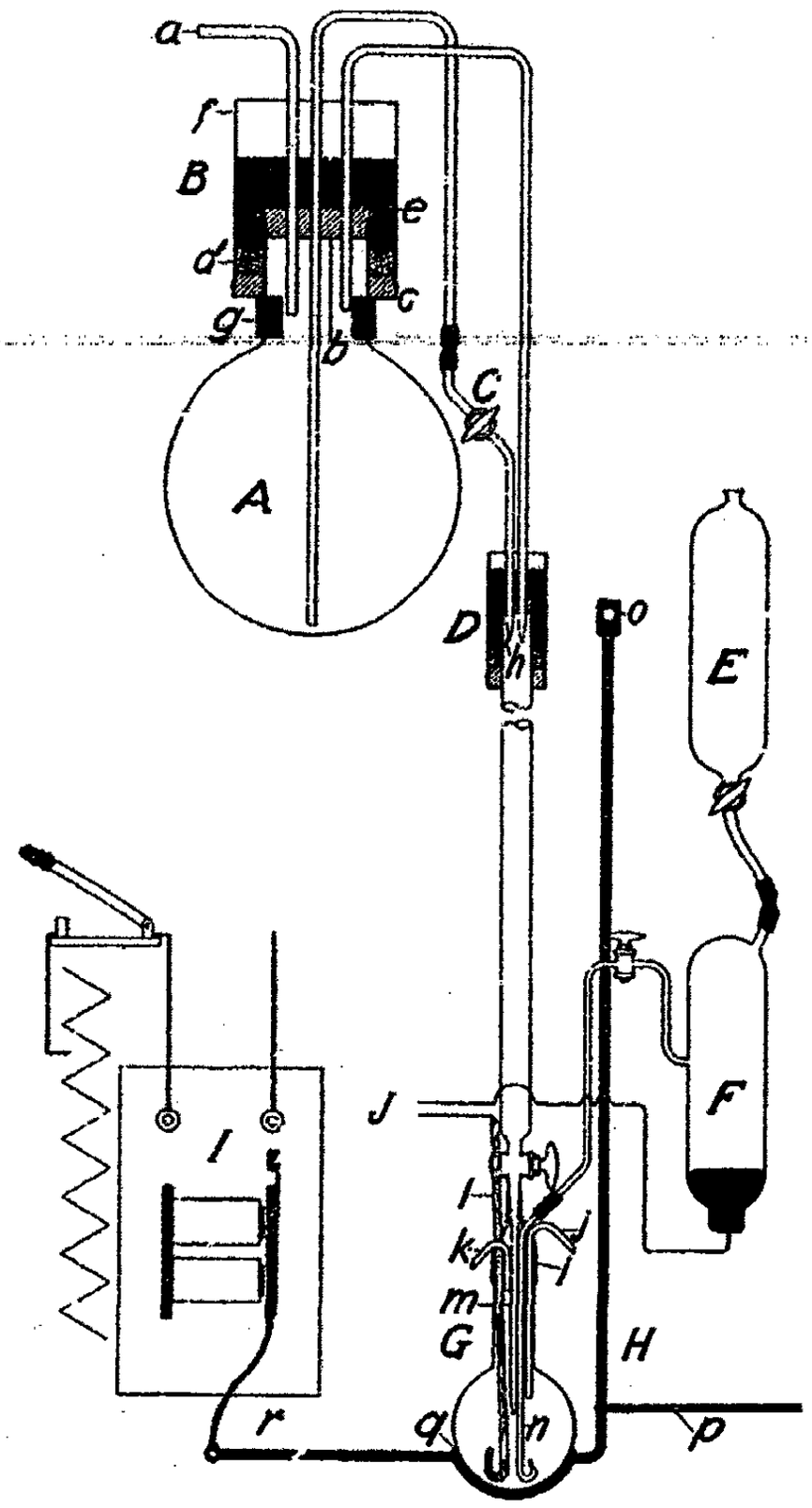



FIG. 1

An electrometric titration apparatus for titrating small volumes of heated solutions which are protected from the action of oxygen of the air.

We have developed a simple electrometric titration apparatus which can be easily assembled out of standard laboratory equipment. We have been able to store titanous sulfate solutions for this work as dilute as 0.001 normal to 0.0003 normal.

## The Apparatus

The apparatus used for the electrometric determinations is shown in Fig. 1 where:

A is a three-liter round-bottom Pyrex flask for storage of the titanous sulfate solutions.
- a is the inlet from the carbon dioxide or hydrogen generator.

B is the mercury seal
- b a rubber stopper
- c a cork stopper
- d paraffin
- e mercury
- f metal collar of seal
- g clamp to support mercury seal

When sealing wax, paraffin or collodion were used at B and D, it was found that the slight jarring of the burette in using caused leaks which admitted enough air to oxidize the titanous solution very rapidly.

C is a well ground stop-cock for filling the burette.
h is a capillary tip touching the side of the burette.

D is a mercury seal similar to B.

E is a storage reservoir for the saturated potassium chloride solution for the calomel cell.

F is the calomel cell.

G is a 100 cc round-bottom long-neck Pyrex flask which was used as the titrating flask.
- i is a rubber nipple with holes punched through and serves as a cap to keep out the air.
- j Carbon dioxide gas inlet
- k Carbon dioxide gas outlet
- l platinum electrode shown in Fig. 2
- m capillary extension tip to burette
- n turned up tip from calomel cell.

H is a shaking device to keep the solution constantly stirred.
- o is a bearing
- p rubber tension fastened here
- q asbestos rest for flask

Constant readings could only be obtained on the potentiometer when a vigorous and uniform stirring was maintained by the shaking device.

I parts of an electric gong with an extension soldered on the clapper at r. A switch in series with "I" makes it possible to start and stop the shaker for the addition of portions of the titanous sulfate solution during the titration. A rheostat in series with the gong controls the speed

J of shaking.

Wires connected to the potentiometer which in our work was a Leeds and Northrup Type K potentiometer.

The electrode shown in Figure 2 was designed to support the very fine platinum wire (0.0085 mm in diameter) and to keep the mercury used for making contact with the platinum wire above the hot solution in which the electrode was used. With an ordinary platinum wire electrode trouble was frequently experienced due to slight cracks developing where the wire was sealed in with sealing glass which allowed the hot acid solution to come in contact with the mercury. This electrode was found to be very satisfactory, to give constant and reproducible readings. It was cleaned and stored in hot chromic acid and washed with distilled water.

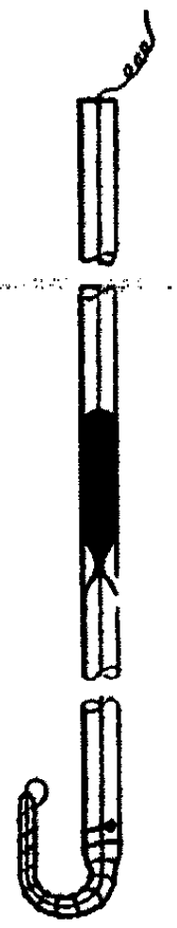


FIG. 2
An electrode of fine platinum wire for use in hot solutions.

Since the solutions were heated when titrated, a small electric fan was used near the burette to keep the air in circulation around the burette during the titration so that there would be no volume change in the solution in the burette. Readings over a period of time were made to establish the fact that the fan served this purpose.

### Preparation and Storage of Dilute Titanous Sulfate Solutions

Knecht and Hibbert[1] and Thornton and Chapman[2] recommend the storage of titanous solutions in an atmosphere of hydrogen gas. Thornton and Chapman report their titanous sulfate solutions remaining constant over a period of 42 days. With the dilute solutions which we used it was necessary to give special attention to the question of storage. We have used both hydrogen and carbon dioxide and with the precautions given below have found that our solutions kept well enough for use with occasional restandardization. The standard titanous sulfate solutions were prepared as follows:

Sulfuric acid solution was boiled for about two hours in a three-liter round bottom Pyrex flask to free it from dissolved oxygen. The solution was made of such a strength that after boiling it was 20 percent (by weight) in sulfuric acid. After boiling, the flask was stoppered and hydrogen was passed through the solution as it cooled. The hydrogen, prepared in a Kipp generator with C. P. zinc and sulfuric acid containing trace of copper sulfate, was purified by passing through four wash bottles, (1) 20% KOH, (2) alkaline permanganate, (3) two bottles of alkaline pyrogallol. To the sulfuric acid solution was then added the correct volume of LaMotte Chemical Company's 15% stock titanous sulfate solution to make an approximate 0.001 normal solution. With hydrogen bubbling through the solution, the flask was then fitted with its mercury seal and attached to the titrating apparatus which itself had been freed from air. The solution thus prepared was compared with a standard ferric iron solution. The standard ferric iron solution was made from a

[1] E. Knecht and E. Hibbert: "New Reduction Methods in Volumetric Analysis."
[2] W. M. Thornton, Jr. and E. Chapman: J. Am. Chem. Soc., 43, 91 (1921).

weighed amount of clear crystals of C. P. ferrous ammonium sulfate from a freshly opened bottle. Enough of the salt was taken to make 500 cc of a solution ten times as strong as the desired standard. The weighed salt was dissolved in a small amount of air free 20 percent sulfuric acid solution and oxidized with 0.1 normal potassium permanganate. This oxidized solution was made up to 500 cc with the special sulfuric acid. 50 cc of this solution was then diluted to 500 cc for use in standardization. The dilutions were carried out in calibrated apparatus in a thermostat. The following data gives a record of the change in strength of a titanous sulfate solution made as above:

On Feb. 3rd a titanous sulfate solution was prepared and when titrated electrometrically against a standard ferric iron solution, it was found that 14.04 cc of the titanous sulfate solution was equivalent to 25 cc of 0.001 normal ferric iron solution. That the solution thus stored was effectually protected from oxidation can be seen from the following tests:

25 cc of 0.001 normal ferric solution equivalent

| Date | cc titanous sulfate solution |
|---|---|
| Feb. 9th | 14.14 |
| 16 | 14.15 |
| 25 | 14.34 |
| Mar. 7 | 14.46 |
| 23 | 14.65 |
| 26 | 14.75 |

During the entire time that these tests were made this solution was being drawn upon for use in analyses.

### Effect of Exclusion of Air during Titration

Although Thornton and Chapman found that they were able to obtain consistent results titrating with titanous solutions exposed to the air when the standardization was made under the same conditions as the analysis, with our more dilute solutions and using the electrometric end point, a series of experiments showed that it would be necessary to protect the solutions during titration from the oxygen of the air.

Curves A, B and C in Figure 3 show the results of the titration of a 0.01 normal ferric iron solution with a 0.02 normal titanous sulfate solution in an open flask. Curve D in the same figure is a typical curve resulting from the titration of the same solutions in a flask with the solution protected from the air with a blanket of carbon dioxide. (Analyses of several samples of the carbon dioxide gas from a tank of the gas used, taken at different times as the tank was being emptied, showed an oxygen content of less than 0.05 percent by volume.) Three such titrations as shown by curve D gave results as follows:

| cc of ferric solution | cc titanous solution |
|---|---|
| 25 | 11.61 |
| 25 | 11.59 |
| 25 | 11.60 |

Since the results with the 0.02 normal titanous sulfate solutions showed that air must be excluded from the flask during titration, we used the carbon dioxide blanket in all the work with the more dilute solutions.

### Effect of Acidity

In their work on the electrometric titration of ferrous iron by potassium dichromate, Hostetter and Roberts found that over a range of 17% to 67%

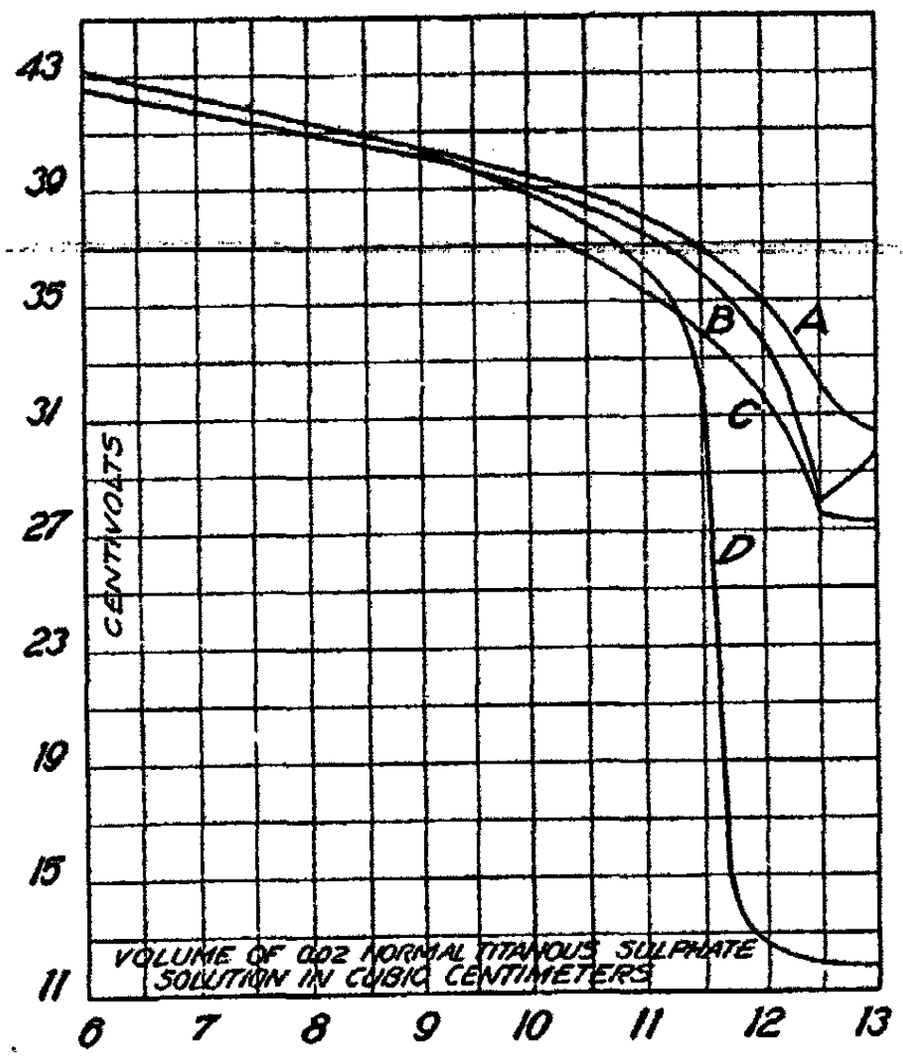



FIG. 3
Curves to show the effect of excluding air from the flask during titration.

sulfuric acid, the potential change at the end point increased with increasing acidity. With 0.001 normal dichromate solutions, they found that a very sharp end point could be realized if both the iron solution and the dichromate solution were made up with 25 percent sulfuric acid. In a series of titrations of ferric iron with titanous sulfate solutions, we studied the effect of increasing the acidity of both solutions from 5% to 20% in sulfuric acid.

A 0.001 normal ferric solution made up with 5% sulfuric acid was titrated with a titanous sulfate solution also made up with 5% sulfuric acid. The titration was run in duplicate with results as follows:

| cc ferric solution | cc titanous solution |
|---|---|
| 25 | 13.54 |
| 25 | 13.54 |

The shape of the curves from which the end points were read off is shown by curve A on Figure 4.

Next a 0.001 normal ferric solution was made up with 20% sulfuric acid and this was titrated with a titanous sulfate solution made up with 20% sulfuric acid. The titration was made in triplicate with the following results:

| cc ferric solution | cc titanous solution |
|---|---|
| 25 | 14.32 |
| 25 | 14.32 |
| 25 | 14.33 |

The shape of the curves from which the end points were read off is shown by curve B in Figure 4.

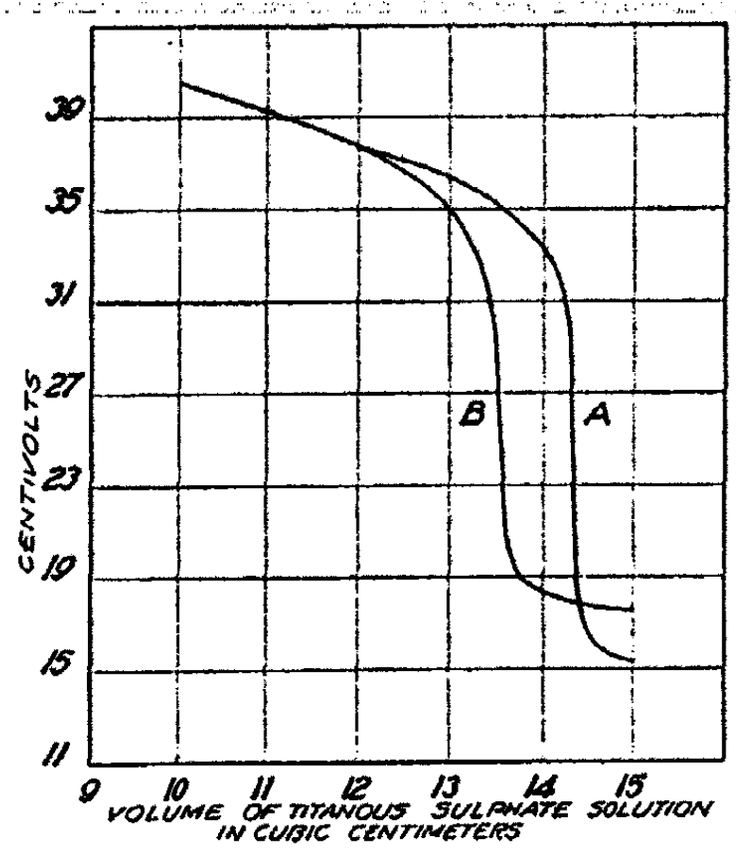



FIG. 4
Curves to show the effect of increasing the acidity of the solutions.

With the 20% sulfuric acid solution, the addition of 0.05 cc of the titanous sulfate solution caused a drop in voltage of 0.120 volts while with the 5% sulfuric acid solution the addition of 0.05 cc of the titanous sulfate solution caused a drop of 0.080 volts. We therefore made use of 20% sulfuric acid in all the rest of the titrations.

### Effect of the Increase in Temperature

The time required to reach equilibrium after each addition of titanous sulfate solution was noticably greater with the dilute solutions. For instance, when working with 0.0003 normal titanous sulfate solution, in one experiment and excess of the titanous sulfate solution was added to the iron solution over the usual period of time. Then the voltage change was taken over a period of ten minutes as follows:

| Time in minutes | volts | Time in minutes | volts |
|---|---|---|---|
| 0 | 0.356 | 6 | 0.187 |
| 1 | 0.341 | 8 | 0.170 |
| 2 | 0.322 | 9 | 0.165 |
| 3 | 0.302 | 10 | constant |
| 5 | 0.213 | | |

Knecht and Hibbert and Kolthoff and Tomicek were successful in titrating with solutions of titanous salts more concentrated than ours at temperatures

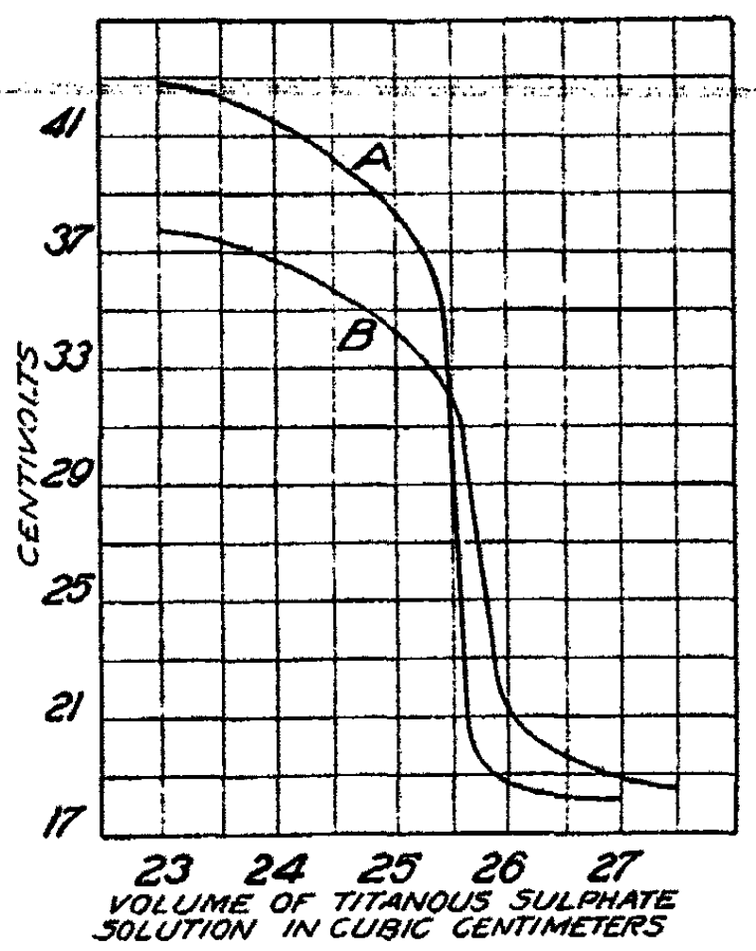



FIG. 5
Curves to show the effect of increase in temperature.

above room temperature. We obtained sharp and reproducible curves with a 0.0003 normal titanous sulfate solution when the 20 percent sulfuric solution of ferric iron was heated to the boiling point (about 106 degrees Centigrade). In Figure 5 are given two curves to show the effect of temperature. Curve B was made from data obtained when the titration was carried out at room temperature with solutions approximately 0.001 normal and curve A was made from data obtained by titrating the same solutions at the boiling point. In the hot solutions not only are the end points sharper but the drop in potential of 0.140 volt is caused by the addition of 0.2 cc of the reagent as against in the solution at room temperature of 0.110 by the addition of 0.5 cc of the reagent.

## Accuracy of Method

In order to test out the accuracy of the method, three series of experiments were carried out with different solutions. Each titration was run in duplicate and the results given in the following table are the average of the two.

Column 1 cc of iron solution used
2 grams of iron in this volume of solution corrected for the iron impurity in the reagents (determined by running a "blank").
3 cc of titanous solution used (read off the voltage—volume graphs).
4 grams of iron equivalent to this volume of titanous solution (i.e. "grams of iron found") The first duplicate analysis in a series is in this case used as the one to "standardize" the titanous sulfate solution.
5 ratio of the volume of ferric solution to the volume of titanous solution.
6 percent error considering the first analysis as the standard.

TABLE OF RESULTS

| | cc. of iron solution | "corrected" grams of iron taken | cc. titanous solution | "grams of iron found" | ratio of volumes | percent error |
|---|---|---|---|---|---|---|
| | | | Series I | | | |
| 1. | 25.00 | 0.001407 | 16.30 | 0.001407 | 1.533 | |
| 2. | 49.98 | 0.002812 | 32.64 | 0.002815 | 1.531 | 0.1 |
| 3. | 34.98 | 0.001966 | 22.82 | 0.001968 | 1.532 | 0.1 |
| 4. | 14.98 | 0.0008429 | 9.72 | 0.0008399 | 1.539 | 0.37 |
| | | | Series II | | | |
| 5. | 25.00 | 0.002153 | 25.21 | 0.002153 | 0.9916 | |
| 6. | 19.98 | 0.001720 | 20.13 | 0.001719 | 0.9925 | 0.07 |
| 7. | 29.98 | 0.002581 | 30.20 | 0.002579 | 0.9927 | 0.08 |
| | | | Series III | | | |
| 8. | 25.00 | 0.0004203 | 24.46 | 0.0004203 | 1.022 | |
| 9. | 19.98 | 0.0003360 | 19.56 | 0.0003361 | 1.022 | 0.03 |
| 10. | 29.98 | 0.0005042 | 29.44 | 0.0005059 | 1.019 | 0.3 |

In Figure 6 are reproduced the curves which resulted from the six analyses giving the data in Series II of the table.

No. 5 is the average of Curve C and D

No. 6 is the average of Curves A and B

No. 7 is the average of Curves E and F

These curves are reproduced for the purpose of showing the sharpness of the end-points in the analyses with a dilute titanous sulfate solution according to the method which was developed.

## Summary

1. An electrometric method has been described for the determination of small amounts of iron.

2. A procedure for satisfactorily storing titanous sulfate solutions as dilute as 0.0003 normal for periods of several weeks has been given.

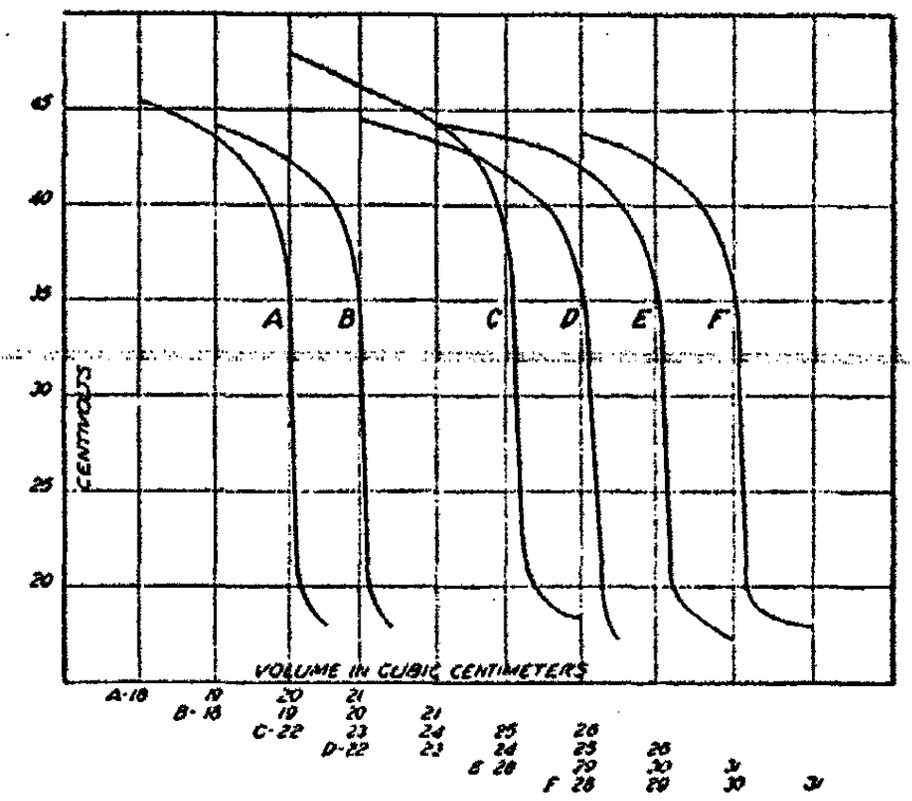




FIG. 6

Typical curves resulting from the titration of a small amount of ferric iron with an approximate 0.001 normal titanous sulfate solution.


3. A simple electrometric titration apparatus has been described where small volumes of a reagent may be shaken, heated, protected from the air by an inert gas and electrometrically titrated.

4. A platinum electrode with fine platinum wire has been designed for use in hot solutions.

5. Results of our work show that it is possible to determine as small an amount of iron as 0.0003 grams in the ferric condition by direct electrometric titration with an accuracy of one part in a thousand.


*Williamstown, Mass.*

BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS
ORSAY

BIBLIOTHEQUES DE L'UNIVERSITÉ DE PARIS
ORSAY

# NAME INDEX

*To Papers*


| | | |
|---|---|---|
| *Adkins, Homer,* | See Lazier and Adkins, | 353 |
| *Åkerlöf, Gösta,* | The solubility of strong, simple electrolytes in water, | 1585 |
| *Andrews, Mary R.,* | Vapor pressure of naphthalene at low temperature, | 1497 |
| *Arenson, S. B., P. E. Roller and D. J. Brown,* | The reactive nature of aldehydes from the standpoint of the apparent electromotive force, | 620 |
| *Arsem, W. C.,* | Gel structure, | 306 |
| *Bachman, P. W.,* | See Patrick and Bachman, | 134 |
| *Bancroft, Wilder D.,* | Blue wood, | 521 |
| *Bancroft, Wilder D.,* | The water equilibrium, | 1194 |
| *Beebe, R. A.,* | Heat of adsorption of carbon monoxide on copper catalyst, | 1538 |
| *Bencowitz, Isaac, and H. T. Hotchkiss, Jr.,* | Vapor pressure lowering as a function of the degree of saturation. II, | 643 |
| *Benton, A. F.,* | A gel of metallic platinum, | 1415 |
| *Benton, A. F. and T. L. Williams,* | The catalytic oxidation of carbon monoxide in contact with quartz glass, | 1487 |
| *Bergstein, M., and Martin Kilpatrick, Jr.,* | The catalytic minimum point, | 1616 |
| *Bergstrom, F. W.,* | Reaction of the type $Cl_2+2KOH=KCl+KClO+H_2O$, | 12 |
| *Booth, H. S.,* | See Germann and Booth, | 369 |
| *Bowen, N. L.,* | Properties of Ammonium Nitrate. I, II, III, | 721, 726, 736 |
| *Brode, W. R.,* | The effect of solvents on the absorption spectrum of a simple azo dye, | 56 |
| *Brode, W. R.* | See Phipps and Brode, | 507 |
| *Brönsted, J. N.,* | The acid-basic function of molecules and its dependency on the electric charge type, | 777 |
| *Brown, D. J.,* | See Arenson, Roller and Brown, | 620 |
| *Brown, F. S., and C. R. Bury,* | Cryoscopic measurements with nitrobenzene. IV. | 694 |
| *Brüzs, B.,* | Velocity of thermal decomposition of carbonates, | 680 |
| *Burk, R. E.,* | A possible mechanism for the lowering of the heat of activation of a reaction by a catalytic surface, | 1134 |
| *Burt-Gerrans, J. T.,* | The electrolysis of acid solutions of copper sulphate. II, | 396 |
| *Bury, C. R., and F. S. Brown,* | Cryoscopic measurements with nitrobenzene. IV, | 694 |
| *Byron, M. L.,* | The peptization of pyroxylin, | 1116 |
| *Cady, H. P.,* | See Groening and Cady, | 1597 |
| *Cantelo, R. C.,* | The thermal decomposition of methane. II, | 899 |
| *Cantelo, R. C.,* | The methane equilibrium. I, | 1641 |
| *Carroll, B. H.,* | The photochemical oxidation of leuco bases, | 130 |
| *Chakravarti, D. N., and N. R. Dhar,* | Viscosity measurements of certain sols in presence of electrolytes, | 1646 |
| *Chen, Hsi-Ching,* | A laboratory latex, | 713 |
| *Collett, A. R., and John Johnston,* | Solubility relations of isomeric organic compounds. VI, | 70 |
| *Cray, F. M.,* | The color change of Congo red in acidified acetone-water solutions, | 1276 |
| *Creighton, H. J. M.,* | Solubility and electrolytic conductance of mesitylene phosphinous acid, | 1209 |

| | | |
|---|---|---|
| *Cunliffe, P. W., R. G. Franklin, R. E. W. Maddison, and L. Reeve,* | Studies in photochemical technique. III, | 1427 |
| *Currie, L. M.,* | Antimony sulphides, | 205 |
| *Davies, E. C. H., and V. Sivertz,* | Rhythmic diurnal bands of gold and platinum in silicic acid gel, | 1467 |
| *Derbigny, I. A.,* | See Nichols and Derbigny, | 491 |
| *Dennis, L. M., and F. E. Hance,* | Germanium. XVI, | 1055 |
| *Dennis L. M. and A. W. Laubengayer,* | Germanium. XVII, | 1510 |
| *Dennis, L. M., W. R. Orndorff and D. L. Tabern,* | Germanium. XV, | 1049 |
| *Dhar, N. R.,* | Influence of temperature on metabolism and the problem of acclimatization, | 480 |
| *Dhar, N. R.,* | Origin of the formation of deposits in gout and other diseases, and the cause of swelling in beriberi, | 277 |
| *Dhar, N. R.,* | Old age and death from a chemical point of view, | 378 |
| *Dhar, N. R.,* | See Chakravarti and Dhar, | 1646 |
| *Dhar, N. R., and S. Ghosh,* | Studies in adsorption. XIII, | 628 |
| *Dhar, N. R.,* | See Ghosh and Dhar, | 294, 820, 1564 |
| *Dhar, N. R.,* | See Mehrotra and Dhar | 1185 |
| *Dhar, N. R.,* | See Palit and Dhar, | 939, 1125 |
| *Draves, C. Z.,* | See Tartar and Draves, | 763 |
| *Dunnicliff, H. B., I. S. Sikka and R. C. Hoon,* | The system: sodium sulphate, sulphuric acid, ethyl alcohol, | 1211 |
| *Engelder, C. J.,* | See Nelson and Engelder, | 470 |
| *Engelder, C. J.,* | See Rudisill and Engelder, | 106 |
| *Engelder, C. J.,* | See Wescott and Engelder, | 476 |
| *Field, M. C.,* | See McBain and Field, | 1545 |
| *Firth, J. B., and W. L. Purse,* | Organogels of silicic acid—the replacement of the water in the hydrogel by alcohol, | 617 |
| *Forbes, G. S., and Philip Albert Leighton,* | Electrolysis of dichromic acid under a mercury vapor lamp of high intensity, | 1628 |
| *Franklin, R. G.,* | See Cunliffe, Franklin, Maddison, and Reeve, | 1427 |
| *Frazer, J. C. W., B. F. Lovelace and R. K. Taylor,* | The vapor pressures of potassium nitrate solutions at 20°C, | 1669 |
| *Freyer, E. B.,* | See Yoe and Freyer, | 1389 |
| *Frivold, O. E.,* | The influence of the ionic charge on the osmotic behavior of alcoholic solutions, | 1153 |
| *Fryling, C. F.,* | Heats of adsorption and the problem of promoter action, | 818 |
| *Fulmer, E. I.,* | See Sherwood and Fulmer, | 738 |
| *Ganguly, P. B.,* | The scattering of light by aqueous sodium silicate solution, | 706 |
| *Garner, Maud,* | Note on the significance of the variation in the Smoluchowski coagulation coefficient ($\beta$), | 1410 |
| *Garner, Maud, and W. C. McC. Lewis,* | The effect of temperature on the rate of coagulation of gold sol, | 1401 |
| *Germann, A. F. O., and H. S. Booth,* | Thermal analysis of the system boron trifluoride-hydrogen sulphide, | 369 |
| *Getman, F. H.,* | The ultraviolet absorption spectra of aqueous solutions of sulphur dioxide and some of its derivatives, | 266 |
| *Ghosh, S. and N. R. Dhar,* | The influence of ageing of a sol on its coagulation, | 1564 |

| | | |
|---|---|---|
| *Ghosh, S., and N. R. Dhar,* | The influence of ions carrying the same charge as the dispersed particles in the inversion of emulsions, | 294 |
| *Ghosh, S., and N. R. Dhar,* | Studies in adsorption. XIV, | 830 |
| *Ghosh, S.,* | See Dhar and Ghosh, | 628 |
| *Goldsmith, Norris,* | See Stenström and Goldsmith, | 1683 |
| *Groening, A. A., and H. P. Cady,* | Decompoeition potentials and metal overvoltages in liquid ammonia and water, | 1597 |
| *Gurchot, Charles,* | Reversible permeability of membranes and its relation to cell metabolism, | 83 |
| *Hampton, W. H.,* | The potential of the iron electrode, | 980 |
| *Hance, F. E.,* | See Dennis and Hance, | 1055 |
| *Harder, O. E.,* | See Reyerson, Harder and Swearingen, | 1623 |
| *Hardy, F.,* | Anomalous flocculation in colloidal clays and soils, | 254 |
| *Harman, R. W.,* | Aqueous solutions of sodium silicates. II, III, | 359, 917 |
| *Harned, H. S.,* | Individual thermodynamic behaviors of ions in concentrated solutions, ine uding a discussion of the thermodynamic method of computing liquid-junction potentials, | 433 |
| *Harned, H. S., and G. M. James,* | The dissociation of water in potassium and sodium bromide solutions, | 1060 |
| *Harris, J. McA., Jr.,* | See Lucasse and Harris, | 930 |
| *Harvey, C. E.,* | See McBain, Harvey and Smith, | 312 |
| *Hendricks, S. B.,* | Equi ibrium in the system: arsenic pentoxide, barium oxide, water, | 248 |
| *Herzog, R. D.,* | The nature of the structure of cellulose and its significance in chemical transformations, | 457 |
| *Hicks, M. M.,* | See Pearce and Hicks, | 1678 |
| *Hoon, R. C.,* | See Dunnicliff, Sikka and Hoon, | 1211 |
| *Hopkins, D. G.,* | See McBain and Hopkins, | 114 |
| *Hotchkiss, H. T., Jr.,* | See Bencowitz and Hotchkiss, | 643 |
| *Howard, H. C., Jr.,* | Mechanism of the catalytic dehydration of methanol, and some properties of the hydrous aluminum oxide catalyst, | 964 |
| *Hylan, M. C.,* | Grain size and the quantum theory of photographic exposure, | 845 |
| *James, G. M.,* | See Harned and James, | 1060 |
| *Johnson, F. M. G.,* | See Munro and Johnson, | 172 |
| *Johnston, John,* | See Collett and Johnston, | 70 |
| *Joss, E. J.,* | The action of metals on nitric acid, | 1222 |
| *Kao, C. H.,* | See Lenher and Kao, | 126 |
| *Kawamura, K.,* | Adsorption by humic acid, | 1364 |
| *Kelley, K. K.,* | See Parks and Kelley, | 47, 1175 |
| *Kilpatrick, Martin, Jr.,* | See Bergstein and Kilpatrick, | 1616 |
| *King, J. F., and R. N. Washburne,* | The electromotive determination of small amounts of ferric iron, | 1688 |
| *Kistiakowsky, G. B.,* | The ionisation potentials of nitrogen and hydrogen on iron and other metals, | 1356 |
| *Klosky, Simon, and Leo Woo,* | Solubility of silver oxide, | 1179 |
| *Koch, W.,* | See Mund and Koch, | 289 |
| *Kraemer, E. O.,* | See Stamm and Kraemer, | 992 |
| *Kunsman, C. H.,* | The thermionic properties of some mixtures used as catalysts in the synthesis of ammonia, | 525 |
| *Lambert, R. H.,* | The ternary system: silver bromide—potassium bromide—water, | 973 |

| | | |
|---|---|---|
| *Laubengayer, A. W., and R. B. Corey,* | Germanium. XIII, | 1043 |
| *Laubengayer, A. W., and D. L. Tabern,* | Germanium. XIV, | 1047 |
| *Lazier, W. A., and Homer Adkins,* | Adsorption of ethylene and hydrogen by zinc oxide, iron oxide, nickel, and copper, | 353 |
| *Lazier, W. A., and Homer Adkins,* | The formation of carbon dioxide from alcohols, | 895 |
| *Leighton, Philip Albert,* | See Forbes and Leighton, | 1628 |
| *Lenher, Victor, and C. H. Kao,* | Studies on the chemistry of gold, | 126 |
| *Lucasse, W. W.,* | The transference numbers of hydrochloric acid in glycerol-water mixtures, | 562 |
| *Lewis, J. McC., Jr.,* | See Garner and Lewis, | 1401 |
| *Lovelace, B. F.,* | See Frazer, Lovelace and Taylor, | 1669 |
| *Lucasse, W. W., and J. McA. Harris, Jr.,* | The transition points of salt hydrates in non-aqueous solutions, | 930 |
| *McAulay, John, Jr.,* | Influence on the solubilities of salts in water by the addition of a non-electrolyte to the solution, | 1202 |
| *McBain, J. W.,* | The apparent viscosity of colloidal solutions and a theory of neutral colloids as solvated micelles capable of aggregation, | 239 |
| *McBain, J. W., C. E. Harvey and L. E. Smith,* | The apparent viscosity of solutions of nitro cotton in various solvents, | 312 |
| *McBain, J. W., and D. G. Hopkins,* | Films of adhesives, | 114 |
| *McBain, J. W., and M. C. Field,* | The equilibrium underlying the soap-boiling process, | 1545 |
| *McHutchinson, J. P.,* | The electrodeposition of Radium D and Radium E, | 925 |
| *Maddison, R. E. W.,* | See Cunliffe, Franklin, Maddison and Reeve, | 1427 |
| *Main, V. R.,* | The viscosity of aqueous solutions of the silicates of soda, | 535 |
| *Marshall, A. L.,* | Photosensitization by optically excited mercury atoms, the hydrogen oxygen reaction, | 34 |
| *Marshall, A. L.,* | Mechanism of the photochemical reaction between hydrogen and chlorine. III, | 757 |
| *Marshall, A. L.,* | Synthetic formaldehyde from carbon monoxide and hydrogen, | 1634 |
| *Mason, C. W.,* | Structural colors in insects. I, | 383 |
| *Mason, R. B., and J. H. Mathews,* | The effect of ultra-violet light on the oxidation of sodium sulphite by atmospheric oxygen, | 414 |
| *Mehrotra, M. R., and N R. Dhar,* | Studies in adsorption. XV, | 1185 |
| *Miller, E. J.,* | Adsorption from solution by ash-free charcoals. I, II, | 1031, 1162 |
| *Mund, W.,* | Ionization by radon in spherical vessels, | 890 |
| *Mund, W., and W. Koch,* | The chemical action of alpha particles on acetylene, | 289 |
| *Munro, L. A., and F. M. G. Johnson,* | The sorption of vapors by alumina, | 172 |
| *Nelson, W. H., and C. J. Engelder,* | The thermal decomposition of formic acid, | 470 |
| *Neville, H. A.,* | Adsorption and reaction. I, II, | 1037, 1181 |
| *Nichols, M. L., and I. A. Derbigny,* | The reduction of nitrous oxide, | 491 |
| *Oakley, H. B.,* | The origin of the charge on colloidal particles, | 902 |

| | | |
|---|---|---|
| *Oliver, Jean, and Pearl Smith,* | The kinetics of agglutiniation of red blood cell suspensions, | 1 |
| *Orndorff, W. R.,* | See Dennis, Orndorff and Tabern, | 1049 |
| *Palit, C. C., and N. R. Dhar,* | Catalytic and induced oxidation of some carbohydrates, uric acid, and inorganic substances, | 939 |
| *Palit, C. C., and N. R. Dhar,* | Action of nitric acid on metals in presence of catalysts, | 1125 |
| *Parks, G. S., and K. K. Kelly,* | The heat capacities of some metallic oxides, | 47 |
| *Parks, G. S., and K. K. Kelly,* | The heat capacity of calcium silicate, | 1175 |
| *Patrick, W. A., and P. W. Bachman,* | The adsorption of ions on a mercury surface, | 134 |
| *Peacock, D. H.,* | The benzylation of amines. III, | 673 |
| *Pearce, J. N., and M. M. Hicks,* | A sensitive electrical precision apparatus for the determination of the boiling-point elevation, | 1678 |
| *Perkins, M. F.,* | See Tartar and Perkins, | 595 |
| *Phipps, T. E., and W. R. Brode,* | A comparative study of two kinds of colored rock salt, | 507 |
| *Posnjak, E.,* | The nature of stannic acids, | 1073 |
| *Pound, J. R.,* | Interfacial tensions between organic liquids and water or aqueous solutions, | 791 |
| *Pray, H. A. H.,* | The stability of diazo-benzene chloride solution. I, II, | 1471, 1477 |
| *Purse, W. L.,* | See Firth and Purse, | 617 |
| *Reeve, L.,* | See Cunliffe, Franklin, Maddison, and Reeve, | 1427 |
| *Reyerson, L. H., and L. E. Swearingen,* | The nature of metal films reduced on the surfaces of silica gel, | 1623 |
| *Rice, O. K.,* | Equilibrium in colloid systems. I, II, | 189, 1660 |
| *Rice, O. K.,* | The surface tension of charged surfaces, | 1348 |
| *Richards, O. W.,* | A nomogram for the van't Hoff-Arrhenius temperature equation, | 1219 |
| *Rogers, William, Jr., and H. S. Taylor,* | The rate of oxidation of linseed oil, | 1334 |
| *Roller, P. E.,* | See Arenson, Roller and Brown, | 620 |
| *Rosenberg, J. E., and Gebbard Stegeman,* | The adsorption of ions by metallic mercury, | 1306 |
| *Rudisill, W. A., and C. J. Engelder,* | Catalytic activation of titania, | 106 |
| *Scott, A. F.,* | A relationship between atomic numbers and the properties of ions in the crystal lattice. II, III, | 577, 1009 |
| *Sherwood, F. F., and E. I. Fulmer,* | The effect of temperature upon the growth of yeast in various media, | 738 |
| *Sikka, I. S.,* | See Dunnicliff, Sikka, and Hoon, | 1211 |
| *Sivertz, S.,* | See Davies and Sivertz, | 1467 |
| *Skogstrom, J. A.,* | See Williams and Skogstrom, | 1170 |
| *Smith, L. E.,* | See McBain, Harvey, and Smith, | 312 |
| *Smith, G. McP.,* | Ionic activity versus concentration in the interpretation of equilibria between amalgams and aqueous sodium and potassium halide mixtures, | 849 |
| *Smith, Pearl,* | See Oliver and Smith, | 1 |
| *Stamm, A. J., and E. O. Kraemer,* | A note on the mechanism of emulsification, | 992 |
| *Stegeman, Gebbard,* | See Rosenberg and Stegeman, | 1306 |
| *Stenström, Wilhelm, and Norris Goldsmith,* | Determination of the dissociation constants of phenol and the hydroxyl group of tyrosine by means of absorption measurements in the ultraviolet, | 1683 |

| | | |
|---|---|---|
| *Stillwell, C. W.,* | The color of the ruby, | 1441 |
| *Swearingen, L. E.,* | See Reyerson and Swearingen, | 1623 |
| *Tabern, D. L.,* | See Laubengayer and Tabern, | 1047 |
| *Tabern, D. L.,* | See Dennis, Orndorff and Tabern, | 1049 |
| *Tartar, H. V., and C. Z. Draves,* | A study of the precipitation of mastic suspensoids, | 763 |
| *Tartar, H. V., and M. F. Perkins,* | A laboratory study of nitrogen fixation in the high tension arc, | 595 |
| *Taylor, H. S.,* | Fourth report of the committee on contact catalysis, | 145 |
| *Taylor, H. S.,* | See Rogers and Taylor, | 1334 |
| *Taylor, R. K.,* | See Frazer, Lovelace and Taylor, | 1669 |
| *Uchida, Shun-ichi,* | On the reaction mechanism of the catalytic oxidation of ammonia, | 1297 |
| *Usher, F. L.,* | Electrokinetic behavior and electrode potential, | 954 |
| *Vieweg, H. F.,* | Frictional electricity, | 865 |
| *Ward, H. Lee,* | The solubility relations of naphthalene, | 1316 |
| *Washburne, R. W.,* | See King and Washburne, | 1688 |
| *Weiser, H. B.,* | The antagonistic action of ions in the neutralization of sols. I, II, | 20, 1527 |
| *Westcott, B. B., and C. J. Engelder,* | The catalytic decomposition of formic acid, | 470 |
| *Williams, J. W., and J. A. Skogstrom,* | Colloidal systems of nitromethane, | 1170 |
| *Williams, T. L.,* | See Benton and Williams, | 1487 |
| *Woo, Leo,* | See Klosky and Woo, | 1179 |
| *Woodman, R. M.,* | The preparation and conditions of formation of the two possible types of emulsion in the system cresylic acid—gelatine—water, | 658 |
| *Woodman, R. M.,* | The system: water, acetic acid, toluene, | 1283 |
| *Yoe, J. H., and E. B. Freyer.* | The effect of hydrogen ion concentration on the viscosity of hydrosols of aluminum, chromic and ferric oxides, | 1389 |


BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS ORSAY

BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS
ORSAY

# NAME INDEX

*To New Books*


| | | |
|---|---|---|
| *Adam, A. T.,* | Wire-Drawing and the Cold-Working of Steel, | 425 |
| *Alexander, Jerome, Editor,* | Colloid Chemistry. Vol. I, | 1287 |
| *Arrhenius, Svante,* | Chemistry in Modern Life, | 282 |
| *Barnard, J. E., and F. V. Welch,* | Practical Photomicrography, | 1149 |
| *Barnett, E. de B.,* | A Text-Book of Organic Chemistry, | 431 |
| *Berliner, Arnold,* | Lehrbuch der Physik, | 1150 |
| *Born, Max,* | The Constitution of Matter, | 571 |
| *Bragg, Sir William,* | Concerning the Nature of Things, | 1433 |
| *Cooper, F. G.,* | Textile Chemistry, | 864 |
| *Eisenlohr, Fritz,* | Der molekulare Brechungskoefficient in der Reihe der Polymethylenverbindungen, | 426 |
| *Ellis, Carleton, and A. A. Wells,* | The Chemical Action of Ultraviolet Rays, | 566 |
| *Ewald, P. P.,* | Kristalle und Röntgenstrahlen, | 1150 |
| *Fajans, K.,* | Radioactivity, | 136 |
| *Fodor, Andor,* | Die Grundlagen der Dispersoidchemie, | 719 |
| *Formanek, J., and J. Knop,* | Untersuchung und Nachweis organischer Farbstoffe auf spektroskopischem Wege, | 1584 |
| *Freundlich, Herbert,* | Fortschritte der Kolloidchemie, | 1151 |
| *Funk, Casimir,* | Mikroanalyse nach der Mikro-Dennstedt Methode, | 1151 |
| *Garard, Ira D.,* | Applied Chemistry, | 720 |
| *Guertler, W.,* | Metallographie, Vol. II, Part IV, | 1583 |
| *Haas, Arthur,* | The New Physics, | 1438 |
| *Hatschek, Emil,* | An Introduction to the Physics and Chemistry of Colloids, | 1584 |
| *Hevesy, George, and Fritz Paneth,* | A Manual of Radioactivity, | 1571 |
| *Hinshelwood, C. N.,* | The Kinetics of Chemical Change in Gaseous Systems | 1432 |
| *Holmes, H. N., Editor,* | Colloid Symposium Monograph, Vol. III, | 861 |
| *Houben, J.,* | Die Methoden der organischen Chemie Vols. I, II, | 138, 863 |
| *Jeffery, G. B.,* | Relativity for Physics Students, | 1440 |
| *Job, P.,* | Les Méthodes physiques appliquées à la Chimie, | 575 |
| *Klein, Wilhelm, and Maria Steuber,* | Die gasanalytische Methodik des dynamischen Stoffwechsels, | 427 |
| *van Laar, J. J.,* | L'Hydrogène et les Gas nobles, | 1151 |
| *Leathes, J. B., and H. S. Raper,* | The Fats, | 1292 |
| *Levene, P. A.,* | Hexosamines and Mucoproteins, | 1436 |
| *Lewis, W. C. McC.,* | A System of Physical Chemistry, Vol. II, | 288 |
| *Lloyd, Dorothy J.,* | Chemistry of the Proteins and its Economic Applications, | 1577 |
| *Loeb, Jacques,* | Regeneration, | 1004 |
| *Lowry, Alexander, and Benjamin Harrow,* | Introduction to Organic Chemistry, | 144 |
| *McEwen, B. C.,* | The Properties of Matter, | 432 |
| *Mason, F. A.,* | An Introduction to the Literature of Chemistry, | 1440 |
| *Masson, Irvine,* | Three Centuries of Chemistry, | 573 |
| *Matthews, J. M.,* | The Textile Fibers, | 140 |

| | | |
|---|---|---|
| *Mellor, J. W.,* | A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. VI,..... | 421 |
| *O'Brien, W. B.,* | Factory Practice in the Manufacture of Azo Dyes,.. | 573 |
| *Ostwald, W.,* | Farbkunde,..... | 286 |
| *Pascal, Paul,* | Explosifs, Poudres, Gaz de Combat,..... | 718 |
| *Planck, Max,* | A Survey of Physics..... | 858 |
| *Popoff, Stephen,* | Quantitative Analysis,..... | 432 |
| *Pummerer, R.,* | Organische Chemie,..... | 576 |
| *Rinne, Friedrich,* | Crystals and the Fine-Structure of Matter,..... | 428 |
| *Russell, Bertrand,* | The A B C of Atoms,..... | 1001 |
| *Speller, F. N.,* | Corrosion: Causes and Prevention,..... | 1141 |
| *Stavenhagen, Alfred,* | Der Wasserstoff,..... | 863 |
| *Stewart, A. W.,* | Recent Advances in Physical and Inorganic Chemistry,..... | 1148 |
| *Sutton, Francis,* | A Systematic Handbook of Volumetric Analysis,.... | 431 |
| *Tammann, Gustav,* | The States of Aggregation,..... | 1006 |
| *Thompson, F. C.,* | A Course of Metallurgy for Engineers,..... | 139 |
| *Thorpe, Sir Edward,* | A Dictionary of Applied Chemistry, Vol. VI,..... | 716 |
| *Walden, Paul,* | Molekulargrössen von Elektrolyten in nichtwässerigen Lösungsmitteln,..... | 427 |
| *Warburg, Emil,* | Ueber Wärmeleitung und andere ausgleichende Vorgänge,..... | 719 |
| *Zsigmondy, R.,* | Ueber Kolloidchemie,..... | 576 |


BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS
ORSAY

BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS
ORSAY

# SUBJECT INDEX

*Exclusive of New Books*

Absorption measurements in the ultra-violet, determination of the dissociation constants of phenol and the hydroxyl group of tyrosine by means of,..... 1683
Absorption spectra, the ultra-violet, of aqueous solutions of sulphur dioxide and some of its derivatives,..... 266
Absorption spectrum of a simple azo dye, the effect of solvents on the,..... 56
Acclimatization, the problem of, influence of temperature on metabolism and,..... 480
Acetic acid, water, toluene, the system:,..... 1287
Acetone-water solutions, acidified, the color change of Congo red in,..... 1276
Acetylene, the chemical action of alpha particles on,..... 289
Acid, acetic, water, toluene, the system:,..... 1287
Acid-basic function of molecules and its dependency on the electric charge type, the, 777
Acid, cresylic, gelatine-water, system, the preparation and conditions of formation of the two possible types of emulsion in the,..... 658
Acid, dichromic, electrolysis of, under a mercury vapor lamp of high intensity,..... 1628
Acid, formic, the catalytic decomposition of,..... 476
Acid, formic, the thermal decomposition of,..... 470
Acid, humic, adsorption by,..... 1364
Acid, hydrochloric, the transference numbers of, in glycerol-water mixtures,..... 562
Acidified acetone-water solutions, the color change of Congo red in,..... 1276
Acid, mesitylene phosphinous, solubility and electrolytic conductance of,..... 1209
Acid, nitric, action of, on metals in presence of catalysts,..... 1125
Acid, nitric, the action of metals on,..... 1222
Acid, silica, gel, rhythmic diurnal bands of gold and platinum in,..... 1467
Acid, silicic, organogels of,—the replacement of the water in the hydrogel by alcohol, 617
Acid solutions of copper sulphate, the electrolysis of..... 396
Acids, stannic, the nature of,..... 1073
Acid, sulphuric, ethyl alcohol, sodium sulphate. the system:,..... 1211
Acid, uric, some carbohydrates and inorganic substances, catalytic and induced oxidation of,..... 939
Action of metals on nitric acid, the,..... 1222
Action of nitric acid on metals in presence of catalysts,..... 1125
Action, promoter, heats of adsorption and the problem of,..... 818
Action, the antagonistic, of ions in the neutralization of sols,.....20, 1527
Action, the chemical, of alpha particles on acetylene,..... 289
Activation, catalytic, of titania,..... 106
Activation, heat of, of a reaction by a catalytic surface, a possible mechanism for the lowering of the,..... 1134
Activity, ionic, versus concentration in the interpretation of equilibria between amalgams and aqueous sodium and potassium halide mixtures,..... 84
Addition of a non-electrolyte to the solution, influence on the solubilities of salts in water by the,..... 1202
Adhesives, films of,..... 114
Adsorbent ash-free charcoals, adsorption from solution by..... 1031, 1162
Adsorption and reaction,..... 1037, 1181
Adsorption by humic acid,..... 1364
Adsorption, heats of, and the problem of promoter action ..... 818
Adsorption from solution by ash-free adsorbent charcoals. .....1031, 1162
Adsorption, heat of, of carbon monoxide on copper catalyst,..... 1538
Adsorption of ethylene and hydrogen by zinc oxide, iron oxide, nickel, and copper,.. 353
Adsorption of ions by metallic mercury, the,..... 1306

Adsorption of ions on a mercury surface, the,..... 134
Adsorption, studies,..... 628, 830, 1185
Age, old, and death, from a chemical point of view,..... 378
Ageing of a sol on its coagulation, influence of,..... 1564
Agglutination, the kinetics of, of red blood cell suspensions,..... 1
Aggregation, a theory of neutral colloids as solvated micelles capable of,..... 239
Alcohol, ethyl, sulphuric acid, sodium sulphate, the system:,..... 1211
Alcoholic solutions, osmotic behavior, the influence of the ionic charge on the,..... 1153
Alcohols, the formation of carbon dioxide from,..... 895
Alcohol, the replacement of the water in the hydrogel by,..... 617
Aldehydes, the reactive nature of, from the standpoint of the apparent electromotive force,..... 620
Alpha particles, the chemical action of, on acetylene,..... 289
Alumina, the sorption of vapors by,..... 172
Aluminum, chromic and ferric oxides, the viscosity of, hydrosols of, the effect of hydrogen ion concentration on,..... 1389
Aluminum oxide catalyst, hydrous, some properties of the,..... 964
Amalgams and aqueous sodium and potassium halide mixtures, the interpretation of equilibria between, ionic activity versus concentration in,..... 849
Amines, the benzylation of,..... 673
Ammonia, catalytic oxidation of, on the reaction mechanism of the,..... 1297
Ammonia, liquid, and in water, decomposition potentials and metal overvoltages in, 1597
Ammonia, mixtures used as catalysts in the synthesis of, the thermionic properties of some,..... 525
Ammonium nitrate, properties of,.....721, 726, 736
Analysis, thermal, of the system boron trifluoride-hydrogen sulphide,..... 369
Anomalous flocculation in colloidal clays and soils,..... 254
Antagonistic action of ions in the neutralization of sols,..... 20, 1527
Antimony sulphides,..... 205
Apparatus, precision, a sensitive electrical, for the determination of the boiling point elevation,..... 1678
Apparent electromotive force, the reactive nature of aldehydes from the standpoint of the,..... 620
Apparent viscosity of colloidal solutions and a theory of neutral colloids as solvated micelles capable of aggregation, the,..... 239
Aqueous sodium and potassium halide mixtures, amalgams and, ionic activity versus concentration in the interpretation of equilibria between,..... 849
Aqueous sodium silicate solutions,..... 706
Aqueous solutions of sodium silicates,..... 359, 917, 1100
Aqueous solutions of sulphur dioxide and some of its derivatives, the ultraviolet absorption spectra of,..... 266
Aqueous solutions of the silicates of soda, the viscosity of,..... 535
Aqueous solutions, water or, interfacial tensions between organic liquids and,..... 791
Arc, high tension, a laboratory study of nitrogen fixation in the,..... 595
Arrhenius-van't Hoff temperature equation, a nomogram for the,..... 1219
Arsenic pentoxide, barium oxide, water, equilibrium in the system:..... 248
Ash-free adsorbent charcoals, adsorption from solution by,..... 1031, 1162
Atmospheric oxygen, the effect of ultra violet light on the oxidation of sodium sulphite by,..... 414
Atomic numbers and the properties of ions in the crystal lattice, a relationship between,..... 577, 1009
Atoms, mercury, optically excited, photosensitization by,..... 34
Azo dye, a simple, the effect of solvents on the absorption spectrum of,..... 56
Bands, rhythmic diurnal, of gold and platinum in silicic acid gel,..... 1467
Barium oxide, water, arsenic pentoxide, equilibrium in the system:,..... 248

Bases, leuco, the photochemical oxidation of,..... 130
Behavior, electrokinetic, and electrical potential,..... 954
Behavior, osmotic, of alcoholic solutions, the influence of the ionic charge on the,.. 1153
Behaviors, individual thermodynamic, of ions in concentrated solutions,..... 433
Benzylation of amines, the,..... 673
Beriberi, cause of swelling in, origin of the formation of deposits in gout and other diseases and the,..... 277
Blood, red, cell suspensions, the kinetics of agglutination of,..... 1
Blue wood,..... 521
Boiling point elevation, a sensitive electrical precision apparatus for the determination of the,..... 1678
Boron trifluoride-hydrogen sulphide, thermal analysis of the system:,..... 369
Bromide-potassium bromide-water, silver, the ternary system:,..... 973
Bromide solutions, potassium and sodium, the dissociation of water in,..... 1060
Bromide-water, silver bromide-potassium, the ternary system:,..... 973
Calcium silicate, the heat capacity of,..... 1175
Capacities, the heat, of some metallic oxides,..... 47
Capacity, the heat, of calcium silicate,..... 1175
Carbohydrates, some, uric acid, and inorganic substances, catalytic and induced oxidation of,..... 939
Carbonates, velocity of thermal decomposition of,..... 680
Carbon dioxide, the formation of, from alcohols,..... 895
Carbon monoxide and hydrogen, synthetic formaldehyde from,..... 1634
Carbon monoxide in contact with quartz glass, the catalytic oxidation of,..... 1487
Carbon monoxide, the heat adsorption of, on copper catalyst,..... 1538
Catalysis, contact, committee on, fourth report of the,..... 145
Catalyst, copper, heat of adsorption of carbon monoxide in,..... 1538
Catalyst, hydrous oxide, some properties of the mechanism of the catalytic dehydration of methanol and,..... 964
Catalysts, action of nitric acid on metals in presence of,..... 1125
Catalysts in the synthesis of ammonia, the thermionic properties of some mixtures used as,..... 525
Catalytic activation of titania,..... 166
Catalytic and induced oxidation of some carbohydrates, uric acid, and inorganic substances,..... 939
Catalytic decomposition of formic acid, the,..... 476
Catalytic dehydration of methanol, mechanism of the, and some properties of the hydrous aluminum oxide catalyst,..... 964
Catalytic minimum point, the,..... 1616
Catalytic oxidation of carbon monoxide in contact with quartz glass, the,..... 1487
Catalytic oxidation of ammonia, on the reaction mechanism of the,..... 1297
Catalytic surface, heat of activation of a reaction by a, a possible mechanism for the lowering of the,..... 1134
Cell metabolism, reversible permeability of membranes and its relation to,..... 83
Cell suspensions, red blood, the kinetics of agglutination of,..... 1
Cellulose, the nature of the structure of, and its significance in chemical transformations,..... 457
Change, color, of Congo red in acidified acetone-water solutions,..... 1276
Charcoals, ash free, adsorbent, adsorption from solution by,..... 1031, 1162
Charged surfaces, the surface tension of,..... 1348
Charge, electric, type, the acid-basic function of molecules and its dependency on the, 777
Charge, ionic, the influence of the, on the osmotic behavior of alcoholic solutions,. 1153
Charge on colloidal particles, the origin of the,..... 902
Charge, same, as the dispersed particles in the inversion of emulsions, the influence of ions carrying the,..... 294

Chemical action of alpha particles on acetylene, the,..... 289
Chemical point of view, old age and death from a,..... 378
Chemical transformations, the nature of the structure of cellulose and its significance in,..... 457
Chemistry of gold, studies on the,..... 126
Chloride, potassium-water potassium laurate, the system:,..... 1545
Chloride solutions, diazo-benzene, the stability of,..... 1417, 1477
Chlorine and hydrogen, mechanism of the photochemical reaction between,..... 757
Chromic, aluminum and ferric oxides, the viscosity of hydrosols of, the effect of hydrogen ion concentration on,..... 1389
Clays, colloidal, and soils, anomalous flocculation in,..... 254
Coagulation coefficient ($\beta$), Smoluchowski, note on the significance of the variation in the,..... 1410
Coagulation, influence of ageing of a sol on its,..... 1564
Coagulation of gold sol, the effect of temperature on the rate of,..... 1401
Coefficient ($\beta$), Smoluchowski coagulation, note on the significance of the variation in the,..... 1410
Colloidal clays and soils, anomalous flocculation in,..... 254
Colloidal particles, the origin of the charge on,..... 902
Colloidal solutions, the apparent visocisty of,..... 239
Colloidal systems in nitromethane,..... 1170
Colloids, neutral, a theory of, as solvated micelles capable of aggregation,..... 239
Colloid systems, equilibrium in,..... 189, 1660
Color change of Congo red in acidified acetone-water solutions,..... 1276
Colored rock salt, two kinds of, a comparative study of,..... 507
Color of the ruby, the,..... 1441
Colors in insects, structural,..... 383
Committee on contact catalysis, fourth report on the,..... 145
Comparative study of two kinds of colored rock salt,..... 507
Compounds, isomeric organic, solubility relations of,..... 70
Computing liquid-junction potentials, a discussion of the thermodynamic method of, 433
Concentrated solutions, individual thermodynamic behaviors of ions in,..... 433
Concentration, hydrogen ion, the effect of, on the viscosity of hydrosols of aluminum, chromic and ferric oxides,..... 1389
Concentration in the interpretation of equilibria between amalgam and aqueous sodium and potassium halide mixtures, ionic activity versus,..... 849
Conditions, the preparation and, of formation of the two possible types of emulsion in the system cresylic acid–gelatine-water,..... 558
Conductance, solubility and electrolytic, of mesitylene phosphinous acid,..... 1209
Congo red, the color change of, in acidified acetone–water solutions,..... 1276
Constants, dissociation, of phenol and the hydroxyl group of tyrosine by means of absorption measurements in the ultra-violet, determination of the,..... 1683
Contact catalysis, fourth report of the committee on, ..... 145
Copper catalyst, heat of adsorption of carbon monoxide on,..... 1538
Copper, nickel, iron oxide, and zinc oxide, adsorption of ethylene and hydrogen by, 353
Copper sulphate, the electrolysis of acid solutions of.,..... 396
Cotton, nitro, in various solvents, the apparent viscosity of solutions of,..... 312
Cresylic acid–gelatine–water, the preparation and conditions of formation of the two possible types of emulsions in the system,..... 658
Cryoscopic measurements with nitrobenzene,..... 694
Crystal lattice, the properties of ions in the, a relationship between atomic numbers and,..... 577, 1009
Curve, the electrocapillary, near its maximum, a study of,..... 1501
Death, old age and, from a chemical point of view,..... 378
Decomposition, the thermal, of formic acid,..... 470

Decomposition, the catalytic, of formic acid,..... 476
Decomposition, the thermal, of methane,..... 899
Decompositions potentials and metal overvoltages in liquid ammonia and in water, 1597
Decompositions, thermal, of carbonates, velocity of,..... 685
Degree of saturation, vapor pressure lowering as a function of the,..... 643
Dehydration, catalytic, of methanol, mechanism of the, and some properties of the hydrous aluminum oxide catalyst,..... 964
Dependency of the acid-basic function of molecules on the electric charge type,.. 777
Deposits in gout and other diseases, origin of the formation of, and the causes of swelling in beriberi,..... 277
Derivatives, the ultraviolet absorption spectra of aqueous solutions of sulphur dioxide and some of its,..... 266
Determination of the boiling point elevation, a sensitive electrical precision apparatus for the,..... 1678
Determination of the dissociation constants of phenol and the hydroxyl group of tyrosine by means of absorption measurements in the ultra-violet,..... 1683
Determination, the electromotive, of small amounts of ferric iron,..... 1688
Diazo-benzene chloride solutions, the stability of,.....1417, 1477
Dichromic acid, electrolysis of, under a mercury vapor lamp of high intensity,..... 1628
Dioxide, carbon, from alcohols, the formation of,..... 895
Dioxide, sulphur, and some of its derivatives, the ultraviolet absorption spectra of aqueous solutions of,..... 266
Discussion of the thermodynamic method of computing liquid-junction potentials,. 433
Diseases, gout and other, origin of the formation of deposits in,..... 277
Dispersed particles in the inversion of emulsions, the influence of ions carrying the same charge as the,..... 294
Dissociation constants of phenol and the hydrosol group of tyrosine, determination of the, by means of absorption measurements in the ultra-violet,..... 1683
Dissociation of water in potassium and sodium bromide solutions, the,..... 1060
Diurnal bands, rhythmic, of gold and platinum in silicic acid gel,..... 1467
Dye, a simple azo, the effect of solvents on the absorption spectrum of,..... 56
Effect of temperature upon the growth of yeast in various media,..... 738
Effect of ultra-violet light on the oxidation of sodium sulphite by atmospheric oxygen, the,..... 414
Electrical precision apparatus, a sensitive, for the determination of the boiling elevation,..... 1678
Electric charge type, the acid-basic function of molecules and its dependency on the, 777
Electricity, frictional,..... 865
Electrocapillary curve near its maximum, a study of the,..... 1501
Electrode, iron, the potential of the,..... 980
Electrodeposition of radium D and radium E, the,..... 925
Electrode potential, electrokinetic behavior and,..... 954
Electrokinetic behavior and electrode potential,..... 954
Electrolysis of acid solutions of copper sulphate,..... 396
Electrolysis of dichromic acid under a mercury vapor lamp of high intensity,..... 1628
Electrolysis of radium D and radium E, experiments on the,..... 1112
Electrolytes, strong, simple, in water, the solubility of,..... 1585
Electrolytes, viscosity measurements of certain sols in presence of,..... 1646
Electrolytic conductance, solubility and, of mesitylene phosphinous acid,..... 1209
Electromotive determination of small amounts of ferric iron, the,..... 1688
Electromotive force, apparent, the reactive nature of aldehydes from the standpoint of the,..... 620
Elevation, boiling point, a sensitive electrical precision apparatus for the determination of the,..... 1678
Emulsification, a note on the mechanism of,..... 992

Emulsion in the system cresylic acid–gelatine–water, the preparation and conditions of formation of the two possible types of,..... 658
Emulsions, inversions of, the influence of ions carrying the same charge as the dispersed particles in the,..... 294
Equation, temperature, van't Hoff-Arrhenius, a nomogram for the,..... 1219
Equilibria between amalgams and aqueous sodium and potassium halide mixtures, ionic activity versus concentration in the interpretation of,..... 849
Equilibrium in colloid systems,..... 189, 1660
Equilibrium in the system: arsenic pentoxide, barium oxide, water,..... 248
Equilibrium, the methane,..... 1641
Equilibrium, the water,..... 1194
Equilibrium underlying the soap-boiling process,..... 1545
Ethyl alcohol, sulphuric acid, sodium sulphate, the system:,..... 1211
Ethylene and hydrogen, adsorption of, by zinc oxide, iron oxide, nickel, and copper, 353
Excited, optically, mercury atoms, photosensitization by,..... 34
Experiments on the electrolysis of radium D and radium E,..... 1112
Exposure, photographic, the quantum theory of, grain size and the,..... 845
Ferric, chromic and aluminum oxides, the viscosity of hydrosols of, the effect of hydrogen ion concentration on,..... 1389
Ferric iron, the electromotive determination of small amounts of,..... 1685
Films, metal, the nature of, reduced on the surfaces of silica gel,..... 1623
Films of adhesives,..... 114
Fixation, nitrogen, in the high tension arc, a laboratory study of,..... 595
Flocculation, anomalous, in colloidal clays and soils,..... 254
Force, electromotive, apparent, the reactive nature of aldehydes from the standpoint of the,..... 620
Formaldehyde, synthetic, from carbon monoxide and hydrogen,..... 1634
Formation of deposits in gout and other diseases, origin of the, and the cause of swelling in Beriberi,..... 277
Formation, the preparation and conditions of, of the two possible types of emulsion in the system cresylic acid—gelatine—water,..... 658
Formation of carbon dioxide from alcohols, the,..... 895
Formic acid, the catalytic decomposition of,..... 476
Formic acid, the thermal decomposition of,..... 470
Fourth report of the committee on contact catalysis,..... 145
Frictional electricity,..... 865
Function, the acid-basic, of molecules and its dependency on the electric charge type, 777
Function of the degree of saturation, vapor pressure lowering as a,..... 643
Gelatine–water–cresylic acid, the preparation and conditions of formation of the two possible types of emulsions in the system,..... 658
Gel of metallic platinum,..... 1415
Gel, silica, the nature of metal films reduced on the surfaces of,..... 1623
Gel, silicic acid, rhythmic diurnal bands of gold and platinum in,..... 1467
Gel structure,..... 306
Germanium,..... 1043, 1047, 1049, 1055, 1510
Glass, quartz, the catalytic oxidation of carbon monoxide in contact with,..... 1487
Glycerol-water mixtures, the transference numbers of hydrochloric acid in,..... 562
Gold and platinum in silicic acid gel, rhythmic dirunal bands of,..... 1467
Gold sol, the rate of coagulation of, the effect of temperature on,..... 1401
Gold, studies on the chemistry of,..... 126
Gout and other diseases, origin of the formation of deposits in, and the cause of swelling in beriberi,..... 277
Grain size and the quantum theory of photographic exposure,..... 845
Group, phenol and hydroxyl, of tyrosine, determination of the dissociation constants of, by means of absorption measurements in the ultra-violet,..... 1683

Growth of yeast in various media, the effect of temperature upon the,..... 738
Halide mixtures, aqueous sodium and potassium, ionic activity versus concentration in the interpretation of equilibria between amalgams and,..... 849
Heat capacities of some metallic oxides,..... 47
Heat capacity of calcium silicate,..... 1175
Heat of activation of a reaction by a catalytic surface, a possible mechanism for the lowering of the,..... 1134
Heat of adsorption of carbon monoxide on copper catalyst,..... 1538
Heats of adsorption and the problem of promoter action,..... 818
High tension arc, a laboratory study of nitrogen fixation in the,..... 595
van't Hoff-Arrhenius temperature equation, a nomogram for the,..... 1219
Humic acid, adsorption by,..... 1364
Hydrates, salt, in non-aqueous solutions, the transition points of,..... 930
Hydrochloric acid in glycerol-water mixtures, the transference numbers of,..... 562
Hydrogel, the replacement of water in the, by alcohol,..... 617
Hydrogen, adsorption of ethylene and, by zinc oxide, iron oxide, nickel, and copper, 353
Hydrogen and chlorine, mechanism of the photochemical reaction between,..... 757
Hydrogen and nitrogen, the ionisation potentials of, on iron and other metals,..... 1356
Hydrogen, carbon monoxide and, synthetic formaldehyde from,..... 1634
Hydrogen ion concentration, the effect of, on the viscosity of hydrosols of aluminum, chromic and ferric oxides,..... 1389
Hydrogen-oxygen reaction,..... 34
Hydrogen sulphide-boron trifluoride, thermal analysis of the system,..... 369
Hydrosols of aluminum, chromic and ferric oxides, the effect of hydrogen ion concentration on the viscosity of,..... 1389
Hydrous aluminum oxide catalyst, some properties of the,..... 964
Hydroxyl and phenol group of tyrosine, determination of the dissociation constants of, by means of absorption measurements in the ultra-violet,..... 1683
Individual thermodynamic behaviors of ions in concentrated solutions of,..... 433
Induced oxidation, catalytic and, of some carbohydrates, uric acid, and inorganic substances,..... 939
Influence of ageing of a sol on its coagulation,..... 1564
Influence of ions carrying the same charge as the dispersed particles in the inversion of emulsions,..... 294
Influence of temperature on metabolism and the problem of acclimatization,..... 480
Influence of the ionic charge on the osmotic behavior of alcoholic solutions,..... 1153
Influence on the solubilities of salts in water by the addition of a non-electrolyte to the solution,..... 1202
Inorganic substances, uric acid and some carbohydrates, catalytic and induced oxidation of,..... 939
*Insects, structural colors in*,..... 383
Intensity, a mercury vapor lamp of high, electrolysis of dichromic acid under,..... 1628
Interfacial tensions between organic liquids and water or aqueous solutions,..... 791
Inversion of emulsions, the dispersed particles in the, the influence of ions carrying the same charge as,..... 294
Ion concentrations, hydrogen, the effect of, on the viscosity of hydrosols of aluminum, chromic and ferric oxides,..... 1389
Ionic activity versus concentration in the interpretation of equilibria between analgams and aqueous sodium and potassium halide mixtures,..... 849
Ionic charge, the influence of the, on the osmotic behavior of alcoholic solutions,... 1153
Ionization by radon in spherical vessels,..... 890
Ionization potentials of nitrogen and hydrogen on iron and other metals,..... 1356
Ions, the influence of, carrying the same charge as the dispersed particles in the inversion of emulsions,..... 294
Ions, individual thermodynamic behaviors of, in concentrated solutions,..... 433

Ions, in the neutralization of sols, the antagonistic action of,.....20, 1523
Ions, the adsorption of, on a mercury surface,..... 134
Ions, the adsorption of, by metallic mercury,..... 1306
Ions, the antagonistic action of, in the neutralization of sols,..... 1527
Ions, the properties of, in the crystal lattice, a relationship between atomic numbers and,.....577, 1009
Iron and other metals, the ionization potentials of nitrogen and hydrogen on,..... 1356
Iron electrode, the potential of the,..... 980
Iron, ferric, the electromotive determination of small amounts of,..... 1688
Iron oxide, zinc oxide, nickel, and copper, adsorption of ethylene and hydrogen by, 353
Isomeric organic compounds, solubility relations of,..... 70
Junction, liquid, potential, thermodynamic method of computing,..... 433
Kinetics of agglutination of red blood cell suspensions,..... 1
Laboratory latex,..... 713
Laboratory study of nitrogen fixation in the high tension arc,..... 595
Lamp, mercury vapor, of high intensity, electrolysis of dichromic acid under a,.... 1628
Latex, a laboratory,..... 713
Lattice, crystal, a relationship between atomic numbers and the properties of ions in the,.....577, 1009
Laurate, potassium, potassium chloride-water, the system,..... 1545
Leuco bases, the photochemical oxidation of,..... 130
Light, the scattering of, by aqueous sodium silicate solutions,..... 706
Light, ultra-violet, the effect of, on the oxidation of sodium sulphite by atmospheric oxygen,..... 414
Linseed oil, the rate of oxidation of,..... 1334
Liquid ammonia, decomposition potentials and metal overvoltages in, and in water, 1597
Liquid-junction potentials, a discussion of the thermodynamic method of computing, 433
Liquids, organic, and water or aqueous solutions, interfacial tensions between,..... 791
Lowering of the heat of activation of a reaction by a catalytic surface, a possible mechanism of the,..... 1134
Low temperatures, vapor pressure of naphthalene at,..... 1497
Lowering, vapor pressure, as a function of the degree of saturation,..... 643
Mastic suspensoids, a study of the precipitation of,..... 763
Maximum, a study of the electrocapillary curve near its,..... 1501
Measurements, absorption, in the ultra-violet, determination of the dissociation constants of phenol and the hydroxyl group of tyrosine by means of,..... 1683
Measurements, cryoscopic, with nitrobenzene,..... 694
Measurements, viscosity, of certain sols in presence of electrolytes,..... 1646
Mechanism for the lowering of the heat of activation of a reaction by a catalytic surface, a possible,..... 1134
Mechanism of emulsification, a note on the,..... 992
Mechanism of reactions photosensitized by mercury vapor,..... 1078
Mechanism of the catalytic dehydration of methanol, and some properties of the hydrous aluminum oxide catalyst,..... 964
Mechanism of the photochemical reaction between hydrogen and chlorine,..... 757
Mechanism, reaction, of the catalytic oxidation of ammonia, on the,..... 1297
Media, various, the effect of temperature upon the growth of yeast in,..... 738
Membranes, reversible, permeability of, and its relation to cell metabolism,..... 83
Mercury atoms, optically excited, photosensitization by,..... 34
Mercury, metallic, the adsorption of ions by,.....134, 1306
Mercury vapor lamp of high intensity, electrolysis of dichromic acid under a,..... 1628
Mercury vapor, reactions photosensitized by, the mechanism of,..... 1078
Mesitylene phosphinous acid, solubility and electrolytic conductance of,..... 1209
Metabolism, cell, reversible permeability of membranes and its relation to,..... 83
Metabolism, influence of temperature on, and the problem of acclimatization,..... 480

Metal films reduced on the surfaces of silica gel, the nature of,..... 1623
Metallic mercury, the adsorption of ions by,..... 1306
Metallic oxides, the heat capacities of some,..... 47
Metallic platinum, a gel of,..... 1415
Metal overvoltages, decomposition potentials and, in liquid ammonia and in water, 1597
Metals, action of nitric acid on, in presence of catalysts,..... 1125
Metals, iron and, other, the ionization potentials of nitrogen and hydrogen on,..... 1356
Metals, the action of, on nitric acid,..... 1222
Methane equilibrium,..... 1641
Methane, the thermal decomposition of,..... 899
Methanol, mechanism of the, catalytic dehydration of, and some properties of the hydrous aluminum oxide catalyst,..... 964
Method, thermodynamic, of computing liquid-junction potentials, a discussion of the, 433
Micelles, solvated, capable of aggregation, the apparent viscosity of colloidal solutions and a theory of neutral colloids as,..... 239
Minimum point, the catalytic,..... 1616
Mixtures, aqueous sodium and potassium halide, ionic activity versus concentration in the interpretation of equilibria between amalgams and,..... 849
Mixtures, glycerol-water, hydrochloric acid in, the transference numbers of,..... 562
Mixtures, some, the thermionic properties of, used as catalysts in the synthesis of ammonia,..... 525
Molecules, the acid-basic function of, and its dependency on the electric charge type, 777
Monoxide, carbon, and hydrogen, synthetic formaldehyde from,..... 1634
Monoxide, carbon, on copper catalyst, heat of adsorption of,..... 1538
Monoxide, carbon, the catalytic oxidation of, in contact with quartz glass,..... 1487
Naphthalene, vapor pressure of, at low temperature,..... 1497
Naphthalene, the solubility relations of,..... 1316
Nature of aldehydes, the reactive, from the standpoint of the apparent electromotive force,..... 620
Nature of metal films reduced on the surfaces of silica gel,..... 1623
Nature of stannic acids,..... 1073
Nature of the structure of cellulose and its significance in chemical transformation, the,..... 457
Neutral colloids as solvated micelles capable of aggregation, a theory of,..... 239
Neutralization of sols, the antagonistic action of ions in the,.....20, 1527
Nickel, iron oxide, zinc oxide, and copper, adsorption of ethylene and hydrogen by,.. 353
Nitrate, ammonium, properties of,.....721, 726, 736
Nitrate, potassium, solutions at 20°C. the vapor pressures of,..... 1669
Nitric acid, action of, on metals in presence of catalysts,..... 1125
Nitric acid, the action of metals on,..... 1222
Nitrobenzene, cryoscopic measurements with,..... 694
Nitro cotton in various solvents, solutions of, the apparent viscosity of,..... 312
Nitrogen and hydrogen, the ionization potentials of, on iron and other metals,..... 1356
Nitrogen fixation in the high tension arc, a laboratory study of,..... 595
Nitromethane, colloidal systems in,..... 1170
Nitrous oxide, the reduction of,..... 491
Nomogram for the van't Hoff-Arrhenius temperature equation,..... 1219
Non-aqueous solutions, the transition points of salt hydrates in,..... 930
Non-electrolyte, the addition of, to the solution, influence on the solubilities of salts in water by,..... 1202
Note on the mechanism of emulsification, a,..... 992
Note on the significance of the variation in the Smoluchowski coagulation coefficient ($\beta$),..... 1410
Numbers, atomic, and the properties of ions in the crystal lattic, a relationship between,.....277, 1009

Numbers, the transference, of hydrochloric acid in glycerol-water mixtures,..... 562
Oil, linseed, the rate of oxidation of,..... 1334
Old age and death from a chemical point of view,..... 378
Optically excited mercury atoms, photosensitization by, the hydrogen oxygen reaction,..... 34
Organic compounds, isomeric, solubility relations of,..... 70
Organic liquids and water or aqueous solutions, interfacial tensions between,..... 791
Organogels of silicic acid—the replacement of the water in the hydrogel by alcohol, 617
Origin of the charge on colloidal particles,..... 902
Origin of the formation of deposits in gout and other diseases, and the cause of swelling in beriberi,..... 277
Osmotic behavior of alcoholic solutions, the influence of the ionic charge on the,... 1153
Overvoltages, metal, decomposition potentials and, in liquid ammonia and in water, 1597
Oxidation of ammonia, catalytic, on the reaction mechanism of the,..... 1297
Oxidation, catalytic and induced, of some carbohydrates, uric acid, and inorganic substances,..... 939
Oxidation of linseed oil, the rate of,..... 1334
Oxidation of sodium sulphite by atmospheric oxygen, the effect of ultra-violet light on the oxidation of sodium sulphite by atmospheric oxygen,..... 414
Oxidation, the catalytic, of carbon monoxide in contact with quartz glass,..... 1487
Oxidation, the photochemical, of leuco bases,..... 130
Oxide, barium, water, arsenic pentoxide, equilibrium in the system:..... 248
Oxide, hydrous aluminum, catalyst, some properties of the,..... 964
Oxide, iron, zinc oxide, nickel and copper, adsorption of ethylene and hydrogen,.. 353
Oxide, nitrous, the reduction of,..... 491
Oxides, chromic, ferric and aluminum, the viscosity of hydrosols of, the effect of hydrogen ion concentration on,..... 1389
Oxide, silver, solubility of,..... 1179
Oxides, some metallic, the heat capacities of,..... 47
Oxide, zinc, iron oxide, nickel and copper, adsorption of ethylene and hydrogen by, 353
Oxygen, atmospheric, the effect of ultra violet light on the oxidation of sodium sulphite by,..... 414
Oxygen, hydrogen, reaction, the,..... 34
Particles, alpha, the chemical action of, on acetylene,..... 289
Particles, colloidal, the origin of the charge on,..... 902
Particles, dispersed, in the inverrion of emulsions, the influence of ions carrying the same charge as the,..... 294
Pentoxide, arsenic, barium oxide, water, equilibrium in the system,..... 248
Peptization of pyroxylin, the,..... 1116
Permeability, reversible, of membranes and its relation to cell metabolism,..... 83
Phenol and the hydroxyl group of tyrosine, determination of the dissociation constants of, by means of absorption measurements in the ultra-violet,..... 1683
Phosphinous acid, mesitylene, solubility and electrolytic conductance of,..... 1259
Photochemical oxidation of leuco bases,..... 130
Photochemical reaction between hydrogen and chlorine, mechanism of,..... 757
Photochemical technique, studies in,..... 1427
Photographic exposure, quantum theory of, grain size and the,..... 845
Photosensitization by optically excited mercury atoms, the hydrogen oxygen reaction,..... 34
Photosensitized, reactions, by mercury vapor, the mechanism of,..... 1078
Platinum and gold, rhythmic diurnal bands of, in silicic acid gel,..... 1467
Platinum, metallic, a gel of,..... 1415
Point of view, chemical, old age and death from a,..... 378
Point, boiling, elevation, a sensitive electrical precision apparatus for the determination of the,..... 1678

Point, the catalytic minimum,..... 1616
Points, the transition, of salt hydrates in non-aqueous solutions,..... 930
Possible mechanism for the lowering of the heat of activation of a reaction bya catalytic surface,..... 1134
Possible types, two, of emulsion in the system cresylic acid–gelatine–water, the preparation and conditions of formation of the,..... 658
Potassium and sodium bromide solutions, the dissociation of water in,..... 1060
Potassium bromide–water, silver bromide–the system:,..... 973
Potassium chloride–potassium laurate–water, the system,..... 1545
Potassium halide mixtures, amalgams and aqueous sodium and, ionic activity versus concentration in the interpretation of equilibria between,..... 849
Potassium laurate–potassium chloride–water, the system,..... 1545
Potassium nitrate solutions at 20° C, the vapor pressurce of,..... 1669
Potential, electrode, electrokinetic behavior and,..... 954
Potential of the iron electrode,..... 980
Potentials, decomposition, and metal overvoltages in liquid ammonia and in water, 1597
Potentials, liquid-junction, a discussion of the thermodynamic method of computing, 433
Potentials, the ionization, of nitrogen and hydrogen on iron and other metals,..... 1356
Precipitation of mastic suspensoids, a study of the,..... 763
Precision apparatus, a sensitive electrical, for the determination of the boiling point elevation,..... 1678
Preparation and conditions of formation of the. two possible types of emulsion in the system cresylic acid—gelatine—water, the,..... 658
Pressures, the vapor, of potassium nitrate solutions at 20°C,..... 1669
Pressure, vapor, lowering as a function of the degree of saturation,..... 643
Pressure, vapor, of naphthalene, at low temperatures,..... 1497
Problem of acclimatization, influence of temperature on metabolism and the,..... 480
Problem of promoter action, heats of adsorption and the,..... 818
Process, the soap-boiling, the equilibrium underlying,..... 1545
Promoter action, heats of adsorption and the problem of,..... 818
Properties of ammonium nitrate,..... 721, 726, 736
Properties of ions in the crystal lattice, a relationship between atomic numbers and the,..... 577, 1009
Properties, some, of the hydrous aluminum oxide catalyst, mechanism of the catalytic dehydration of methanol and,..... 964
Properties, the thermionic, of some mixtures used as catalysts in the synthesis of ammonia,..... 525
Pyroxylin, the peptization of,..... 1116
Quantum theory of photographic exposure, grain size and the,..... 845
Quartz glass, the catalytic oxidation of carbon monoxide in contact with,..... 1487
Radium D and Radium E, the electrodeposition of,..... 925
Radium D and Radium E, experiments on the electrolysis of,..... 1112
Radon, ionization by, in spherical vessels,..... 890
Rate of coagulation of gold sol, the effect of temperature on the,..... 1401
Rate of oxidation of linseed oil, the,..... 1334
Reaction, adsorption and,..... 1037, 1181
Reaction, heat of activation of a, by a catalytic surface, a possible mechanism for the lowering of the,..... 1134
Reaction, mechanism of the catalytic oxidation of ammonia on the,..... 1297
Reaction, photochemical, mechanism of the, between hydrogen and chlorine,..... 757
Reaction, photosensitized by mercury vapor, the mechanism of,..... 1078
Reactions of the type $Cl_2 + 2\ KOH = KCl + KClO + H_2O$,..... 12
Reaction, the hydrogen-oxygen,..... 34
Reactive nature of aldehydes from the standpoint of the apparent electromotive force,..... 620

Red blood cell suspensions, the kinetics of agglutination of,..... 1
Red, Congo, the color change of, in acidified acetone-water solutions,..... 1276
Reduction of nitrous oxide,..... 491
Relationship between atomic numbers and the properties of ions in the crystal lattice,..... 577, 1069
Relations, solubility, of isomeric organic compounds,..... 70
Relations, the solubility, of naphthalene,..... 1316
Replacement of the water in the hydrogel by alcohol, the organogels of silicic acid,. 617
Report, fourth, of the committee on contact catalysis,..... 145
Reversible permeability of membranes and its relation to cell metabolism,..... 83
Rhythmic diurnal bands of gold and platinum in silicic acid gel,..... 1467
Rock salt, colored, two kinds of, a comparative study of,..... 507
Ruby, the color of the,..... 1441
Salt hydrates, the transition points of, in non-aqueous solutions,..... 930
Salt, rock, colored, two kinds of, a comparative study of,..... 507
Salts in water, influence on the solubilities of, by the addition of a non-electrolyte to the solution,..... 1202
Saturation, degree of, vapor pressure lowering as a function of the,..... 643
Scattering of light by aqueous sodium silicate solutions,..... 706
Sensitive electrical precision apparatus for the determination of the boiling point elevation,..... 1678
Significance of the variation in the Smoluchowski coagulation coefficient ($\beta$),..... 1410
Significance, the nature of the structure of cellulose and its, in chemical transformation,..... 457
Silica gel, the nature of metal films reduced on the surfaces of,..... 1623
Silicate, calcium, the heat capacity of,..... 1175
Silicates of soda, the viscosity of aqueous solutions of the,..... 535
Silicates, sodium, aqueous solutions of,..... 358, 917, 1100
Silicate solutions, aqueous sodium, the scattering of light by,..... 706
Silicic acid gel, rhythmic diurnal bands of gold and platinum in,..... 1467
Silicic acid, organogels of—the replacement of the water in the hydrogels by alcohol, 617
Silver bromide-potassium bromide-water, the ternary system:..... 973
Silver oxide, solubility of,..... 1179
Simple azo dye, the effect of solvents on the absorption spectrum of a,..... 56
Simple, strong electrolytes in water, the solubility of,..... 1585
Size, grain, and the quantum theory of photographic exposure,..... 845
Smoluchowski coagulation coefficient ($\beta$), note on the significance of the,..... 1410
Soap-boiling process, the equilibrium underlying the,..... 1545
Soda, the silicates of, the viscosity of aqueous solutions of,..... 585
Sodium and potassium bromide solutions, the dissociation of water in,..... 1060
Sodium, aqueous, and potassium halide mixtures, ionic activity versus concentration in the interpretation of equilibria between amalgams and,..... 849
Sodium silicates, aqueous solutions of,..... 359, 917, 1100
Sodium silicate solutions, aqueous, the scattering of light by,..... 706
Sodium sulphate, sulphuric ac , ethyl alcohol, the system:,..... 1211
Sodium sulphite, the oxidation the effect of ultra-violet light on the, by atmospheric oxygen,..... 414
Soils, colloidal clays and, anomalous flocculation in,..... 254
Sol, gold, the rate of coagulation of, the effect of temperature on,..... 1401
Sol, influence of ageing of a, on its coagulation,..... 1564
Sols, the neutralization of, the antagonistic action of ions in the,..... 20, 1527
Sols, viscosity measurements of certain, in presence of electrolytes,..... 1646
Solubilities of salts in water, influence on the, by the addition of a non-electrolyte to the solution,..... 1202
Solubility and electrolytic conductance of mesitylene phosphinous acid,..... 1209

Solubility of silver oxide,..... 1179
Solubility of strong, simple electrolytes in water,..... 1585
Solubility relations of isomeric organic compounds,..... 70
Solubility relations of naphthalene,..... 1316
Solution, adsorption from, by ash-free charcoals,.....1031, 1162
Solution, influence on the solubilities of salts in water by the addition of a non-electrolyte to the,..... 1202
Solutions, acidified acetone-water, the color change of Congo red in, ..... 1276
Solutions, acid, the electrolysis of, of copper sulphate,..... 396
Solutions, aqueous, interfacial tensions between organic liquids and water or,.... 791
Solutions, aqueous, of sodium silicates,..... 359, 917, 1100
Solutions, aqueous, of sulphur dioxide and some of its derivatives, the ultraviolet absorption spectra of,..... 266
Solutions, aqueous sodium silicate, the scattering of light by,..... 706
Solutions, aqueous, the viscosity of, of the silicates of soda,..... 535
Solutions, alcoholic, the influence of the ionic charge on the osmotic behavior of,.. 1153
Solutions, colloidal, the apparent viscosity of,..... 239
Solutions, concentrated, individual thermodynamic behaviors of ions in,..... 433
Solutions, diazo-benzene chloride, the stability of,.....1417, 1477
Solutions, non-aqueous, salt hydrates in, the transition points of,..... 930
Solutions of nitro cotton in various solvents, the apparent viscosity of,..... 312
Solutions, potassium nitrate at 20° C, the vapor pressures of, ..... 1669
Solutions, sodium and potassium bromide, the dissociation of water in,..... 1060
Solvated micelles capable of aggregation, a theory of neutral colloids as,..... 239
Solvents, the effect of, on the absorption spectrum of a simple azo dye,..... 56
Solvents, various, the apparent viscosity of solutions of nitro cotton in various solvents,..... 312
Some mixtures, the thermionic properties of, used as catalysts in the synthesis of ammonia,..... 525
Sorption of vapors by alumina, the,..... 172
Spectra, absorption, the ultra-violet, of aqueous solutions of sulphur dioxide and some of its derivatives,..... 266
Spectrum, the absorption, of a simple azo dye, the effect of solvents on the,..... 56
Spherical vessels, ionization by radon in,..... 890
Stability of diazo-benzene chloride solutions,.....1417, 1477
Standpoint of the apparent electromotive force, the reactive nature of aldehydes from the,..... 620
Stannic acids, the nature of,..... 1073
Strong, simple electrolytes in water, the solubility of,..... 1585
Structural colors in insects,..... 383
Structure, gel,..... 306
Structure of cellulose, the nature of the, and its significance in chemical transformations,..... 457
Studies in adsorption,.....628, 830, 1185
Studies in photochemical technique,..... 1427
Studies on the chemistry of gold,..... 126
Study of nitrogen fixation in the high tension arc, a laboratory,..... 595
Study of the electrocapillary curve near its maximum, a,..... 1501
Study of the precipitation of mastic suspensoids,..... 763
Study of two kinds of colored rock salt, a comparative,..... 507
Substances, inorganic, uric acid, and some carbohydrates, catalytic and induced oxidation of,..... 939
Sulphate, copper, acid solutions of, the electrolysis of,..... 396
Sulphate, sodium, sulphuric acid, ethyl alcohol, the system:,..... 1211
Sulphides, antimony,..... 205

Sulphide, the system boron trifluoride-hydrogen, thermal analysis of,..... 369
Sulphite, sodium, oxidation of, the effect of ultra-violet light on the, by atmospheric oxygen,..... 414
Sulphur dioxide and some of its derivatives, aqueous solutions of, the ultraviolet absorption spectra of,..... 266
Sulphuric acid, ethyl alcohol, sodium sulphate, the system:,..... 1211
Surface, a catalytic, heat of activation of, a possible mechanism for the lowering of the,..... 1134
Surface, mercury, the adsorption of ions on a,.....134, 1306
Surface of silica gel, the nature of metal films reduced on the,..... 1623
Surfaces, charged, the surface tension of,..... 1348
Surface tension of charged surfaces, the,..... 1348
Suspensions, red blood cell, the kinetics of agglutination of,..... 1
Suspensoids, mastic, a study of the precipitation of,..... 763
Swelling in beriberi, cause of,..... 277
Synthesis of ammonia, mixtures used as catalysts in the, the thermionic properties of some,..... 525
Synthetic formaldehyde from carbon monoxide and hydrogen,..... 1634
System: boron, trifluoride–hydrogen sulphide, thermal analysis of the,..... 369
System: cresylic acid–gelatine–water, the preparation and conditions of formation of the two possible types of emulsion in the,..... 658
System, equilibrium in the, arsenic pentoxide, barium oxide, water,..... 248
System: potassium laurate–potassium chloride–water, the equilibrium underlying the soap-boiling process, the,..... 1545
System: sodium sulphate, sulphuric acid, ethyl alcohol,..... 1211
System, the ternary, silver bromide–potassium bromide–water,..... 973
System, water, acetic acid, toluene,..... 1287
Systems, colloidal, in nitromethane,..... 1170
Systems, colloid, equilibrium in,.....189, 1660
Technique, photochemical, studies in,..... 1427
Temperature equation, van't Hoff-Arrhenius, a nomogram for the,..... 1219
Temperature, influence of, on metabolism and the problem of acclimatization,..... 480
Temperature, low, vapor pressure of naphthalene at,..... 1497
Temperature, the effect of, on the rate of coagulation of gold sol,..... 1401
Temperature, the effect of, upon the growth of yeast in various media,..... 738
Tension, high, arc, a laboratory study of nitrogen fixation in the,..... 595
Tensions, interfacial, between organic liquids and water or aqueous solutions,..... 791
Tension, the surface, of charged surfaces,..... 1348
Ternary system: silver bromide–potassium bromide–water, the,..... 973
Theory of neutral colloids as solvated micelles capable of aggregation, the apparent viscosity of colloidal solutions and a,..... 239
Theory, quantum, of photographic exposure, grain size and the,..... 845
Thermal analysis of the system: boron trifluoride–hydrogen sulphide,..... 369
Thermal decomposition of carbonates, velocity of,..... 680
Thermal decomposition of formic acid, the,..... 470
Thermal decomposition of methane,..... 899
Thermionic properties of some mixtures used as catalysts in the synthesis of ammonia, the,..... 525
Thermodynamic behaviors, individual, of ions in concentrated solutions,..... 433
Thermodynamic method of computing liquid-junction potentials,..... 433
Titania, catalytic activation of,..... 106
Toluene, acetic acid, water, the system:..... 1287
Transference numbers of hydrochloric acid in glycerol–water mixtures, the,..... 562
Transformations, chemical, the nature of the structure of cellulose and its significance in,..... 457

Transition points of salt hydrates in non-aqueous solutions,..... 930
Two kinds of colored rock salt, a comparative study of,..... 507
Two possible types of emulsion in the system cresylic acid–gelatine–water, the preparation and conditions of formation ot the,..... 658
Type, $Cl_2 + 2KOH = KCl + KClO + H_2O$, reaction of the,..... 12
Type, electric charge, the acid-basic function of molecules and its dependency on the, 777
Types, two possible, of emulsion in the system cresylic acid–gelatine–water, the preparation and conditions of formation of the,..... 658
Tyrosine, phenol and the hydroxyl group of, determination of the dissociation constants of, by means of absorption measurements in the ultra-violet,..... 1683
Ultra-violet absorption spectra of aqueous solutions of sulphur dioxide and some of its derivatives, the,..... 266
Ultra-violet, determination of the dissociation constants of phenol and the hydroxyl group of tyrosine by means of absorption measurements in the,..... 1683
Ultra-violet light, the effect of, on the oxidation of sodium sulphate by atmospheric oxygen,..... 414
Uric acid, some carbohydrates, and inorganic substances, catalytic and induced oxidation of,..... 939
Vapor lamp, mercury, of high intensity, electrolysis of dichromic acid under a,.... 1628
Vapor, mercury, the mechanism of reactions photosensitized by,..... 1078
Vapor pressure lowering as a function of the degree of saturation,..... 643
Vapor pressure of naphthalene at low temperatures,..... 1497
Vapor pressures of potassium nitrate solutions at 20°C,..... 1669
Vapors, the sorption of, by alumina,..... 172
Variation in the Smoluchowski coagulation coefficient ($\beta$), note on the significance of the,..... 1410
Various media, the effect of temperature upon the growth of yeast in,..... 738
Velocity of thermal decomposition of carbonates,..... 680
Vessels, spherical, ionization by radon in,..... 890
View, chemical point of, old age and death from a,..... 378
Violet light, ultra, the effect of, on the oxidation of sodium sulphite by atmospheric oxygen,..... 414
Viscosity measurements of certain sols in presence of electrolytes,..... 1646
Viscosity of aqueous solutions of the silicates of soda,..... 535
Viscosity of hydrosols of aluminum, chromic and ferric oxides, the effect of hydrogen ion concentration on the,..... 1389
Viscosity, the apparent, of solutions of nitro cotton in various solvents,..... 312
Water, acetic acid, toluene, the system:,..... 1287
Water, barium oxide, arsenic pentoxide, equilibrium in the system:,..... 248
Water equilibrium, the,..... 1194
Water–gelatine–cresylic acid the preparation and conditions of formation of the two possible types of emulsion in the system,..... 658
Water, liquid ammonia and in, decomposition potentials and metal overvoltages in, 1597
Water or aqueous solutions, interfacial tensions between organic liquids and,..... 791
Water–potassium chloride–potassium laurate, the system:,..... 1546
Water, salts in, influence on the solubilities of, by the addition of a non-electrolyte to the solution,..... 1202
Water, the dissociation of, in potassium and sodium bromide solutions,..... 1060
Water, the replacement of the, in the hydrogels by alcohol,..... 617
Water, the solubility of strong, simple electrolytes in,..... 1585
Wood, blue.....
Yeast in various media, growth of, the effect of temperature upon the growth of,.. 738
Zinc oxide, iron oxide, nickel, and copper, adsorption of ethylene and hydrogen by,

BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS
ORSAY