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# THE SIZE-FREQUENCY DISTRIBUTION OF PARTICLES OF SILVER HALIDE IN PHOTOGRAPHIC EMULSIONS AND ITS RELATION TO SENSITOMETRIC CHARACTERISTICS*

## PART III

BY E. P. WIGHTMAN, A. P. H. TRIVELLI AND S. E. SHEPPARD**

### Introduction

The present paper is a continuation of an investigation of the size-frequency distribution of photographic emulsions, both commercial and specially prepared, and the determination of the relations of the variations in grain size to the light sensitivity and other characteristics of the emulsions.

In preliminary papers by two of us[1] some general aspects of the subject of the title were discussed, and some recent work by Svedberg[2] was considered in detail. In the first paper we pointed out that to obtain any relation of the grain, in the statistical sense, or dispersity, to the sensitometric properties of emulsions requires methods of assay and determination of the size-frequency curves.

A discussion of the methods already developed in this direction by ourselves and by others was presented in the second paper of this series. In that paper, a description was also given of a fairly rapid but necessarily somewhat coarse sedimentation method, and we anticipated using the Odén sedimentation method.[3] A purely microscopical method of

* Presented in abstract form at the American Chemical Society Meeting, New York, September, 1921.

** Communication No. 148 from the Research Laboratory of the Eastman Kodak Company.

[1] E. P. Wightman and S. E. Sheppard: Jour. Phys. Chem., **25**, 181, 561 (1921); Brit. Jour. Phot., **68**, 169 (1921).

[2] T. Svedberg: Zeit. wiss. Phot., **20**, 38 (1920).

[3] S. Odén: Bull. Geol. Inst. Upsala (1917–19); Koll. Zeit., **26**, 190 (1920).

studying random samples placed on a microscopical slide was likewise described.

The last method has been so much improved and has been made so much more rapid, that it was thought best to continue with it until sufficient data had been collected to be of real value. It should be said that in perfecting this method certain features of Svedberg's procedure, to be discussed later, have been adopted.

Since our last paper went to press, some "*Remarks on the Relation between Sensitiveness and Grain Size in Photographic Emulsions*," by F. F. Renwick,[1] have appeared, in which he states that over twenty years' experience of emulsion making has convinced him that there is no direct relation between grain size and sensitiveness, but as to whether only a limited range of sizes is possible for a given sensitiveness, and conversely, he has still an open mind. The same idea was expressed in a different way in our first paper, in which we said that "a first result of our experimental work is to show that the frequency curve alone is of less value in relation to the sensitometric curve, than the projective area curve obtained by plotting the product of frequency by the mean projective area of each class size against the corresponding classes."

He says that "all the evidence I have seen goes to show that grain size and sensitiveness are not mutually interdependent qualities, though in practice we have not yet learned to vary them independently. The potentialities of an emulsion, i. e., its possible optimum speed, its density-giving properties and its grain characteristics are largely and possibly completely determined at the instant of mixing the reagents." Undue stress, he believes, has been laid on the subsequent stages of the process; they are ripening processes and little more.

In a note on Renwick's remarks two of us[2] commented on his statements, and agreed that while a strict proportionality between grain size and sensitiveness need not exist as

[1] F. F. Renwick: Phot. Jour., 61, 333 (1921).

[2] S. E. Sheppard and A. P. H. Trivelli: Ibid., 61, 400 (1921).

between different emulsions, that a probability relation might exist in one and the same emulsion. It was also pointed out that in practice coarse grained emulsions are sometimes less sensitive than fine grained; some examples were given.

Issue was taken, in the same paper, with Svedberg's definition of the term sensitiveness, in which he regards this (sensitiveness) as entirely conditioned by "a silver nucleus large enough to act as a condensation center in development." The importance of the nucleus as a catalytic agent, and the probable formation of an adsorption complex preceding reduction by the developer were discussed. We shall have occasion later to discuss this more fully, in defining "grain sensitivity;" from the statistical standpoint the evidence quoted is still inconclusive, and we shall, therefore, return to the statistical examination in an entirely agnostic attitude as to the relation in question.

Renwick has given data and photomicrographs of some emulsions which are exceptions to the general rule previously mentioned. However, Dr. Slater Price in discussing Renwick's remarks believed, as we do, that the emulsions which the latter described as identical in preparation, but widely different in grain appearance and sensitometric characteristics, must have undergone some, perhaps slight, difference of treatment which was not noticed.

In the course of our present work we were very desirous of knowing whether the fog which Renwick comments upon as so high in Svedberg's work, was chemical fog induced by the method of treatment, i. e., removal of the emulsion from one plate and coating it in a thinner layer on another, or whether it was due to excessive exposure to the red light of the dark room during treatment. The question also arose, could this fog be eliminated nearly or entirely?

We are happy to state that by taking proper precautions as to exposure and other factors, we were able to very largely eliminate the fog. The entire exposure of even a slow emulsion to the red light during removal of the emulsion from the original plate or film, coating, drying, examining, boxing,

etc., did not exceed five to ten minutes, at a distance from the safelight of more than 50 cm. Tests showed that more than 15 minutes exposure at 30 cm was detrimental. The safelight used was a Wratten Series No. 2.

One other factor which had to be considered was temperature. During the removal of the emulsion, the temperature was never allowed to rise above 40° C, although as high as 50° C could have been used without inducing fog.[1]

We believe, therefore, that the large amount of fog in Svedberg's original experiments was probably due to lack of sufficient precautions as to exposure to the red light, or temperature, or both.

The various questions involved here, and their relation to sensitivity and to the action of the light on the grains are being made the subject of a subsequent paper. In the mean time, a paper on the general theory of the action of light on the photographic emulsion by Dr. L. Silberstein, based on the assumption that light is transmitted in discrete quanta has just been sent to press.[2]

## EXPERIMENTAL PART

### I. Apparatus

Two different sets of microscopic apparatus were employed in the work described below; they consisted of the following:

1. A Zeiss photomicrographic bench; microscope, and camera. The microscope was fitted with 1.9 mm B. and L. oil immersion, 1.30 N. A., and 2 mm Zeiss apochromatic oil immersion, 1.40 N. A., objectives; No. 6 Zeiss compensating ocular; Zeiss Abbé aplanatic substage condenser, 1.4 N. A. Additional parts of the outfit were a 100 C. P. "Pointolite" lamp, with B. and L. aplanatic condenser; H filter; water cell containing quinine bisulphate; "Graflex" shutter. The optical bench was placed on heavy wooden platform supported

[1] These conditions may vary with the emulsion.

[2] Published since this was written Phil. Mag., 44, 257; cf. also Silberstein and Trivelli: 956 (1922).

on an inner tube of an automobile truck tire. Vibrations were thus reduced to a minimum.

2. B. and L. microscope, fitted with 1.9 mm oil immersion 1.30 N. A. objective; Zeiss No. 12 compensating ocular with camera lucida attachment; B. and L. Abbé substage condenser, 1.4 N. A.; a special mechanical substage arranged to take a sensitometric strip, 2.54×12.7 cm in such a way that the latter can be examined even in the corners; tracing linen.

Other apparatus consisted of:

3. A projection printer for enlarging photomicrographs or camera lucida drawings.

4. A polar planimeter.

5. A special rule for measuring the class-size of the particles. The rule was made of steel, 10 cm long, 1 mm thick, and 1.5 cm wide. The two upper lengthwise edges were beveled and these beveled edges were ruled with three sets of rulings, two on one side and one on the other. In each set the rulings represented class limits measured in mm at 10,000 × magnification. Table I gives these distances in mm together with the limiting class sizes and mean class sizes expressed as areas in $\mu^2$ and the corresponding class numbers. The reason for using three sets of class sizes will be discussed later. It will be noticed that the sizes of classes under II are just twice those under I. As a means of distinguishing them easily we call them the single and double scales.

6. A non-intermittent sensitometer,[1] giving a series of exposures both in powers of 2 and $\sqrt{2}$.

7. A neutral gray wedge with range of density from 0 to 6. The wedge was 5×5 inches square, made from dyed gelatin on optical glass, and was as near neutral as it has been possible to obtain by any method. The methods of calibrating it will be described below, along with the sensitometric determinations by means of it.

8. A Freas constant temperature electric oven.

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[1] L. A. Jones: Jour. Franklin Inst., **189**, 303 (1920).

TABLE I
Classification of Grain Sizes

| Class no. | I | | | II | | |
|---|---|---|---|---|---|---|
| | Limit class size in $\mu^2$ | Limit class size, in $\mu \times 10$ | Mean class size in $\mu^2$ | Limit class size in $\mu^2$ | Limit class size, $\mu \times 10$ | Mean class size in $\mu^2$ |
| 1 | 0.03–0.1 | 2.00–3.53 | 0.065 | 0.03–0.2 | 2.00–5.05 | 0.11 |
| 2 | 0.1–0.2 | 3.53–5.05 | 0.15 | 0.2–0.4 | 5.05–7.13 | 0.3 |
| 3 | 0.2–0.3 | 5.05–6.18 | 0.25 | 0.4–0.6 | 7.13–8.74 | 0.5 |
| 4 | 0.3–0.4 | 6.18–7.13 | 0.35 | 0.6–0.8 | 8.74–10.09 | 0.7 |
| 5 | 0.4–0.5 | 7.13–7.98 | 0.45 | 0.8–1.0 | 10.09–11.28 | 0.9 |
| 6 | 0.5–0.6 | 7.98–8.74 | 0.55 | 1.0–1.2 | 11.28–12.36 | 1.1 |
| 7 | 0.6–0.7 | 8.74–9.44 | 0.65 | 1.2–1.4 | 12.36–13.35 | 1.3 |
| 8 | 0.7–0.8 | 9.44–10.09 | 0.75 | 1.4–1.6 | 13.35–14.27 | 1.5 |
| 9 | 0.8–0.9 | 10.09–10.69 | 0.85 | 1.6–1.8 | 14.27–15.14 | 1.7 |
| 10 | 0.9–1.0 | 10.69–11.28 | 0.95 | 1.8–2.0 | 15.14–15.95 | 1.9 |
| 11 | 1.0–1.1 | 11.28–11.83 | 1.05 | 2.0–2.2 | 15.95–16.74 | 2.1 |
| 12 | 1.1–1.2 | 11.83–12.36 | 1.15 | 2.2–2.4 | 16.74–17.48 | 2.3 |
| 13 | 1.2–1.3 | 12.36–12.86 | 1.25 | 2.4–2.6 | 17.48–18.19 | 2.5 |
| 14 | 1.3–1.4 | 12.86–13.35 | 1.35 | 2.6–2.8 | 18.19–18.88 | 2.7 |
| 15 | 1.4–1.5 | 13.35–13.82 | 1.45 | 2.8–3.0 | 18.88–19.54 | 2.9 |
| 16 | 1.5–1.6 | 13.82–14.27 | 1.55 | 3.0–3.2 | 19.54–20.18 | 3.1 |
| 17 | 1.6–1.7 | 14.27–14.71 | 1.65 | 3.2–3.4 | 20.18–20.80 | 3.3 |
| 18 | 1.7–1.8 | 14.71–15.16 | 1.75 | 3.4–3.6 | 20.80–21.40 | 3.5 |
| 19 | 1.8–1.9 | 15.16–15.56 | 1.85 | 3.6–3.8 | 21.40–22.00 | 3.7 |
| 20 | 1.9–2.0 | 15.56–15.95 | 1.95 | 3.8–4.0 | 22.00–22.57 | 3.9 |
| 21 | 2.0–2.1 | 15.95–16.35 | 2.05 | 4.0–4.2 | 22.57–23.12 | 4.1 |
| 22 | 2.1–2.2 | 16.35–16.74 | 2.15 | 4.2–4.4 | 23.12–23.67 | 4.3 |
| 23 | 2.2–2.3 | 16.74–17.11 | 2.25 | 4.4–4.6 | 23.67–24.20 | 4.5 |
| 24 | 2.3–2.4 | 17.11–17.48 | 2.35 | 4.6–4.8 | 24.20–24.72 | 4.7 |
| 25 | 2.4–2.5 | 17.48–17.84 | 2.45 | 4.8–5.0 | 24.72–25.22 | 4.9 |
| 26 | 2.5–2.6 | 17.84–18.19 | 2.55 | 5.0–5.2 | 25.22–25.73 | 5.1 |
| 27 | 2.6–2.7 | 18.19–18.55 | 2.65 | 5.2–5.4 | 25.73–26.22 | 5.3 |
| 28 | 2.7–2.8 | 18.55–18.88 | 2.75 | 5.4–5.6 | 26.22–26.70 | 5.5 |
| 29 | 2.8–2.9 | 18.88–19.21 | 2.85 | 5.6–5.8 | 26.70–27.17 | 5.7 |
| 30 | 2.9–3.0 | 19.21–19.54 | 2.95 | 5.8–6.0 | 27.17–27.04 | 5.9 |
| 31 | —— | —— | — | 6.0–6.2 | 27.64–28.10 | 6.1 |
| 32 | —— | —— | — | 6.2–6.4 | 28.10–28.55 | 6.3 |
| 33 | —— | —— | — | 6.4–6.6 | 28.55–28.99 | 6.5 |
| 34 | —— | —— | — | 6.6–6.8 | 28.99–29.42 | 6.7 |
| 35 | —— | —— | — | 6.8–7.0 | 29.42–29.85 | 6.9 |
| 36 | —— | —— | — | 7.0–7.2 | 29.85–30.27 | 7.1 |

9. A "chill-box." This piece of apparatus is so constructed that pieces of glass can be laid on a level glass plate above a safe light. After coating they can be slid onto a level metal plate on a track. The plate then can be shoved, on its tracks, into a cooling chamber, this being kept cool by means of a jacket filled with cracked ice.

10. A light-tight drying cabinet provided with level shelves, and cooled dry air.

11. Volumetric flasks covered with asphaltum paint to protect the emulsion contained in them from the light.

12. Developing trays, pipettes, and other general laboratory appliances.

## II. Method of determining Size-Frequency Distribution

The sensitive emulsion on a photographic plate or film to be examined is removed and treated as follows:

1. *Preparation of the Emulsion*

To remove the sensitive emulsion from the original plate or film it is first soaked for ½ hour in distilled water at not over 20° (preferably at 15°). This expands and softens the gelatin but does not remove any of it. The water is then poured off and 45 cc of 1% solution of gelatin in 15% ethyl alcohol-water at 40° are added. The whole is then placed in an oven at 40° for 10 minutes, taken out from time to time to rock the tray and thus remove the melted emulsion. After pouring the mixture into a volumetric flask, covered as above stated, 25 cc more of the gelatin solution in alcohol-water is added, and the tray is again placed in the oven for about two minutes. The second lot is poured into the flask and the process is repeated a third time with 25 cc of the gelatin solution. The whole suspension in the flask is finally cooled to about 25° and made up to 100 cc with the gelatin solution. With some kinds of emulsion it is necessary to use a larger volume, 250 cc or even 500 cc, because of the excessively large number of particles contained in a unit quantity of it. The size of plate or film ordinarily employed is 5×7 inches, i. e., 12.7×17.8 cm.

2. *Coating and preparing One-Grain-Layer Slides*

A number of 2×5 inch strips, cut from larger "subbed" plates,[1] were placed on the glass platform of the chill-box

[1] "Subbed" plates are plates which have been specially cleaned and coated on one side with a thin coating of hard gelatin to serve as a binder for the subsequently coated emulsion. Some very clean glass plates without this sub coat were tried but the development and other treatment of the emulsion caused the latter to loosen and float off the surface.

and 1 cc of the emulsion suspension was spread evenly on each strip. The strips were immediately slid onto the level metal plate which was then slid into the cooling chamber. Here they remained for $^1/_2$ hour, by which time the gelatin was "set" sufficiently so that it would dry completely without remelting. The drying was completed on level shelves in a light-tight drying cabinet, in which the temperature was kept below 20°. This required several hours. When dry, the plates were examined for uniformity of coating, and were boxed for future use. The grains on slides prepared in this manner are almost if not exactly in one plane. The varying thicknesses of the grains themselves prevents them from being so exactly.

A quicker method of preparing the emulsion for determining size-frequency only, was to melt the original emulsion off the plate (no special size, though a 12.7×17.8 cm plate was usually used) in about 100 cc of distilled water at 40° about 200 cc of 1% gum arabic solution was then prepared also at 30° to 40° and about $^1/_4$ of the emulsion suspension was poured into it and thoroughly stirred. A drop of the mixture on the end of the stirring rod was then placed on a microscopic slide on a leveled plate and after spreading quickly into a circle about 1.5 cm in diameter was allowed to dry. Immediately following the setting aside of the first one to dry, another quarter of the emulsion suspension was added to the gum arabic solution and the process was repeated on a second slide. A third and then the final quarter were added in the same way, so that all together four slides were prepared, and when dry, that one was chosen for photomicrographing which had the most suitable concentration of grains for the frequency determination.

3. *Magnification of the Particles on a Slide*

From two of these strips, either photomicrographs or camera lucida drawings were made from several fields on each strip. Table II gives data for the two systems used:

The magnifications were actually measured by placing a standard Grayson ruling (1000 to 60,000 lines per inch =

393.7 to 23,622 lines per cm) and a standard B. and L. ruling (.10 and .010 mm) on the microscope stage, and comparing the image on the ground glass (or drawn by means of the camera lucida) with the known distances between the rulings.

The resolving power of the two systems was calculated from the formula

$$d = \frac{1}{2} \cdot \frac{\lambda}{n \sin \alpha} = \frac{1}{2} \cdot \frac{\lambda}{\text{N. A.}} \qquad (1)$$

The effective value of $\lambda$ for the pointolite source with H filter lies about 480 $\mu\mu$, as shown in Table II. Since the source

TABLE II

| | Photomicrographic system | Camera Lucida system |
|---|---|---|
| 1. Effective $\lambda$ for light source used | 480 $\mu\mu$ | 580 $\mu\mu$ |
| 2. N. A. for each system | 1.3 N. A. (sometimes 1.4 N. A.) | 1.3 N. A. |
| 3. Theoretical resolving power | 0.19 $\mu$ | 0.22–0.30 $\mu$ |
| 4. Magnification (on ground glass or linen) | 2500 diams. | 4000 diams. |
| 5. Enlargement (of original negative or drawing) | 4 X | 2.5 X |
| 6. Total magnification | 10,000 diams. | 10,000 diams. |
| 7. Bellows length (eye point tc ground glass) | 56 cm | |
| 8. Total field of microscope (on ground glass or drawing linen) | 292.6 $cm^2$ = 19.3 cm, diam. | |
| 9. Part of total field used (in center) | (12.7 × 17.78) $cm^2$ = 225.8 $cm^2$ | 12.7 cm (diam. circle) = 126.7 $cm^2$ |
| 10. Enlarged field | 3612.8 $cm^2$ = 67.8 cm, diam. | 792.2 $cm^2$ = 31.75 cm, diam. |
| 11. Part of enlarged field used | (24.2 × 29.2) $cm^2$ = 706.6 $cm^2$ = 30.0 cm, diam. | 792.2 $cm^2$ |
| 12. Actual field on microscopic slide | $7.066 \times 10^{-6}$ $cm^{-2}$ | $7.922 \times 10^{-6}$ $cm^2$ |

of light in the visual system was a concentrated filament 100 W tungsten lamp at a voltage of about 110, the effective value of $\lambda$ was 580 $\mu\mu$. It should be noted that since critical illumination was not used in the latter system, $d$ was somewhat larger than the theoretically calculated value.

One thing which adds greatly to the ease of measurement and allows us to reach nearly the theoretical limit of resolving power possible in the present work, is the great difference in refractive index of the silver halides as compared with that of glass and oil (2.25 for AgBr as against about 1.55 for the glass), which thus allows considerable contrast between the object and its surrounding medium.

In the case of both microscopic systems, enlargements were made from the photomicrographic negatives or drawings, with the projection printer, so as to give a final total magnification of 10,000 diameters. The various magnification values are given in the table above. It can be seen that only a small central portion of each total field is utilized which practically eliminates distortion and aberrations.

4. *Measurement of the Grains*

With the first emulsions treated, measurements were made of the grain sizes largely by means of the polar planimeter, except the circular grains, the diameters of which were measured and converted to areas. This method was found to be too slow, and so a number of schemes were tried to shorten the process. The method finally adopted was to measure the majority of grains by means of the special class-rule described above. Only the largest grains and those of unusual shape (e. g., needle-shaped grains, etc.) were planimetered. By using the "double" class-size, the chances of error in classification, i. e., of throwing a particle in the wrong class, were not large. In the case of the angular grains the mean of two dimensions, the longest and shortest across the particle, was found sufficient to classify them. The three most general shapes of angular grains in the commercial emulsions were found to be the tabloid equilateral hexagon; tabloid unequilateral hexagon, nearly triangular; and tabloid unequilateral hexagon, nearly a trapesium. Other shapes occur less often, and all the angular grains are frequently rounded at the corners instead of being perfectly angular.

A series of particles of various shapes was measured by means of the planimeter and by the rule, and only in a few

instances did the class number differ, and since a large number of particles was always measured for the frequency determinations, and the chances for positive errors were about equal to those for negative errors, these may be considered to more or less counterbalance each other. More will be said below about the errors.

It may be of interest to mention in connection with the shapes of the grains, that we have found in the commercial emulsions investigated a few rare examples of (210)+(111) combination crystals, one example of the triakisoctahedron skeleton, and one example of a triakisoctahedron superimposed on the unequilateral hexagon tabloid form all types of which have previously been described in connection with experimental emulsions.[1]

5. *Reproducibility and Sources of Error of the Frequency Determinations*

Green,[2] in a recent paper on "A Photomicrographic Method for the Determination of Particle Size of Paint and Rubber Pigments" has enumerated and discussed what he considers the principal errors involved in this method. He divides them into four general classes. (I) Errors of magnification; (II) Errors in obtaining the average diameter of particles, aside from those in (I); (III) Negligible errors; and (IV) Mistakes. His method of dealing with these errors appears to us somewhat awkward and to a certain extent erroneous, in that he does not seem to have clearly distinguished probable error of observations from percentage average deviation. Moreover, excessive space is devoted to the determination of the error in estimating "grain size" which is not clearly defined, so that actual instrumental errors are swallowed up in errors of classification.

In Table III we give what we believe to be a more suitable classification for our own work, in which are enumerated, not

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[1] A. P. H. Trivelli and S. E. Sheppard: "Monograph on the Silver Bromide Grain of Photographic Emulsions," Research Laboratory of the Eastman Kodak Company, No. 1, pp. 101, 102 (1921).

[2] Henry Green: Jour. Franklin Inst., 192, 637 (1921).

all the possible errors, but what appear to us as the most probable ones. Since the percentage average deviation for the errors in the present work on the average amounts to about

TABLE III

Classification of Experimental Errors

| | | |
|---|---|---|
| **I. Determinate errors** | | |
| 1. Instrumental errors in or due to | (*a*) Graduation of mm rules | Negl. |
| | (*b*) Graduation of classification rules | Negl. |
| | (*c*) Graduation of scale on microscopic bench | Negl. |
| | (*d*) Graduation of Grayson ruling | Negl. |
| | (*e*) Spherical aberration of image on ground glass | Negl. |
| | (*f*) Spherical aberration of image on focussing glass | Negl. |
| | (*g*) Chromatic aberration of image on ground glass | Negl. |
| | (*h*) Chromatic aberration of image on focussing screen | Negl. |
| | (*i*) Insufficient or excessive illumination | Negl. |
| | (*j*) Under or over development of negative | Negl. |
| | (*k*) Under or over development of positive | Negl. |
| | (*l*) Distortion of photographic emulsion on drying | Negl. |
| 2. Errors in method and theoretical errors | (*a*) Estimating area of grains of different shape from mean diameters | |
| | (*b*) Drawing particles on linen by means of camera lucida, instead of photomicrographically | |
| 3. Personal errors | Owing to the nature of the work these would not play an important part, except in estimating sizes of grains, and here the method was checked by more than one person | Negl. |
| **II. Indeterminate errors** | | |
| 1. Accidental errors | (*a*) Determination of the exact edge of magnified image of the grain on the print | Negl. |
| | (*b*) Poor focussing | Negl. |
| | (*c*) Determination of microscopic magnification | Negl. |
| | (*d*) Determination of projection magnification | |
| | (*e*) Using limited number of fields | |
| | (*f*) Using limited number of grains | |
| 2. Residual errors | These include errors from all of the above methods including small personal errors | |

$\pm 7\%$, the deviations in component factors $\overline{<}$ $\pm 1.0\%$, may be considered negligible. Any errors enumerated in the table which are less than $\pm 0.5\%$ we have indicated, as negligible.

In this table errors (*e*), (*f*), (*g*), (*h*) under I (1) may be considered negligible since only a small portion at the center of the microscopic field was used, as seen from Table II above, and since compensating eyepieces for the microscopes, and

a high grade apochromatic, anastigmatic lens on the projector apparatus were employed.

Errors (*i*), (*j*), (*k*), (l) in I (1) are negligible, since intensity and time of illumination, development time, and method of drying negatives and prints, when once determined remained the same throughout the work.

Error II (1) (*b*) is likewise negligible since negatives which showed poor focussing were discarded, and in the camera lucida method, the images of particles being drawn were always brought to an exact focus.

Before taking up the remaining errors, let us designate the notation employed. Let M = any indirectly determined magnitude.

$\Delta$ = the precision of M expressed as average deviation.[1]

$m_1, m_2, \ldots . m_n$ = means of single observations of directly measured components of M.

$\delta_1, \delta_2 \ldots . \delta_n$ = precision of $m_1, m_2, \ldots .$ respectively, expressed as average deviations (a. d. = $\frac{\Sigma d}{n}$, for a single observation)

$d_1, d_2, \ldots . d_n$ = actual deviations of single observations from the mean of n measurements, $a_1, a_2, \ldots . a_n$ (whence $\frac{\Sigma a}{n} = m_1$, etc.)

$\Delta_1, \Delta_2, \ldots . \Delta_n$ = average deviation in M produced by deviations $\delta_1, \delta_2, \ldots .$ in the components $m_1, m_2, m \ldots .$

$p_1, p_2 \ldots . p_n$ = weights of the different observations.

When M can be expressed as a function of the form

$$M = k \, . \, m_1^a \, . \, m_2^b \ldots m_n^p \qquad (2)$$

where $k, a, b, \ldots . p$ are constants either positive, negative, fractional, or integral, which is the case in most of the present work, then the precision of the final result may be expressed in the form of percentage average deviation as follows:

$$P = 100 \frac{\Delta}{M} = \sqrt{(100\, a \frac{\delta_1}{m_1})^2 + (100\, b \frac{\delta_2}{m_2})^2 + \ldots + (100\, p \frac{\delta_n}{m_n})^2} \qquad (3)$$

[1] The ± sign, whenever omitted from in front of an average deviation is implied.

The values, the precision of which interests us most, are (a) the frequencies for different class sizes; (b) the precision constant and other constants in the equation representing the distribution of the grains; (c) the total areas of each class size; (d) the average grain size; and (e) the number of grains per unit area of the original film or plate.

(a) The reproducibilities of the frequencies are fairly good, as can be seen from Table IV, where we have reproduced a typical series of values for one of the emulsions. Four sets of observed values (of the frequencies) for the emulsion were obtained by measuring a certain number of grains on each of two or more slides containing some of the same emulsion coated in a single layer. The sixth column contains the averages of these four sets of values, and the seventh column the calculated frequencies (obtained as stated below in Section 6). The next four columns contain the deviations of the four sets of frequencies from the observed means. Column 12 gives the average deviation, and 13 the percentage average deviation of each frequency. If we choose as weights the mean frequencies, that is,

$$p_1 = m_1 = y_1,\ p_2 = m_2 = y_2, \ldots . p_n = m_n = y_n$$

and multiply each of the percentage average deviations by these respectively, and divide the sum of the products by the sum of the weights, then we get the precision or weighted mean percentage average deviation of the entire set of frequencies. Thus we have

$$\frac{100\,\delta}{m} = \frac{100\frac{\Sigma\, d}{n}}{m} = D \qquad (4)$$

for the percentage average deviation of the single frequencies, and

$$\frac{p_1 D_1 + p_2 D_2 + \ldots + p_n D_n}{p_1 + p_2 + \ldots + p_n} = \pm 6.4\,\% \qquad (5)$$

for the weighted mean percentage average deviation of the entire set.

TABLE IV
Reproducibility of Frequencies

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| x = class size in $\mu^2$ | $a' = y' =$ freq. per 1000 grains | $a'' = y'' =$ freq. per 1000 grains | $a''' = y''' =$ freq. per 1000 grains | $a'''' = y'''' =$ freq. per 1000 grains | $m = y$ (obs.) = mean freq. per 1000 grains | y(calc.) freq. per 1000 grains | $m - a' = d' =$ devia. of $y'$ from obs. mean |
| 0.1 | 51.0 | 40.5 | 51.8 | 45.9 | 47.3 | 53.2 | − 3.7 |
| 0.2* | 128.4 | 115.3 | 112.0 | 119.5 | 118.8 | 109.9 | − 9.6 |
| 0.3 | 169.2 | 196.8 | 138.3 | 153.7 | 164.5 | 189.9 | − 4.7 |
| 0.4* | 261.0 | 259.3 | 227.0 | 235.0 | 245.6 | 274.2 | − 15.4 |
| 0.5 | 347.8 | 324.1 | 314.2 | 306.0 | 323.0 | 331.2 | − 24.8 |
| 0.6* | 366.0 | 345.0 | 341.2 | 348.1 | 350.0 | 334.4 | − 16.0 |
| 0.7 | 285.0 | 287.0 | 316.0 | 317.9 | 301.5 | 282.3 | + 16.5 |
| 0.8* | 186.5 | 203.0 | 209.3 | 202.2 | 200.5 | 199.2 | + 14.0 |
| 0.9 | 105.6 | 130.0 | 136.2 | 127.4 | 124.8 | 117.6 | + 19.2 |
| 1.0* | 51.2 | 60.2 | 72.0 | 71.8 | 63.8 | 58.0 | + 12.6 |
| 1.1 | 17.8 | 15.9 | 32.2 | 35.3 | 25.3 | 24.0 | + 7.5 |
| 1.2* | 9.2 | 6.5 | 20.6 | 14.1 | 12.6 | 8.3 | + 3.4 |
| 1.3 | 7.2 | 3.5 | 5.4 | 9.2 | 6.3 | 2.4 | − 0.9 |
| 1.4* | 6.1 | 1.8 | 3.8 | 3.0 | 3.7 | 0.6 | − 2.4 |
| 1.5 | —— | —— | 3.0 | 1.4 | 1.1 | 0.1 | + 1.1 |
| No. Grs. Measur. | 1056 | 1065 | 1026 | 1063 | 4210 | | |

TABLE IV (*Continued*)
Reproducibility of Frequencies

| 1a | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|
| x = class size in $\mu^2$ | $m - a'' = d''$ | $m - a''' = d'''$ | $m - a'''' = d''''$ | $\delta = \frac{\Sigma d}{n}$ (obs.) | $D = 100\frac{\delta}{m}$ (obs.) | $d$(calc.) = $yc - y_o$ | $100\frac{d}{y}$ |
| 0.1 | + 6.8 | − 4.5 | + 1.4 | ± 4.1 | ± 8.7 | + 5.9 | ± 11.1 |
| 0.2* | + 3.5 | + 6.8 | − 0.7 | ± 5.2 | ± 4.4 | − 8.9 | ± 8.1 |
| 0.3 | −32.3 | +26.2 | + 9.8 | ±18.2 | ± 11.1 | +27.9 | ± 14.7 |
| 0.4* | −13.7 | +18.6 | +10.6 | ±14.6 | ± 5.6 | +28.6 | ± 10.4 |
| 0.5 | − 1.1 | + 8.8 | +17.0 | ±12.9 | ± 4.0 | + 8.2 | ± 2.5 |
| 0.6* | + 5.0 | + 8.8 | + 1.9 | ± 7.9 | ± 2.3 | −15.6 | ± 4.7 |
| 0.7 | +14.5 | −14.5 | −16.4 | ±15.5 | ± 5.1 | −19.2 | ± 6.8 |
| 0.8* | − 2.5 | − 8.8 | − 1.7 | ± 6.8 | ± 3.0 | + 2.7 | + 1.4 |
| 0.9 | − 5.2 | −11.4 | − 2.6 | ± 9.6 | ± 7.7 | − 2.8 | ± 2.4 |
| 1.0* | + 3.6 | − 8.2 | − 8.0 | ± 8.1 | ± 12.7 | − 5.8 | ± 10.0 |
| 1.1 | + 9.4 | − 6.9 | −10.0 | ± 8.5 | ± 33.6 | − 1.3 | ± 5.4 |
| 1.2* | + 6.1 | − 8.0 | − 1.5 | ± 4.8 | ± 38.1 | − 4.3 | ± 51.8 |
| 1.3 | + 2.8 | + 0.9 | − 2.9 | ± 1.9 | ± 30.2 | − 3.9 | ±162 |
| 1.4* | + 1.9 | − 0.1 | + 0.7 | ± 1.3 | ± 35.1 | − 3.1 | —— |
| 1.5 | + 1.1 | − 1.9 | − 0.3 | ± 1.1 | ±100.0 | − 1.0 | —— |
| Average percentage Average deviation of any set | | | | | ± 6.4** | * —— | ± 7.0† |

* Frequencies for these class-sizes lie within the limits of the class units employed, but since they do not represent the mean frequency for the class they were not counted in determining the number of grains per 1000.

** This is the weighted mean percentage average deviation for all classes calculated from equation (5) above.

† This is the weighted average percentage average deviation of the observed calculated from the mean frequency.

In the case of the smallest class-size, and of the largest class-sizes when the number of grains is comparatively small, the percentage average deviations of the individual frequencies are quite large, which is to be expected, since in the former many small grains just at or below the limit of resolving power are likely to have been missed, and in the latter the chances of misplacing grains in classifying, as well as of finding too great or too small a number of a given size in the limited number of fields observed, is much greater than where the grains approach the average size.

The accuracy of the frequency in each class depends upon ($\alpha$) the determination of the size of the individual particles in that class, and particularly, of those on the border of each neighboring class; ($\beta$) their uniformity of distribution; and, since it is not possible to obtain perfect uniformity, upon ($\gamma$) the number of grains measured.

An error in ($\alpha$) may be due either to an error in the magnification [Table III, I. 2 (b) and II. 1 (c) and (d)] or to an error in measuring its average diameter [Table III., I. 2 (a), I. 3, II. 1 (a) and II. 2], or to both.

The magnification error can be shown to be negligible as follows:

$$\text{Let } M = \text{total magnification} = m_1 \times m_2 \tag{6}$$

where $m_1$ and $m_2$ are the microscopic and projection magnification, respectively.

But,

$$m_1 = K m_3 \tag{7}$$

where $m_3$ is the bellows length $= 560 \pm 0.1$ mm, hence $100 \frac{\delta_3}{m_3} = \pm 0.02\%$

and

$$K = \frac{m_4}{m_5 \cdot m_6} \tag{8}$$

where $m_4$ is the length of the image of the standard ruling on the ground glass, $= 63.50 \pm 0.1$ mm, hence $100 \frac{\delta_4}{m_4} = \pm 0.2\%$; $m_5$ is one of several bellows lengths used in determining K: average deviation less than $\pm 0.05\%$ (negligible); $m_6$ is the actual length between lines of the standard ruling $= 0.02540 \pm 0.00025$

(the error here is less than can be observed, i. e., less than one half the wave length of the light used), hence $100\,\frac{\delta_6}{m_6} = 0.5\%$; then from (3),

$$100\,\frac{\Delta}{K} = 100\,\frac{\delta K}{K} = 100\,\frac{\delta_1}{m_1} = \sqrt{(0.2)^2+(0.5)^2} = \pm .5\% \qquad (9)$$

Now,

$$m_2 = \frac{a_2 \pm d_2}{a_1 \pm d_1} = \frac{1000 \pm 0.2 \text{ mm}}{250 \pm 0.05 \text{ mm}} \qquad (10)$$

i. e., the projection magnification, $m_2$, is the ratio of the distance between two ruled lines on the negative to the distance apart of their images on the screen, and from the above figures it is seen that $100\,\frac{d_2}{a_2}$ and $100\,\frac{d_1}{a_1}$ are both negligible and hence $100\,\frac{\delta_2}{m_2}$ is negligible.

Therefore,

$$100\,\frac{\Delta}{M_1} = 100\,\frac{\delta_1}{m_1} = \pm 0.5\%$$

A similar calculation for the camera lucida method shows that it also has a deviation in the magnification that is negligible in itself, but in drawing the grains, errors as great as $\pm 5\%$ in diameter may occur, especially in the smaller grains. In a large number of grains measured, however, the probability is that these errors will largely eliminate each other.

Now consider the case of the measurement of the average diameter of the magnified grains. A series of measurements with the classification rule was made as described above, i. e., the mean of the maximum and minimum class size dimensions was taken and compared with careful measurements of each grain made with a polar planimeter, which could be trusted, for the larger sized grains, to a precision of $\pm 0.5\%$ (percentage average deviation) and for the medium ones, to about $\pm 1\%$, by taking the average of several determinations on each. The small grains were mostly circular or nearly so, and, therefore, were more accurately measured by the rule than with the planimeter. The comparison showed that for what we have termed a "double" classification, i. e., where the extent

of each class size was $0.2\mu^2$, only about one in 15 to 20 grains were misplaced, and the misplacement was about as often in one direction as in the other.

To calculate the various errors involved here would be a rather complicated process and would have no great value after they were obtained, since we already know what the approximate reproducibility of the frequencies is. It is safe to say, however, that in this part of the work the greatest sources of error in the frequency lie. It is possible to reduce these considerably by more careful measurements of the grain sizes, but it would be at the expense of considerable time and much energy, since, in the present work alone more than 25,000 grains have been measured, and in some other work which is being undertaken, the number of grains being measured runs into hundreds of thousands.

As to ($\beta$), the errors in the uniformity of distribution, they are probably a little less than those just mentioned, but are of the same order. They may, however, be to some extent reduced in future work by more careful coating of the plates, and by coating on optical glass instead of the glass used in commercial plates, which from the standpoint of high-power microscopy and one-grain-layer studies, do not have truly plane surfaces.

In connection with ($\gamma$), the number of grains measured, it should be noted here that the wider the range of sizes of grains in an emulsion the greater the number of grains which it is necessary to count. In some cases a few hundred will suffice, i. e., where the frequency distribution is confined to a narrow range of class sizes; whereas, in others it is not safe to count less than 2000 grains in order to obtain the true distribution. In every emulsion which we have measured we have made sure that sufficient grains have been counted to reduce the error due to lack of uniformity to within reasonable bounds. The number of grains measured for each emulsion is given below together with the other data concerning them.

(b) The reproducibility of the constants in the equations by which the calculated frequencies were determined depends

upon the reproducibility of the observed frequencies. Since they are found by the least squares method, however, they are the most precise values which can be obtained for the arbitrarily chosen form of equation which has been applied to the observations.

(c) Since the area-class-size curve is obtained by multiplying the values of y (=frequency) on the calculated frequency curve, by the corresponding values of x (=mean class size), and by a constant, N representing the number of grains per sq. cm. of the plate divided by 1000, then the precision of the total area of each class size depends upon the precision of these factors. The magnitude of the first of these sources of error is seen from Table IV above. The reproducibility of $x$ is of course constant, since it represents the mean class size, although there is an error in assuming the mean class size instead of integrating between the class limits. We have not attempted to determine the size of this error, yet it is apparent that it would not be large with such narrow class limits as we have chosen. It is probably safe to consider it as negligible compared to the other errors. Data for the third factor are given below under (e). We have then as the weighted average percentage average deviation

$$100\,\frac{\Delta}{Y} = \pm\sqrt{(100\,\frac{\Delta_y}{Y})^2 + (100\,\frac{\Delta_N}{Y})^2}$$

$$= \pm\sqrt{(7.0)^2 + (4.0)^2} = \pm 8.0\% \qquad (11)$$

(d) The determination of the error in the average grain size can be obtained readily from Table V by calculating the

TABLE V
Deviations in the Average Grain Size

| Series no. | $\bar{x}$ in $\mu^2$ | $d$ | $100\,\frac{d_m}{m}$ |
|---|---|---|---|
| 1 | 0.562 | 0.018 | |
| 2 | 0.566 | 0.014 | |
| 3 | 0.596 | 0.016 | ±2.8% |
| 4 | 0.596 | 0.016 | |
| M | 0.580 | 0.016 | |

average size particle for each of the four series of measurements and determining the deviations from the mean of these.

This deviation of course is calculated from the observed values. The deviation of observed from the calculated average grain size (=0.561) amounts to ±3.4%.

(e) Since the number of grains per unit area of the original plate is

$$N = a\, m\, l$$

where $a$ = the ratio of microscopic field area to the unit area of the original plate, $m$ = the average number of grains per microscopic field on two or more one-grain-layer plates, and $l$ = the dilution from the original emulsion to the one-grain-layer emulsion; and since $a$ may be considered to have a negligible error then

$$100\,\frac{\Delta}{N} = \pm\, 100\,\sqrt{\left(\frac{\delta_m}{m}\right)^2 + \left(\frac{\delta_l}{l}\right)^2} = \pm\, 4.0\% \qquad (12)$$

Table VI gives values of $m$, $d$, $\delta_m$, $\delta_l$ and of $100\,\frac{\Delta}{N}$ for a typical emulsion.

TABLE VI

Errors in the Number of Grains per Unit Area of Original Emulsion

| Field no. | $m$ = No. grains | $d_m$ = Devia. from mean | $\frac{\Sigma d_m}{n\sqrt{n}} = \delta_m =$ |
|---|---|---|---|
| 1 | 149 | 9.9 | ±3.8 |
| 2 | 139 | 0.1 | $100\,\frac{\delta_m}{m} =$ |
| 3 | 143 | 3.9 | |
| 4 | 116 | 23.1 | ±2.7 |
| 5 | 155 | 15.9 | |
| 6 | 144 | 4.9 | $100\,\frac{\delta_l}{l} =$ |
| 7 | 148 | 8.9 | |
| 8 | 119 | 20.1 | ±3.0 |
| Mean | 139.1 | 10.9 | $100\,\frac{\Delta}{N} = \pm\, 4.0\%$ |

The errors in dilution include losses in removing the emulsion from the plate, errors in measurement of the volume of the emulsion suspension and in pipetting to the slide, and errors in contraction of the emulsion slightly from the edge of the plate in drying.

It is not claimed that the errors considered above are the maximum ones obtained in this work, but the errors throughout the work are in general of about the same order of magnitude as those for the particular cases cited.

6. *Results and Mathematical Expression of Frequency Curves*

The emulsions whose size-frequency distribution and sensitometric characteristics were measured are the following:

1. Process A (Lantern Slide)
2. Process B
3. Process C
4. Positive Emulsion
5. Medium Speed A
6. Medium Speed B
7. Medium Speed C
8. High Speed A
9. High Speed B
10. Experimental Emulsion No. 1
11. Experimental Emulsion No. 2

Here we have a series ranging from the slowest to the fastest commercial emulsions. The experimental emulsions are slow emulsions.

As the grains on each of these were measured they were classified, most of them on the basis of "equivalent" diameter, with uniform class divisions in $0.2\mu$. The method of converting these to a uniform area classification for the total area-size curves is stated below. A few of the emulsions were classified directly in uniform class divisions of $0.2\mu^2$. Some additional reclassifying into subdivisions of the $0.2\mu$ or $0.2\mu^2$ classes was necessary in the neighborhood of the inflexion points of the distribution curves. With the classification

rule described it was possible to classify directly on an area basis which is more useful in applying or correlating the data. All future work will be done on the area basis.

To obtain the calculated frequency, the observed frequency values were plotted against mean-class-sizes, and since the trend of the curve drawn indicated that some simple standard equation of an error function could be applied to it with a fairly good approximation, the function it most resembled was chosen, and the values of the constants in this equation were quickly calculated as a first approximation, and then by the method of Least Squares, were corrected in order to obtain the best fitting curve of that form. By this is not meant the *best fitting curve possible*. To obtain such a curve would be impracticable so far as the present work is concerned.

Either one or the other of the two following equations were found to fit fairly well the data classified on a uniform diameter basis:

$$y = y_0 e^{-kz} \tag{13}$$

or

$$y = y_0 e^{-k(z-\alpha)^2} \tag{14}$$

in which $y$ represents the frequency (per 1000 grains), $y_0$ the intersection of the curve with the $y$-axis in (13) and the maximum ordinate in (14), $k$ the "precision" or "deviation" constant, $z$ the class size in diameter, and $\alpha$ the constant indicating the position of the mode or maximum ordinate on the class-size-axis.

Curiously enough, equations of the same form appear to be applicable to the uniform area classification, i. e.,

$$y = y_0 e^{-kx} \tag{15}$$

and

$$y = y_0 e^{-k(x-\alpha)^2} \tag{16}$$

in which $x$ represents the class-size in area.

Some of the emulsions, for example the High Speed A, Medium Speed C and the Positive, are quite evidently not

"simple" emulsions. Their size-frequency curves are composites of two or more curves, due to variations in some of the factors involved in the formation of the emulsions, during the course of their preparation.

Starting from the frequency data and working backwards it is difficult to say just what these composite curves are. But some of the possibilities have been calculated and are reproduced below.

From the size-frequency curves are obtained the size-area curves per unit area of the original plate or film, thus:
from (13)

$$Y = \frac{N}{1000}\frac{\pi}{4}z^2 y = \frac{\pi}{4}z^2\frac{N}{1000}y_0 e^{-kz} = Cz^2 e^{-kz} \qquad (17)$$

from (14)

$$Y = \frac{N}{1000}\frac{\pi}{4}z^2 y = \frac{\pi}{4}z\frac{N}{1000}y_0 e^{-k(z-a)^2} = Cz^2 e^{-k(z-a)^2} \qquad (18)$$

where N represents the total number of grains per unit area of the film or plate.

Equations (15) and (16) become

$$Y = \frac{N}{1000}x y = c x e^{-kx} \qquad (19)$$

$$Y = \frac{N}{1000}x y = c x e^{-k(x-a)^2}. \qquad (20)$$

In order to obtain the average size particle for emulsions whose size-frequency curves are similar to equation (15), we have only to integrate equation (19) (with the factor $\frac{N}{1000}$ omitted), for the total area between limits $x_1$ and $x_n$, i. e., between the minimum limit of the smallest and the maximum limit of the largest class size, and divide this area $A_{1000}$, by the number of grains, i. e., 1000, lying within these limits (the number of grains can be determined exactly by inte-

grating equation (15) although it should equal close to 1000).

$$A_{1000} = a\int_{x_1}^{x_2}(xe^{-kx})\,dx = \frac{a}{k^2}\left\{(1+kx_2)e^{-kx_2} - (1+kx_1)e^{-kx_1}\right\} \quad (21)$$

$$N_{1000} = a\int_{x_1}^{x_2}(e^{-kx})\,dx = \frac{a}{k}\int_{x_1}^{x_2}(e^{-kx})\,d(kx) = \frac{a}{k}\left[e^{-kx_2} - e^{-kx_1}\right] \quad (22)$$

Hence,

$$\bar{x} = \frac{A_{1000}}{N_{1000}} = \frac{1}{k}\left\{\frac{(1+kx_2)\,e^{-kx_2} - (1+kx_1)\,e^{-kx_1}}{e^{-kx_2} - e^{-kx_1}}\right\} \quad (23)$$

To get the average size particle for the other equations, we must resort either to a graphic method, or to an approximation of the form

$$\bar{x} = \frac{\Sigma\left(\frac{\pi}{4}z^2y\right)}{\Sigma y} = \frac{\frac{\pi}{4}z_1^2y_1 + \frac{\pi}{4}z_2^2y_2 + \frac{\pi}{4}z_3^2y_3 + \ldots + \frac{\pi}{4}z_m^2y_n}{y_1 + y_2 + y_3 \ldots + y_n} \quad (24)$$

or

$$\bar{x} = \frac{\Sigma(xy)}{\Sigma y} = \frac{x_1y_1 + x_2y_2 + \ldots x_ny_n}{y_1 + y_2 + \ldots y_n}. \quad (25)$$

where $x_1, x_2, \ldots x_n$ are the mean class sizes, and $y_1, y_2, \ldots y_n$ are the calculated frequencies. The values of $z_1$, $z_2$, etc., in (23) are the diameters corresponding to the areas $x_1$, $x_2$, $x_3$, etc., in (24).

For the graphic method we plot any one of the curves on mm cross-section paper, and planimeter the area subtended by it between the desired limits, and divide this area by the number of particles (approximately = 1000) within those limits.

The size-frequency curves of the above-named emulsions are shown in Figs. 1 to 11 inclusive, together with a photomicrograph or camera lucida drawing of each at ×2500 diameters (in the original, and reduced to a little less than one half this in reproducing). Tables VII to XI give the data from

TABLE VII

| | | | Process A | | Process C | | | |
|---|---|---|---|---|---|---|---|---|
| Class no. | z = class size in $\mu$ | Corresp. area in $\mu^2$ | y(obs.) = no. grains per 1000 | y(calc.) = curve A | y(obs.) = no. grains per 1000 | y(calc.) = curve A | x = class size in $\mu_1$ | Corresp. diam. in $\mu$ |
| 1 | 0.3 | 0.071 | 700 | 700 | 172.0 | 172.0 | 0.1 | 0.353 |
| 1*a* | — | — | — | — | — | — | 0.2 | 0.505 |
| 2 | 0.5 | 0.196 | 219 | 219 | 278.0 | 265.0 | 0.3 | 0.618 |
| 2*a* | — | — | — | — | — | — | 0.4 | 0.713 |
| 3 | 0.7 | 0.385 | 73.3 | 68.6 | 280.0 | 280.0 | 0.5 | 0.798 |
| 3*a* | — | — | — | — | — | — | 0.6 | 0.874 |
| 4 | 0.9 | 0.636 | 9.3 | 21.4 | 162.0 | 202.8 | 0.7 | 0.944 |
| 4*a* | — | — | — | — | — | — | 0.8 | 1.01 |
| 5 | 1.1 | 0.950 | 0 | 3.4 | 66.7 | 100.7 | 0.9 | 1.07 |
| 5*a* | — | — | — | — | — | — | 1.0 | 1.13 |
| 6 | 1.3 | 1.327 | — | — | 26.7 | 34.3 | 1.1 | 1.18 |
| 6*a* | — | — | — | — | — | — | 1.2 | 1.24 |
| 7 | 1.5 | 1.767 | — | — | 8.0 | 8.0 | 1.3 | 1.29 |
| 7*a* | — | — | — | — | — | — | 1.4 | 1.34 |
| 8 | 1.7 | 2.270 | — | — | 3.6 | 1.3 | 1.5 | 1.38 |
| 9 | 1.9 | 2.835 | — | — | 2.7 | 1.4 | 1.7 | 1.47 |
| 10 | — | — | — | — | — | — | 1.9 | 1.56 |
| 11 | — | — | — | — | — | — | 2.1 | 1.64 |
| 12 | — | — | — | — | — | — | 2.3 | 1.71 |
| 13 | — | — | — | — | — | — | 2.5 | 1.78 |
| 14 | — | — | — | — | — | — | 2.7 | 1.86 |
| 15 | — | — | — | — | — | — | 2.835 | 1.90 |
| Sum | | | 1001.6 | 1012.4 | 999.7 | 1064.2 | | |

TABLE VII (*Continued*)

| | Process B | | Positive | | Proc. A | Proc. B | Proc. C | Posit. |
|---|---|---|---|---|---|---|---|---|
| Class no. | y(obs.) = no. grains per 1000 | y(calc.) = curve A | y(obs.) = no. grains per 1000 | y(calc.) = Curve A | $Y.10^{-6}$ = Curve B | $Y.10^{-6}$ = Curve B | $Y.10^{-6}$ = Curve B | $Y.10^{-6}$ = Curve B |
| 1 | 47.3 | 53.2 | 355.7 | 399.0 | 207.0 | 3.6 | 7.0 | 74.0 |
| 1*a* | 118.8 | 109.9 | — | 309.3 | — | 14.7 | — | 114.7 |
| 2 | 162.0 | 189.9 | 235.2 | 240.9 | 142.0 | 38.1 | 26.5 | 132.1 |
| 2*a* | 245.6 | 274.2 | — | 187.2 | — | 73.3 | — | 139.8 |
| 3 | 323.0 | 331.2 | 176.7 | 145.4 | 37.0 | 110.6 | 36.8 | 134.8 |
| 3*a* | 350.0 | 334.4 | — | 113.0 | — | 133.8 | — | 125.7 |
| 4 | 301.5 | 282.3 | 114.7 | 87.8 | 47.0 | 132.0 | 39.0 | 112.0 |
| 4*a* | 196.5 | 199.2 | — | 68.2 | — | 106.5 | — | 101.1 |
| 5 | 124.8 | 117.6 | 84.5 | 53.0 | 19.0 | 70.7 | 31.8 | 88.4 |
| 5*a* | 63.8 | 58.0 | — | 41.2 | — | 38.8 | — | 76 4 |
| 6 | 25.3 | 24.0 | 20.3 | 32.0 | — | 17.6 | 23.6 | 65.3 |
| 6*a* | 12.6 | 8.3 | — | — | — | 6.7 | — | — |
| 7 | 6.3 | 2.4 | 8.2 | 19.3 | — | 2.1 | 14.9 | 46.5 |
| 7*a* | 3.7 | 0.6 | — | — | — | 0.6 | — | — |
| 8 | 1.1 | 0.1 | 2.8 | 11.7 | — | 0.1 | 8.3 | 32.6 |
| 9 | — | — | 1.1 | 7.0 | — | — | 4.8 | 22.1 |
| 10 | — | — | 0.5 | 4.3 | — | — | 2.4 | 15.2 |
| 11 | — | — | 0.2 | 2.6 | — | — | 1.2 | 10.2 |
| 12 | — | — | — | — | — | — | 0.4 | — |
| 13 | — | — | — | — | — | — | 0.30 | — |
| 14 | — | — | — | — | — | — | 0.19 | — |
| 15 | — | — | — | — | — | — | 0.12 | — |
| Sum | 999.6 | 1000.3 | Total | Area | 502.0 | 374.8 | 197.3 | 733.2 |

which these were plotted, and Table XII a summary of these data. Fig. 11a shows some of the grains of Experimental Emulsion No. 2. magnified 5,000 diameters.

Most of the tables are self explanatory. The values in the last three columns under $y_0$, $K$, and $\alpha$ in Table XII represent the parameters in the equations given above.

It should be noted here that the values of the number of grains in the emulsions determined by the method above described agree quite well with values obtained by the sedimentation method described in the second paper of this series.

The idea has been expressed, particularly by Slade and

TABLE VIII

| Class no. | $z$ = class size in $\mu$ | Corresp. area in $\mu^2$ | Medium Speed A | | Medium Speed B | | Medium Speed C | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | y(obs.) = no. grains per 1000 | y(calc.) curve A | y(obs.) = no. grains per 1000 | y(calc.) curve A | y(obs.) = no. grains per 1000 | y(calc.) curve A | $y'$ (calc.) curve A' |
| 1 | 0.3 | 0.071 | 397.0 | 437.4 | 220.0 | 220.0 | 80.0 | 80.0 | — |
| 2 | 0.5 | 0.196 | 305.0 | 241.2 | 276.0 | 276.0 | 180.0 | 155.2 | — |
| 3 | 0.7 | 0.385 | 133.0 | 133.0 | 228.0 | 245.9 | 214.0 | 214.0 | — |
| 4 | 0.9 | 0.636 | 54.0 | 73.4 | 118.3 | 155.8 | 169.0 | 209.6 | — |
| 5 | 1.1 | 0.950 | 34.0 | 40.4 | 70.0 | 70.0 | 146.0 | 146.0 | — |
| 6 | 1.3 | 1.327 | 22.3 | 22.3 | 34.0 | 22.4 | 73.0 | 72.3 | 0.7 |
| 7 | 1.5 | 1.767 | 20.2 | 12.3 | 24.3 | 5.1 | 41.0 | 25.4 | 6.6 |
| 8 | 1.7 | 2.270 | 13.8 | 6.8 | 8.7 | 0.8 | 30.0 | 6.4 | 23.6 |
| 9 | 1.9 | 2.835 | 9.5 | 3.7 | 7.8 | 0.09 | 23.0 | 1.1 | 31.6 |
| 10 | 2.1 | 3.464 | 5.3 | 2.1 | 5.8 | 0 | 16.0 | — | 16.0 |
| 11 | 2.3 | 4.155 | 4.2 | 1.13 | .97 | — | 13.0 | — | 2.4 |
| 12 | 2.5 | 4.909 | 1.10 | 0.63 | 2.91 | — | 4.0 | — | 0.2 |
| 13 | 2.7 | 5.726 | 1.1 | 0.35 | 2.91 | — | 4.0 | — | — |
| 14 | 2.9 | 6.605 | — | — | — | — | 2.6 | — | — |
| 15 | 3.1 | 7.548 | — | — | — | — | 4.6 | — | — |
| 16 | — | — | — | — | — | — | — | — | — |
| 17 | — | — | — | — | — | — | — | — | — |
| 18 | — | — | — | — | — | — | — | — | — |
| 19 | — | — | — | — | — | — | — | — | — |
| 20 | — | — | — | — | — | — | — | — | — |
| 21 | — | — | — | — | — | — | — | — | — |
| 22 | — | — | — | — | — | — | — | — | — |
| 23 | — | — | — | — | — | — | — | — | — |
| 24 | — | — | — | — | — | — | — | — | — |
| 25 | — | — | — | — | — | — | — | — | — |
| Sum | | | 1000.5 | 974.71 | 999.7 | 996.1 | 1000.2 | 991.1 | |

TABLE VIII (*Continued*)

| Class no. | x = class size in $\mu^3$ | Corresp. diam. in $\mu$ | Medium Speed A | Medium Speed B | Medium Speed C | |
|---|---|---|---|---|---|---|
| | | | $Y.10^{-6}$ = curve B | $Y.10^{-6}$ = curve B | $Y.10^{-6}$ = curve B | $Y.10^{-6}$ = curve B' |
| 1 | .11 | 0.353 | 78.0 | 20.0 | 20.0 | — |
| 2 | .30 | 0.618 | 107.0 | 82.0 | 77.4 | — |
| 3 | .50 | 0.798 | 105.5 | 93.6 | 191.8 | — |
| 4 | .70 | 0.944 | 94.5 | 90.0 | 202.3 | — |
| 5 | .90 | 1.069 | 83.5 | 70.2 | 208.1 | — |
| 6 | 1.1 | 1.183 | 73.0 | 46.7 | 200.2 | — |
| 7 | 1.3 | 1.286 | 63.0 | 30.1 | 160.0 | 0.9 |
| 8 | 1.5 | 1.382 | 55.8 | 38.2 | 107.5 | 4.7 |
| 9 | 1.7 | 1.471 | 48.3 | 10.0 | 75.8 | 13.1 |
| 10 | 1.9 | 1.556 | 42.0 | 5.7 | 51.3 | 27.5 |
| 11 | 2.1 | 1.635 | 36.5 | 3.0 | 32.8 | 51.0 |
| 12 | 2.3 | 1.711 | 31.5 | 1.4 | 19.7 | 86.0 |
| 13 | 2.5 | 1.784 | 27.5 | 1.0 | 11.0 | 112.5 |
| 14 | 2.7 | 1.855 | 24.0 | 0.6 | 6.3 | 122.3 |
| 15 | 2.9 | 1.921 | 21.3 | 0.09 | 5.0 | 124.1 |
| 16 | 3.1 | 2.002 | 18.5 | — | — | 118.4 |
| 17 | 3.3 | 2.050 | 12.0 | — | — | 103.4 |
| 18 | 3.5 | 2.111 | 4.2 | — | — | 76.5 |
| 19 | 3.7 | 2.171 | — | — | — | 50.8 |
| 20 | 3.9 | 2.230 | — | — | — | 30.8 |
| 21 | 4.1 | 2.285 | — | — | — | 17.6 |
| 22 | 4.3 | 2.340 | — | — | — | 9.4 |
| 23 | 4.5 | 2.394 | — | — | — | 5.0 |
| 24 | 4.7 | 2.446 | — | — | — | 2.4 |
| 25 | 4.909 | 2.5 | — | — | — | 1.5 |
| Sum | | | 926.1 | 492.6 | 2327.1 | |

Higson,[1] that process plates are distinguished by a uniform grain size. So far as our own data go, this statement appears misleading, and requires considerable qualification.

The size-frequency distribution is more or less symmetrical with respect to the average size grain, nevertheless, quite a large number of grains lie at an appreciable distance on both sides of this average. True the range is not great when compared with the High Speed A or B and if we choose our unit of class size large enough, we can swallow up all the grains in one class, and apparently they have perfect uniformity, but on closer examination we find that the grains still have a dis-

[1] R. E. Slade and G. I. Higson: Phot. Jour., 59, 260 (1919); Proc. Roy. Soc., 98A, 154 (1921).

tribution of sizes within that class. Our class units must, therefore, be chosen small enough to show the true form of the distribution of particles differing an appreciable amount in size. In the case of the Process B for example, the grains in the largest class (as we have classified them) have in the neighborhood of *twenty five times* the area of those in the smallest, and approximately 15% of all the grains are more than twice as large as the average grain, and 20% of all the

TABLE IX

| | | | High speed B | | | | |
|---|---|---|---|---|---|---|---|
| Class no. | z = class size in $\mu$ | Corresp. area in $\mu^2$ | y(obs.) = no. grains per 1000 | y(calc.) = no. grains per 1000 curve A | y'(calc.) = no. grains per 1000 curve A' | x = class size in $\mu^2$ | Corresp. diam. in $\mu$ |
| 1 | 0.3 | 0.071 | 68.0 | 111.6 | — | .11 | 0.353 |
| 2 | 0.5 | 0.196 | 174.0 | 166.2 | — | .30 | 0.618 |
| 3 | 0.7 | 0.385 | 181.0 | 198.0 | — | .50 | 0.798 |
| 4 | 0.9 | 0.636 | 189.0 | 189.0 | — | .70 | 0.944 |
| 5 | 1.1 | 0.950 | 146.0 | 144.4 | — | .90 | 1.069 |
| 6 | 1.3 | 1.327 | 80.0 | 88.4 | — | 1.1 | 1.183 |
| 7 | 1.5 | 1.767 | 43.0 | 43.0 | 4.4 | 1.3 | 1.286 |
| 8 | 1.7 | 2.270 | 31.0 | 17.0 | 14.0 | 1.5 | 1.382 |
| 9 | 1.9 | 2.835 | 25.0 | 5.4 | 26.3 | 1.7 | 1.471 |
| 10 | 2.1 | 3.464 | 31.0 | 1.3 | 29.7 | 1.9 | 1.556 |
| 11 | 2.3 | 4.155 | 11.0 | 0.07 | 20.0 | 2.1 | 1.635 |
| 12 | 2.5 | 4.909 | 8.0 | 0.00 | 8.0 | 2.3 | 1.711 |
| 13 | 2.7 | 5.726 | 3.0 | — | 1.9 | 2.5 | 1.784 |
| 14 | 2.9 | 6.605 | 2.0 | — | 0.3 | 2.7 | 1.855 |
| 15 | 3.1 | 7.548 | 3.0 | — | 0.00 | 2.9 | 1.921 |
| 16 | 3.3 | 8.553 | 2.0 | — | — | 3.1 | 2.002 |
| 17 | 3.5 | 9.621 | 1.0 | — | — | 3.3 | 2.050 |
| 18 | 3.7 | 10.75 | 0.0 | — | — | 3.5 | 2.111 |
| 19 | 3.9 | 11.95 | 1.0 | — | — | 3.7 | 2.171 |
| 20 | — | — | — | — | — | 3.9 | 2.230 |
| 21 | — | — | — | — | — | 4.1 | 2.285 |
| 22 | — | — | — | — | — | 4.3 | 2.340 |
| 23 | — | — | — | — | — | 4.5 | 2.394 |
| 24 | — | — | — | — | — | 4.7 | 2.446 |
| 25 | — | — | — | — | — | 4.9 | 2.498 |
| 26 | — | — | — | — | — | 5.1 | 2.548 |
| 27 | — | — | — | — | — | 5.3 | 2.598 |
| 28 | — | — | — | — | — | 5.5 | 2.646 |
| 29 | — | — | — | — | — | 5.7 | 2.694 |
| 30 | — | — | — | — | — | 5.9 | 2.740 |
| 38 | — | — | — | — | — | 7.5 | 3.10 |
| Sum | | | 999.0 | 1068.6 | | | |

TABLE IX (*Continued*)

| Class no. | High speed A | | | | | | High speed B | |
|---|---|---|---|---|---|---|---|---|
| | y (obs.) = no. grains per 1000 | y (calc.) = curve A | y′ (calc.) = curve A′ | y + y′ = A + A′ | Y.10⁻⁶ = curve B | Y.10⁻⁶ = curve B′ | Y.10⁻⁶ = curve B | Y′.10⁻⁶ = curve B′ |
| 1 | 326.0 | 99.2 | 214.8 | 314.0 | 7.16 | 15.5 | 6.0 | — |
| 2 | 169.5 | 82.8 | 113.4 | 196.2 | 16.3 | 22.3 | 27.5 | — |
| 3 | 134.4 | 68.4 | 57.9 | 126.3 | 22.5 | 19.0 | 49.1 | — |
| 4 | 91.2 | 56.5 | 29.6 | 86.1 | 26.0 | 13.57 | 63.3 | — |
| 5 | 57.1 | 46.7 | 15.1 | 61.8 | 27.6 | 8.31 | 68.4 | — |
| 6 | 38.9 | 38.6 | 7.7 | 46.3 | 27.9 | 5.56 | 65.8 | — |
| 7 | 35.3 | 31.9 | 3.9 | 35.8 | 27.2 | 3.35 | 59.2 | — |
| 8 | 27.8 | 26.4 | 2.0 | 28.4 | 25.9 | 1.99 | 50.4 | — |
| 9 | 21.1 | 21.8 | 1.03 | 22.8 | 24.3 | 1.15 | 41.2 | 3.0 |
| 10 | 19.4 | 18.0 | 0.42 | 18.4 | 22.6 | 0.52 | 32.7 | 5.0 |
| 11 | 14.3 | 14.9 | 0.27 | 15.2 | 20.5 | 0.37 | 24.9 | 9.0 |
| 12 | 12.1 | 12.9 | 0.14 | 13.0 | 19.4 | 0.21 | 18.1 | 16.4 |
| 13 | 10.5 | 10.2 | 0.07 | 10.3 | 16.7 | 0.12 | 12.7 | 25.0 |
| 14 | 7.46 | 8.4 | — | 8.4 | 14.9 | — | 9.1 | 33.5 |
| 15 | 6.48 | 6.9 | — | 6.9 | 13.2 | — | 6.2 | 39.5 |
| 16 | 3.96 | 5.7 | — | 5.7 | 11.7 | — | 4.5 | 45.8 |
| 17 | 4.62 | 4.7 | — | 4.7 | 10.26 | — | 2.8 | 50.0 |
| 18 | 4.13 | 3.9 | — | 3.9 | 9.01 | — | 2.0 | 51.0 |
| 19 | 4.22 | 3.2 | — | 3.2 | 7.87 | — | 1.6 | 50.0 |
| 20 | 2.46 | 2.7 | — | 2.7 | 6.86 | — | 1.0 | 47.0 |
| 21 | 2.26 | 2.2 | — | 2.2 | 5.95 | — | .4 | 42.6 |
| 22 | 1.77 | 1.8 | — | 1.8 | 5.05 | — | 0.00 | 37.3 |
| 23 | 1.77 | 1.5 | — | 1.5 | 4.46 | — | — | 31.2 |
| 24 | 0.63 | 1.25 | — | 1.25 | 3.86 | — | — | 25.5 |
| 25 | 0.84 | 1.03 | — | 1.03 | 3.31 | — | — | 20.0 |
| 26 | 0.16 | 0.85 | — | 0.85 | 2.84 | — | — | 15.2 |
| 27 | 0.48 | 0.70 | — | 0.70 | 2.43 | — | — | 11.0 |
| 28 | 0.32 | 0.58 | — | 0.58 | 2.09 | — | — | 8.0 |
| 29 | 0.48 | 0.48 | — | 0.48 | 1.80 | — | — | 5.5 |
| 30 | 0.53 | 0.40 | — | 0.40 | 1.55 | — | — | 4.0 |
| 38 | 0.23 | 0.04 | — | 0.05 | 0.15 | — | — | 0.00 |
| Sum | 999 | 1023.3 | | 1023.3 | 489.7 | | 1123.0 | |

grains are less than half as large as the average. In using the term larger, we refer, of course, to the projective area.

As to the relative effect of the large and small grains, a small number of grains larger than the average would, as Slade and Higson state, produce a greater effect on density, than an *equal number* of grains smaller than the average. Where the effective source of the areas of large grains is equal to that of the small grains, before development, we have preliminary evidence to show that the opacity of the film does

not become greater for the larger grains. As a rule in the process emulsions which we have measured, there are a larger number, and a greater range of grains on the large side of the maximum frequency than on the small side.

TABLE X

Experimental Emulsion No. 1

| Class no. uniform diam. | z = diam. in $\mu$ | Corresp. area in $\mu^2$ | y(obs.) | y(calc.) | Class no. uniform area | x = area in $\mu^2$ | Corresp. diam. in $\mu$ | $\frac{1}{x}$ in $\frac{1}{\mu^2}$ | $Y.10^{-7}$ = area/sq. cm. orig. plate | $\frac{Y}{M}.10^{-6}$ area/sq. cm. 1 layer plate |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.30 | 0.071 | 572.0 | 572.0 | 1 | 0.11 | 0.353 | 9.09 | 24.0 | 8.44 |
| | 0.407 | 0.13 | — | 344.2 | – | 0.13 | 0.407 | 7.69 | 35.5 | 8.96 |
| | 0.437 | 0.15 | — | 298.6 | – | 0.15 | 0.437 | 6.67 | 25.5 | 8.96 |
| 2 | 0.50 | 0.196 | 307.6 | 221.4 | – | 0.20 | 0.505 | 5.00 | 24.6 | 8.65 |
| | 0.505 | 0.20 | — | 216.2 | – | 0.25 | 0.564 | 4.00 | 23.2 | 8.16 |
| | 0.564 | 0.25 | — | 163.4 | 2 | 0.30 | 0.618 | 3.33 | 21.6 | 7.59 |
| 3 | 0.70 | 0.385 | 85.7 | 85.7 | 3 | 0.50 | 0.798 | 2.00 | 16.4 | 5.53 |
| 4 | 0.90 | 0.636 | 27.6 | 33.2 | 4 | 0.70 | 0.944 | 1.43 | 10.2 | 3.59 |
| 5 | 1.10 | 0.950 | 7.6 | 12.8 | 5 | 0.90 | 1.069 | 1.11 | 7.1 | 2.50 |
| 6 | 1.30 | 1.327 | 0.9 | 4.9 | 6 | 1.10 | 1.183 | 0.91 | 5.2 | 1.83 |
| | — | — | — | — | 7 | 1.30 | 1.286 | 0.77 | 4.0 | 1.41 |
| Sum* | | | 1001.4 | 930.0 | | | | | 88.5 | 30.89 |

* The frequencies or areas opposite class-numbers only are added. M in the last column signifies the dilution factor.

In the examples of the process emulsions shown by Slade and Higson in both the papers cited, the fairly wide range of sizes is actually quite as apparent as in the examples which we have measured.

Another point which we wish to make clear, concerning those emulsions in which the grains are very minute, or have what appear to be a circular or spherical form, is that an X-ray analysis made for us by Mr. R. B. Wilsey of this Laboratory showed that these apparently non-crystalline grains have the usual cubical lattice structure. Even silver bromide precipitated in colloidal form has been found in this way to have a definite cubical lattice structure

It is worth noting here that previous estimates of the thickness of the grains of the silver halide in photographic

TABLE XI
Experimental Emulsion No. 2

| Class no. (diams.) | z = diam. in $\mu$ | Corresp. area in $\mu^2$ | y (obs.) | y (calc.) | Class no. (areas) | x = area in $\mu^2$ | Corresp. diam. in $\mu$ | $\frac{1}{x}$ in $\frac{1}{\mu^2}$ | $Y.10^{-4}$ = area/sq. cm. orig. plate | $\frac{Y}{M}.10^{-4}$ = area/sq. cm. 1 layer plate |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.3 | 0.071 | 186.7 | 186.7 | 1 | 0.11 | 0.353 | 9.09 | 32.9 | 8.2 |
| 2 | 0.5 | 0.196 | 216.2 | 231.2 | — | 0.13 | 0.407 | 7.69 | 46.6 | 11.7 |
| 3 | 0.7 | 0.385 | 224.2 | 224.2 | — | 0.15 | 0.437 | 6.67 | 55.2 | 13.8 |
| 4 | 0.9 | 0.636 | 188.8 | 170.3 | — | 0.20 | 0.505 | 5.00 | 77.0 | 19.3 |
| 5 | 1.1 | 0.950 | 104.2 | 101.2 | — | 0.25 | 0.564 | 4.00 | 97.6 | 29.1 |
| 6 | 1.3 | 1.327 | 47.1 | 47.1 | 2 | 0.30 | 0.618 | 3.33 | 116.5 | 29.1 |
| 7 | 1.5 | 1.767 | 20.8 | 17.2 | — | 0.35 | 0.668 | 2.86 | 132.2 | 33.1 |
| 8 | 1.7 | 2.270 | 8.3 | 4.9 | 3 | 0.50 | 0.798 | 2.00 | 167.7 | 41.9 |
| 9 | 1.9 | 2.835 | 2.6 | 1.1 | — | 0.55 | 0.837 | 1.818 | 174.1 | 43.5 |
| | — | — | — | — | — | 0.60 | 0.874 | 1.667 | 178.2 | 44.3 |
| | — | — | — | — | — | 0.65 | 0.910 | 1.538 | 180.1 | 45.0 |
| | — | — | — | — | 4 | 0.70 | 0.944 | 1.428 | 180.2 | 45.1 |
| | — | — | — | — | — | 0.80 | 1.010 | 1.250 | 175.3 | 43.3 |
| | — | — | — | — | 5 | 0.90 | 1.069 | 1.111 | 166.1 | 41.5 |
| | — | — | — | — | 6 | 1.10 | 1.183 | 0.909 | 141.5 | 35.4 |
| | — | — | — | — | 7 | 1.30 | 1.286 | 0.769 | 108.5 | 27.1 |
| | — | — | — | — | 8 | 1.50 | 1.382 | 0.667 | 79.4 | 19.9 |
| | — | — | — | — | 9 | 1.70 | 1.471 | 0.588 | 56.9 | 14.2 |
| | — | — | — | — | 10 | 1.90 | 1.556 | 0.526 | 38.1 | 9.5 |
| | — | — | — | — | 11 | 2.10 | 1.635 | 0.476 | 25.2 | 6.3 |
| | — | — | — | — | 12 | 2.30 | 1.711 | 0.435 | 17.3 | 4.3 |
| | — | — | — | — | 13 | 2.50 | 1.784 | 0.400 | 11.5 | 2.6 |
| | — | — | — | — | 14 | 2.70 | 1.855 | 0.370 | 7.0 | 1.8 |
| | — | — | — | — | — | 2.835 | 1.90 | 0.353 | 5.2 | 1.3 |
| Sum* | | | 998.9 | 983.9 | | | | | 1149 | 287 |

* The frequencies or areas opposite class-numbers only are added. M in the last column signifies the dilution factor.

TABLE XII
Grain Characteristics

| Type of film or plate | No. grains per sq. cm. = N | Gms Ag-halide per sq. cm. of film or plate | % conc. Ag-halide in emul. on 1 $cm^2$ of plate or film | Av. Size grain | |
|---|---|---|---|---|---|
| | | | | Equiv. diam. in $\mu$ | Projective area in $\mu^2$ |
| Process A (lantern slide) | $4.30 \times 10^9$ | 0.000840 | 31.4 | 0.383 | 0.115 |
| Process B | $0.668 \times 10^9$ | 0.001366 | 33.6 | 0.844 | 0.560 |
| Process C* | $3.08 \times 10^9$ | 0.001422 | 35.4 | 0.874 | 0.60 |
| Positive emulsion | $1.853 \times 10^9$ | 0.000870 | 36.8 | 0.704 | 0.389 |
| Med. Speed A | $2.11 \times 10^9$ | 0.001213 | 33.4 | 0.757 | 0.450 |
| Med. Speed B | $0.94 \times 10^9$ | 0.001300 | 32.5 | 0.799 | 0.502 |
| Med. Speed C | $1.50 \times 10^9$ | 0.001677 | 33.9 | 1.41 | 1.567 |
| High Speed A | $0.656 \times 10^9$ | 0.001350 | 37.1 | 0.966 | 0.732 |
| High Speed B | $0.478 \times 10^9$ | 0.001470 | 33.7 | 1.67 | 2.198 |
| Experimental emulsion No. 1 | $5.690 \times 10^9$ | ——— | — | 0.461 | 0.167 |
| Experimental emulsion No. 2 | $1.660 \times 10^9$ | ——— | — | 0.950 | 0.710 |

TABLE XII (*Continued*)
Grain Characteristics

| Type of film or plate | Average size grain: Equiv. vol. in $\mu^3$ | Wt. in gms $\times 10^{11}$ | Thickness in $\mu$: for spheres | Thickness in $\mu$: for plates | Ratio thick. diam. | Max. grain size obs. in $\mu^3 = M$ | $\gamma_0$ | K | $\alpha$ |
|---|---|---|---|---|---|---|---|---|---|
| Process A (lantern slide) | 0.0301 | 0.195 | 0.386 | 0.262 | 1:1 | 1.2 | 4000.0 | 5.81 | 0 |
| Process B | 0.317 | 2.05 | 0.846 | 0.566 | 1:1 | 1.6 | 340.4 | 8.95 | 0.555 |
| Process C* | 0.0711 | 0.46 | 0.710 | 0.767 | 1:1.2 | 3.2 | 286.7 | 4.72 | 0.630 |
| Positive emulsion | 0.0726 | 0.47 | 0.518 | 0.187 | 1:3.8 | 2.2 | 573.5 | 2.52 | — |
| Med. Speed A | 0.0889 | 0.575 | 0.554 | 0.198 | 1:3.8 | 6.2 | 1068.0 | 2.98 | — |
| Med. Speed B | 0.213 | 1.38 | 0.740 | 0.424 | 1:1.9 | 6.2 | 276.9 | 4.27 | 0.533 |
| Med. Speed C | 0.173 | 1.12 | 0.691 | 0.110 | 1:12.8 | 8.4 | 221.6<br>32.2 | 4.27<br>12.20 | 0.790<br>1.860 |
| High Speed A | 0.318 | 2.06 | 0.846 | 0.435 | 1:2.2 | 8.6 | 110.2<br>310.9 | 0.953<br>3.36 | —<br>— |
| High Speed B | 0.476 | 3.08 | 0.976 | 0.216 | 1:7.7 | 12.6 | 200.0<br>30.3 | 2.78<br>6.45 | 0.758<br>2.046 |
| Exper. emuls. No.1 | — | — | — | — | — | 1.4 | 2375.3 | 4.75 | — |
| Exper. emuls. No. 2 | — | — | — | — | — | 2.8 | 235.2 | 3.06 | 0.575 |

* This is a panchromchromatic emulsion.

emulsions have been in many cases too low. If, from the weight of silver halide and the number of grains per sq. cm. of plate, we determine the equivalent volume of the average particle, assuming the density to be that of pure silver bromide (the error in doing this is not greater than 3 or 4 percent even with fairly large amounts of iodide present), it is then easy to get the approximate thickness of the average grain (1) where the grains are spherical by determining their diameter

$$d = \sqrt[3]{\frac{6v}{\pi}}$$

and (2) where they are flat by dividing the average volume by the average projective area.

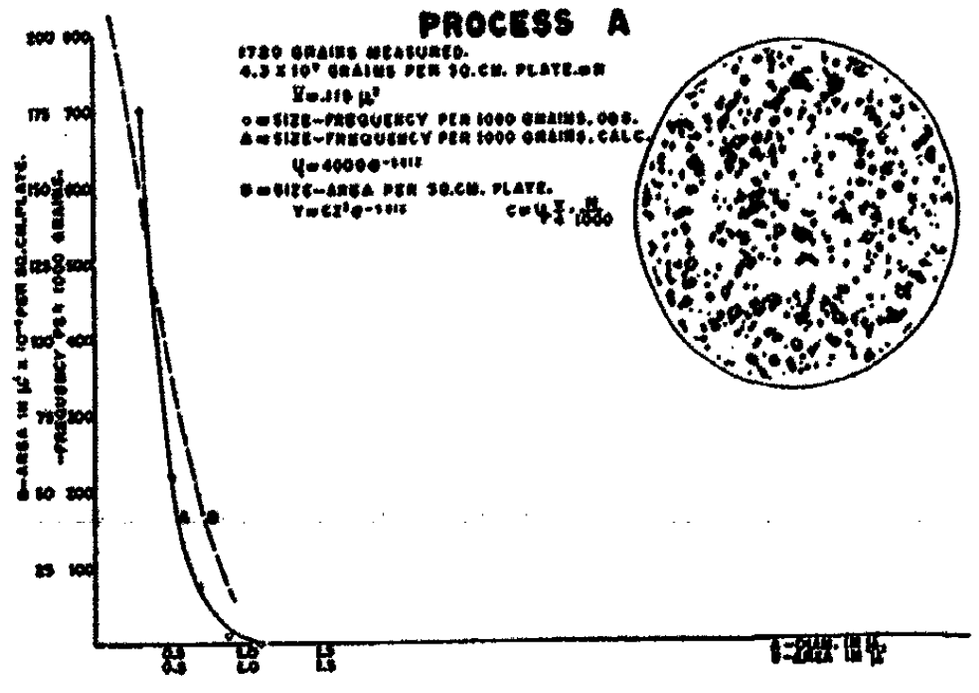

PROCESS A
1730 GRAINS MEASURED.
Ψ=.519 μ²
o=SIZE-FREQUENCY PER 1000 GRAINS. OBS.
Δ=SIZE-FREQUENCY PER 1000 GRAINS. CALC.
B=SIZE-AREA PER SQ.CM. PLATE.

Fig. 1

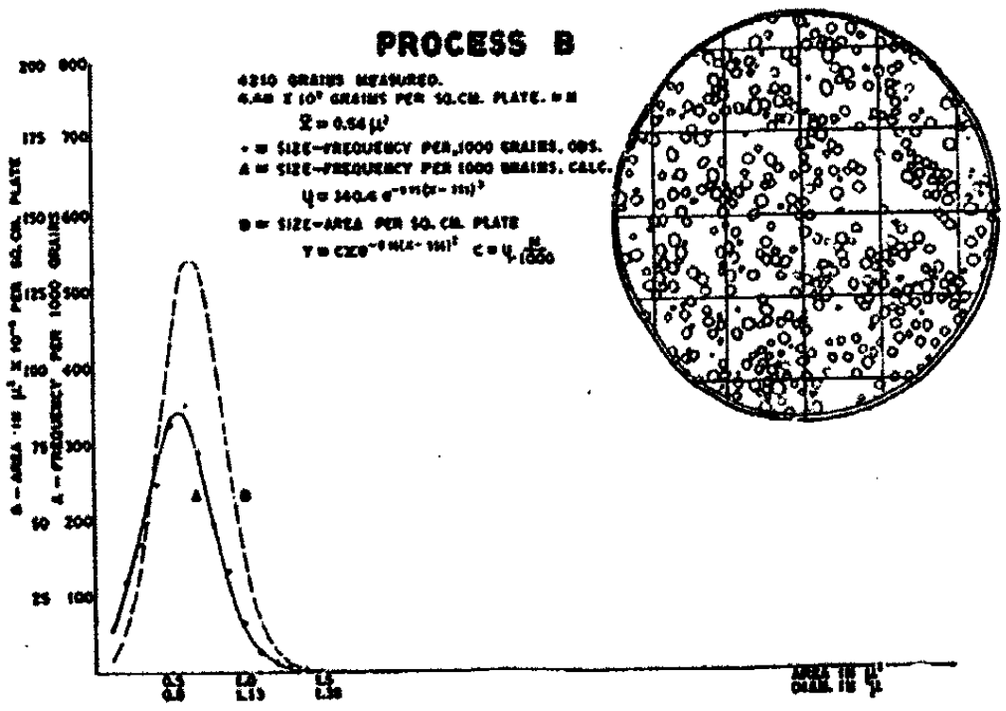

PROCESS B
4210 GRAINS MEASURED.
Ψ = 0.54 μ²
• = SIZE-FREQUENCY PER 1000 GRAINS. OBS.
Δ = SIZE-FREQUENCY PER 1000 GRAINS. CALC.
B = SIZE-AREA PER SQ. CM. PLATE

Fig. 2

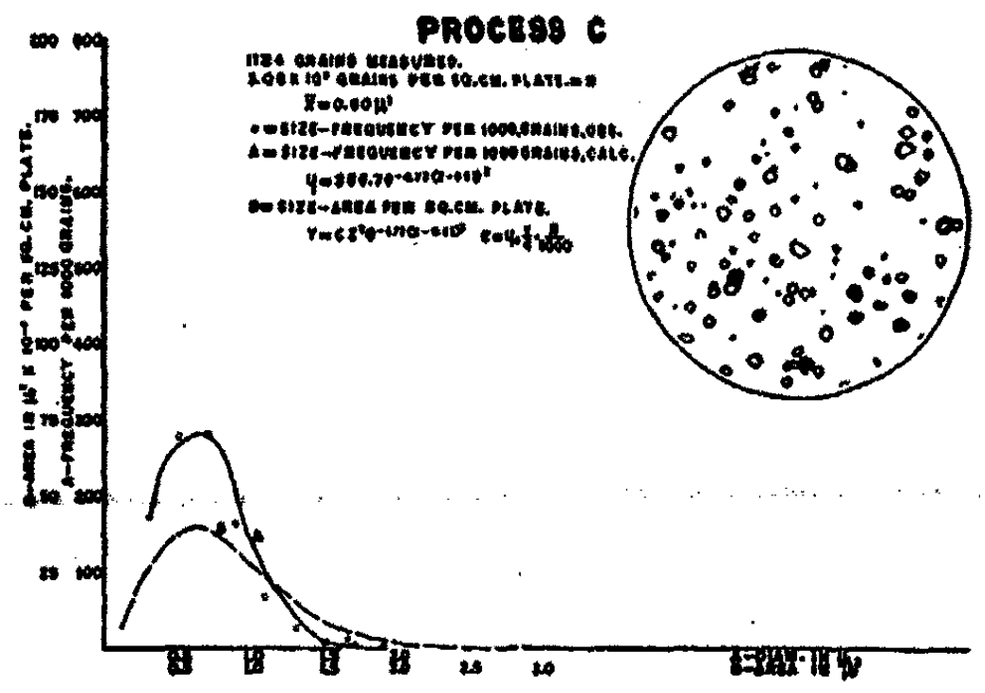



Fig. 3

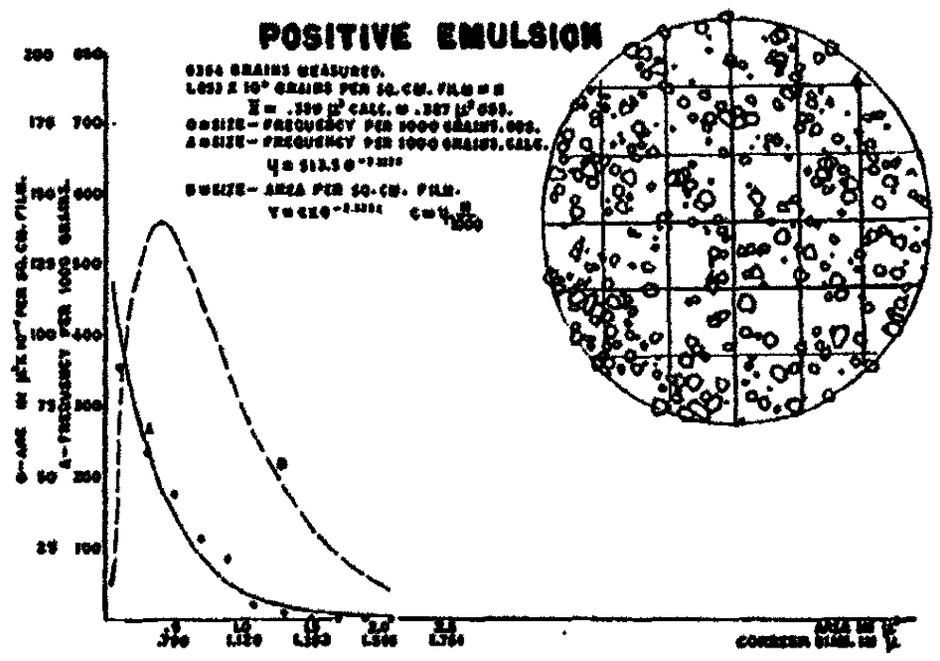



Fig. 4

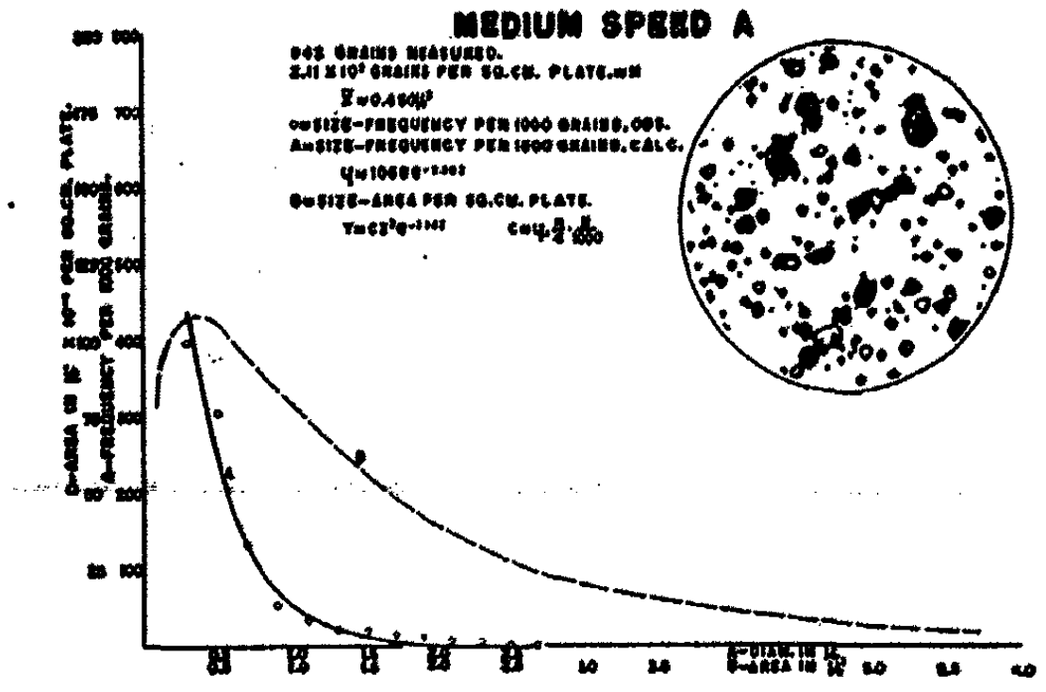



Fig. 5

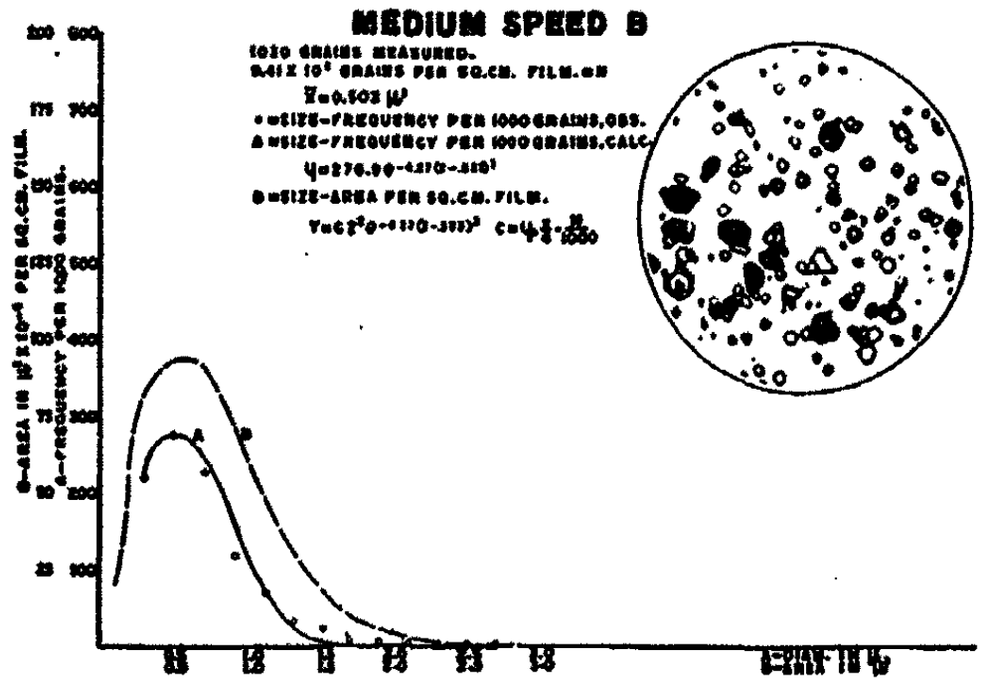



Fig. 6

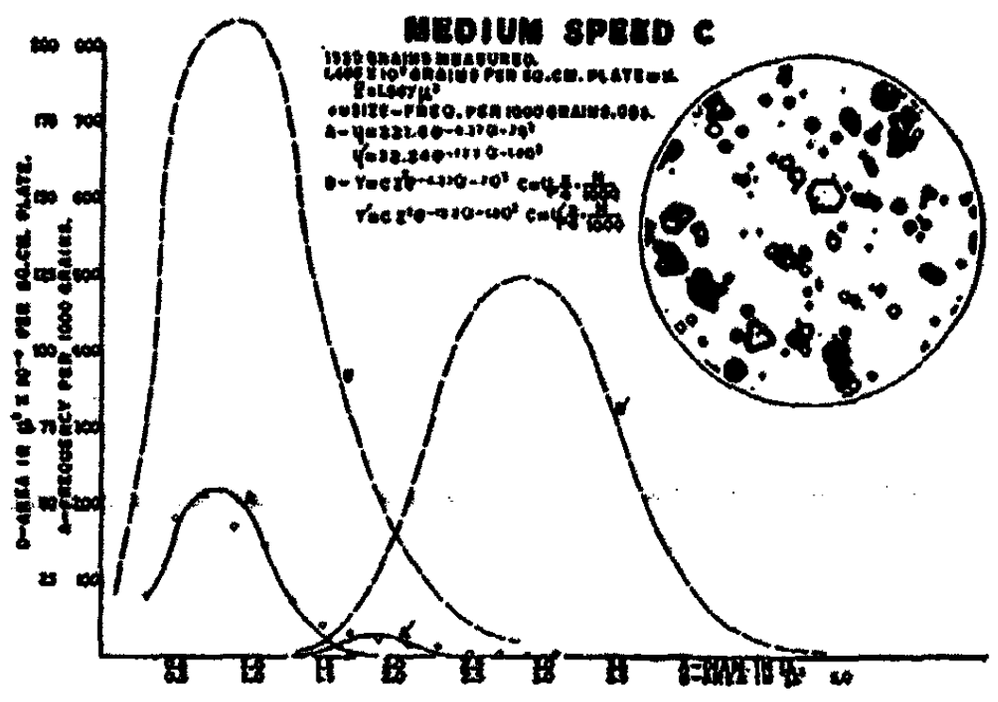



Fig. 7

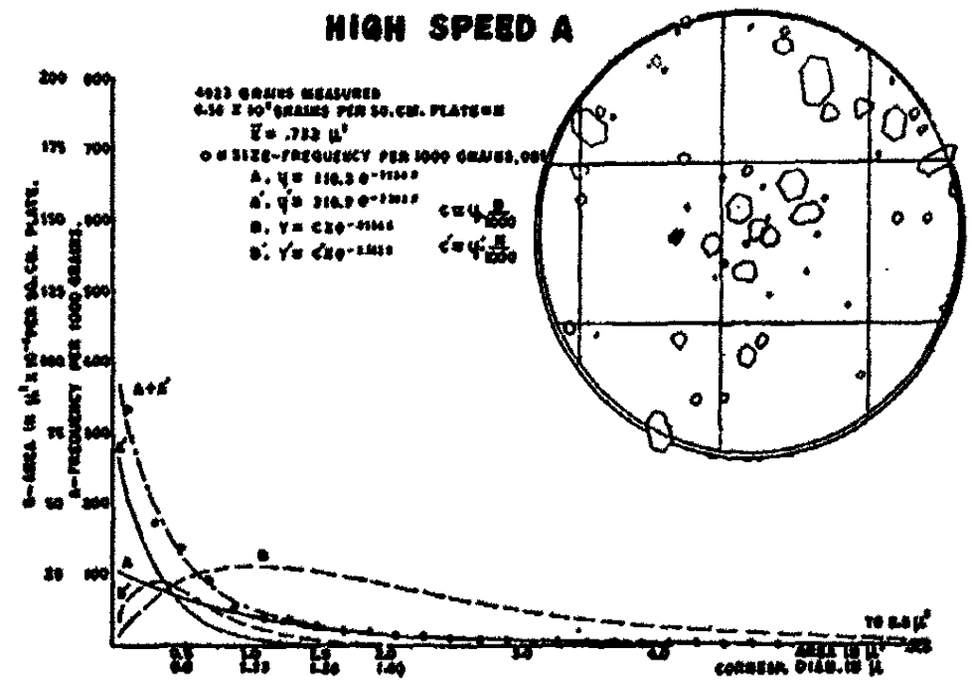



Fig. 8

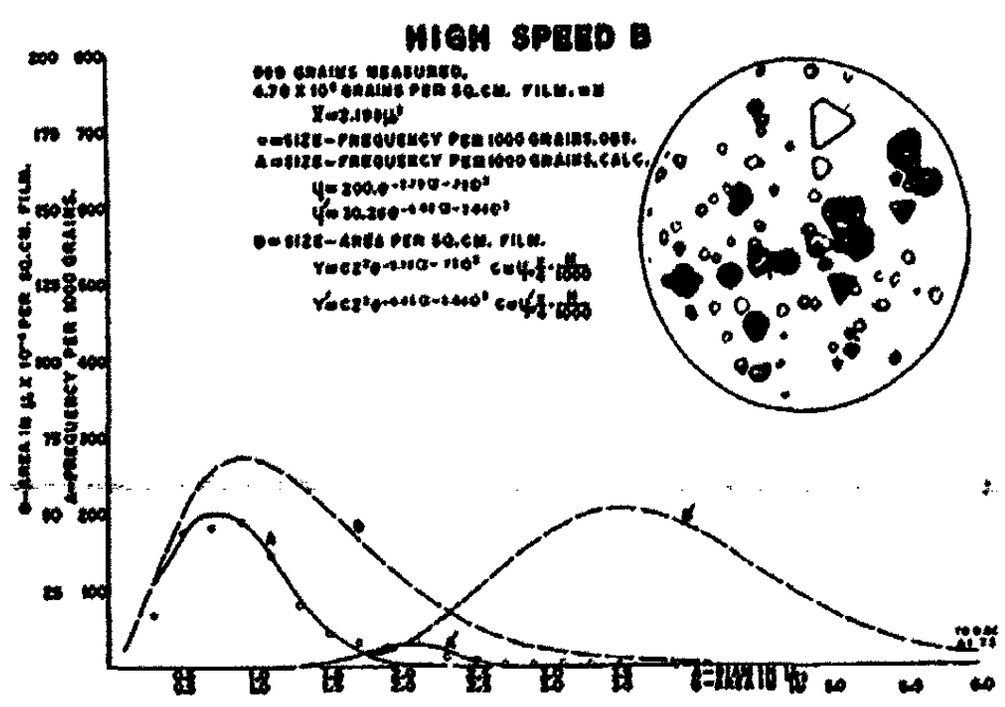

HIGH SPEED B
999 GRAINS MEASURED.
4.70 X 10⁹ GRAINS PER SQ.CM. FILM.=N
X=2.199μ²
•=SIZE-FREQUENCY PER 1000 GRAINS.OBS.
A=SIZE-FREQUENCY PER 1000 GRAINS.CALC.
B=SIZE-AREA PER SQ.CM. FILM.
B-AREA IN μ² X 10⁻⁹ PER SQ.CM. FILM.
A-FREQUENCY PER 1000 GRAINS.

Fig. 9

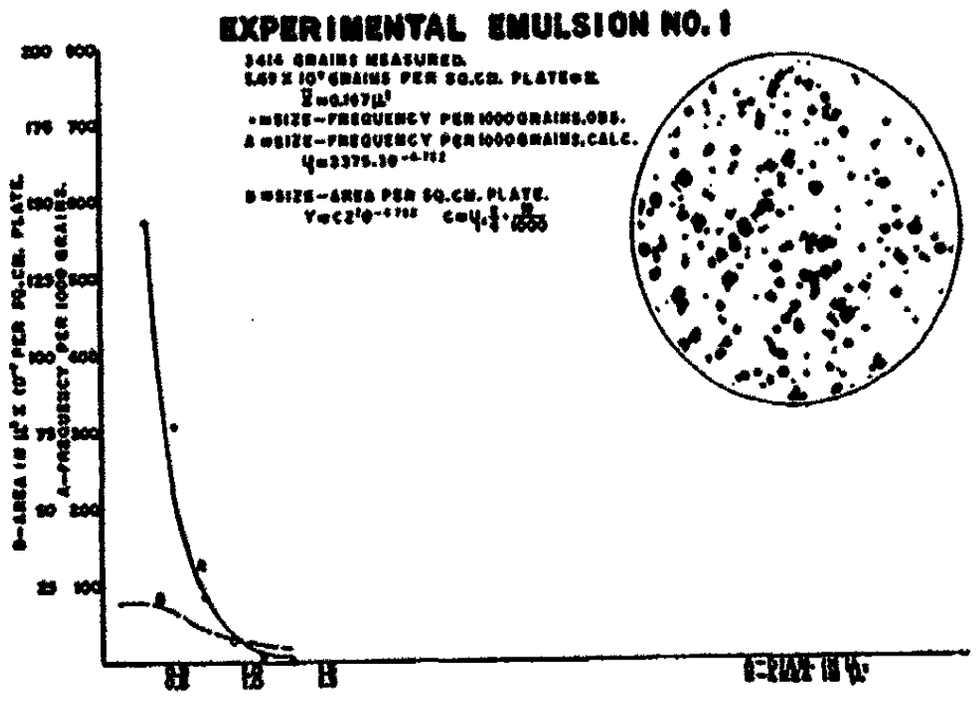

EXPERIMENTAL EMULSION NO. 1
3414 GRAINS MEASURED.
•=SIZE-FREQUENCY PER 1000 GRAINS.OBS.
A=SIZE-FREQUENCY PER 1000 GRAINS.CALC.
B=SIZE-AREA PER SQ.CM. PLATE.
B-AREA IN μ² X 10⁻⁹ PER SQ.CM. PLATE.
A-FREQUENCY PER 1000 GRAINS.

Fig. 10

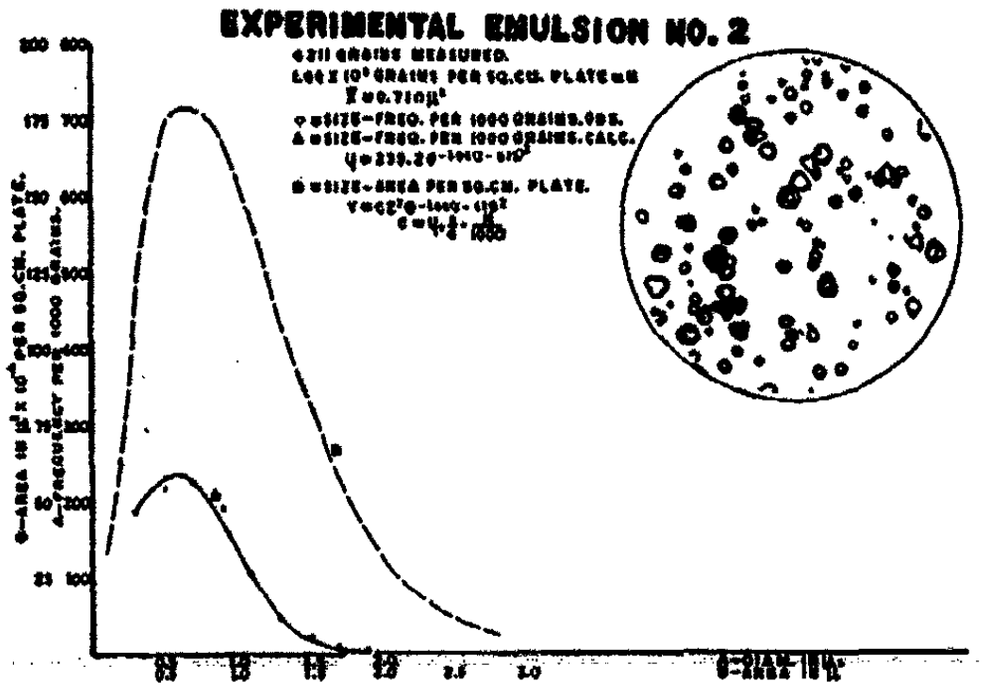



Fig. 11

In two of the process emulsions studied, which have almost entirely spherical grains, calculated diameter corresponds very closely to the average diameter determined statistically by the microscopic method. The third process emulsion (Process C), which is seen by examination of the photomicrographs to have a number of angular grains (usually indicating flatness) has a calculated equivalent diameter somewhat smaller than the average projective diameter. For all the medium and high speed emulsions the calculations were made assuming the grains to be flat. The ratios of thickness to projective diameter are given in Table XII.

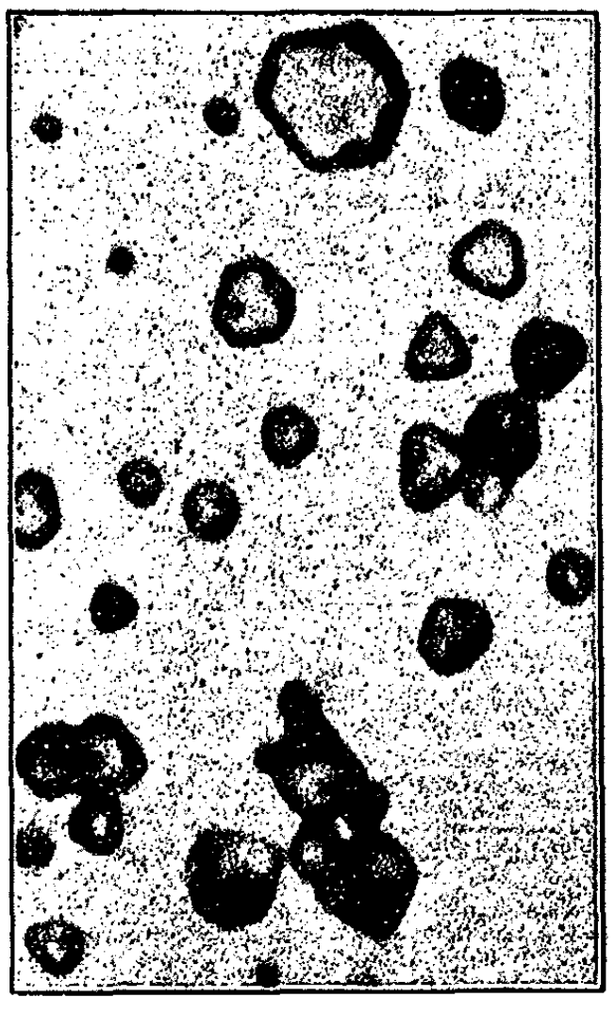


Fig. 11*a*.

## III. The Sensitometric Characteristics

The characteristic curves for the emulsions examined were determined in two ways:

(*a*) By an intensity scale, using a Goldberg wedge and Higson's modification of the Luther crossed-wedge method.

(*b*) By a time scale, using a Jones non-intermittent sensitometer, measuring the densities and plotting the curves.

In each case curves were obtained for different times of development, to ensure absence (or correction) for regression effects.

1. *Determination of the Sensitometric Characteristics of Single-Layer Plate.*—Strips 40.8×127 mm, coated with one layer of grains as above described were cut in half lengthwise, and the half strips were exposed in a non-intermittent sensitometer, each step having double the time of exposure of the one preceding it. There are nine steps in all,[1] and two or more strips are necessary to cover the entire range of exposure; and, owing to the difficulty of getting uniform coating, and exactly equal concentrations on each strip, several series of strips were used. In the present paper, however, we do not give such an extensive series of measurements since the sensitometric work on single-layer plates is to be the subject of another paper. In this later paper will be considered also the effects of clumping of the grains, of the concentration of the grains, and of the gelatin, etc. Some preliminary work of this character has just been presented in connection with a paper by Dr. L. Silberstein[2] on his theory of the action of light on the photographic plate.[3]

[1] A special plate containing about 24 neutral gray squares of consecutively increasing transparency is being constructed, and when prepared, will be used so as to give the whole sensitometric curve from under to over-exposure at one exposure. It will, of course, vary intensity instead of time. This arrangement has the advantage over a wedge in one respect in that it makes possible the studying of each step microscopically with much greater ease and rapidity than in the latter.

[2] L. Silberstein: Phil. Mag. **44**, 257, 956 (1922); cf. also A. P. H. Trivelli and L. Rigliter, Ibid., 252 (1922).

[3] The "clumping" effect is of particular interest in connection with the recent work of T. Svedberg, (Phot. Jour., **44**, 183 (1922)) in which he concluded

The ordinary method of measuring density when applied to single layer plates is very inaccurate. All measurements of density on such thin emulsions will be made shortly by means of a densitometer using a thalofide cell which is being constructed in this Laboratory. The data given in this paper, however, were obtained by the ordinary method. The approximate sensitometric curves are shown in Fig. 12 for two experimental emulsions.

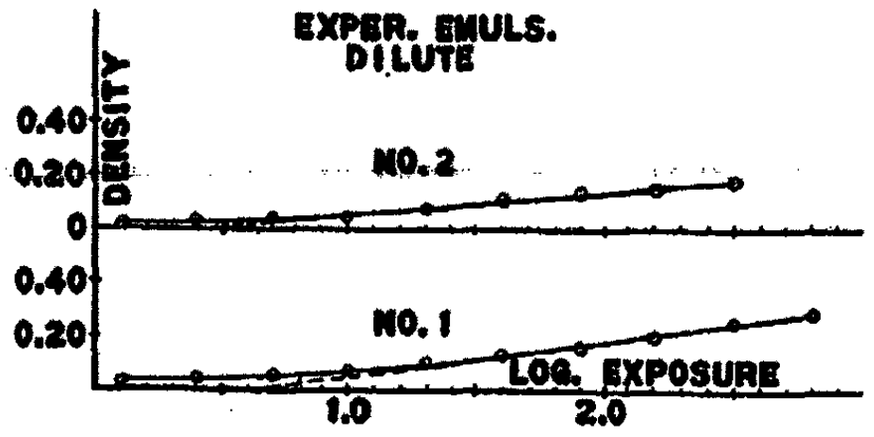



Fig. 12

2. *Determination of the Sensitometric Characteristics for Ordinary Plates by the Wedge Method.*—This method is by no means free from error although it is believed that it is possible to make it as exact as any other method. Its principal advantages lie in the fact that it gives a complete, continuous curve of the emulsion in question, and does not depend upon visual measurements of density. Its principal disadvantages are that it is difficult to obtain a truly permanent, neutral transparent wedge, that the printing

---

that when two grains lie close together there is no "spreading" effect in development it being possible to develop one without the adjacent one or more being developed. It has been found in this Laboratory that this is not necessarily correct. In the type of emulsion which he used, i. e., an emulsion with almost entirely small spherical grains with a narrow range of sizes, there is only a small amount of "clumping" and "spreading" but as the emulsions are studied which have wider and wider range of sizes and more diversified shapes of grains, the "clumping" and "spreading" becomes greater and greater in amount, until in the highest speed emulsions the proportion of these effects is quite high. The "clumping" likewise depends upon other conditions such as concentration of gelatine and of the silver halide grains, method of preparations, etc.

materials are not always perfectly uniform, which would of course give a false curve, and that the method is considerably slower than the H. and D. method.

Briefly, the method as we have adapted it is as follows:

A series of 6 plates or films containing the emulsion to be examined were exposed behind a 12.7 $cm^2$ neutral wedge[1] for 20 seconds at 0.5 m from a light source equivalent to 500 C. M. (corrected for reflections) at that distance. These were developed at 20° in 1 : 1 pyro of the following formula:

Negative Developer

| | | | | | |
|---|---|---|---|---|---|
| A. | $Na_2SO_3$ (anhyd.) | 256 gms | B. | $Na_2CO_3$ (anhyd.) | 300 gms |
| | $NaHSO_3$ | 70 gms | | KBr | 4 |
| | Pyrogallol | 80 gms | | $H_2O$ to | 44 l. |
| | $H_2O$ to | 4 l. | | | |

The combined volume of developer used was 500 cc, and fresh developer was used for each pair of plates or films.

Immediately after development the plates were immersed in fresh 1% acetic acid solution for 15 seconds and then were washed 15 seconds in distilled water. Next they were fixed in fresh 15% acid-hypo. Finally, they were washed for 0.5 hour, before drying. The times of development were 1, 2, 3, 4, 6 and 10 min., and the method of rocking the tray was made as uniform as possible throughout the work.

Each of these wedge negatives was crossed at 90° with the original wedge and a print made behind the two on process film, with a similar but more intense light source, the exposure being 3 min. Before developing, cross rulings with log exposure and relative density scales were flashed onto the film. The development was carried out in a contrast (process) developer (1 B:40 A):

Negative Process Developer

| | | | | | |
|---|---|---|---|---|---|
| A. | Pyrogallol | 10 gms | B. | NaOH | 1000 gms |
| | $Na_2SO_3$ | 750 gms | | $H_2O$ to | 10 l. |
| | $Na_2CO_3$ | 250 gms | | | |
| | KBr | 50 gms | | | |
| | $H_2O$ to | 10 l. | | | |

[1] We are having a new wedge constructed 20 $cm^2$ so as to cover more completely the entire sensitometric curve of plates of all different speeds.

The remaining treatment was the same as for the wedge negatives.

From these process film prints, a second series of prints was made on Contrast Velvet Velox paper, exposure $^1/_2$ min. to the same light source as for the film prints, and 1 min. development in the following developer, other conditions as previously:

M-Q Process Developer

| | |
|---|---|
| Elon | 20 gms |
| Hydroquinone | 180 gms |
| $Na_2SO_4$ | 150 gms |
| $K_2CO_3$ | 500 gms |
| KBr | 100 gms |
| $H_2O$ | 20 l. |

One of these prints is shown in Fig. 13. From a series of these prints (1 to 10 min. development) of a process film

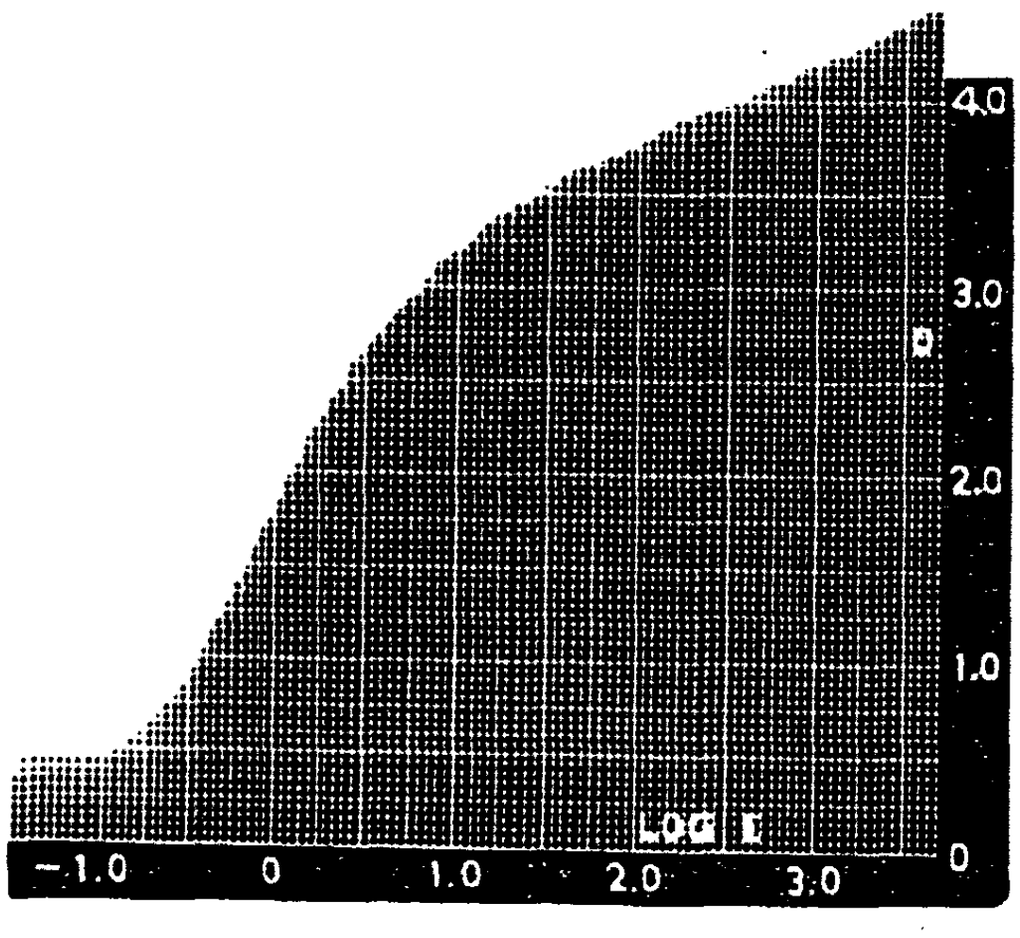



Fig. 13

or plate, which shows very little if any fog at 1 min. development, it is possible to estimate the true 0 density. For comparative purposes, it is of no importance whether or not

the arbitrarily chosen 0 is the true zero. We believe, however, that the 0 value used in obtaining the data given below (Table XIII) for the emulsions studied is very close to the true zero.

After the six prints of any series were made they were then trimmed roughly along the line indicating the characteristic curve of the plate and superimposed on each other before drawing (with a sharp pencil) the lines as finally determined. It should be noted here that in nearly every case the straight line portions in each series, when extended, converged in a point, in some cases, on the "zero" density axis, and in the others below the axis.

For illustration purposes, and to make it easier to determine the various sensitometric characteristics, all the curves of each series were drawn on a print of the same scale as that flashed on the process negatives.

The results are shown in Figs. 14 to 22 inclusive.

For the determination of $\gamma_\infty$, Renwick's method[1] of plotting the time-gamma curve was employed, $K$ being calculated from the equation

$$\frac{\tan \alpha_1 - \tan \alpha_2}{\gamma_2 - \gamma_1}$$

in which tan $\alpha_1$ and tan $\alpha_2$ represent two tangents to the time-gamma curve, fairly wide apart, and are found by dividing the ordinate in gamma units by the abscissa in time units. Having calculated K, read off from the curve the value of $\gamma$ corresponding to $\frac{1}{K}$ (minutes), multiply this by 1.58, and the result is $\gamma_\infty$[2].

In our determinations we examined to see that K was really constant by using two other pairs of values in place of tan $\alpha_1$, $\gamma_1$.

In Table XIII, we give the values of K and as $\gamma_\infty$ well as the relative H. and D. speed, the latitude, the approximate $D_{max}$, and Nietz's $a$ and $b$ values for those emul-

[1] F. F. Renwick: Phot. Jour., **54**, 163 (1914).

[2] For the complete derivation see the original article by Renwick: loc. cit.

TABLE XIII
Sensitometric Characteristics

| Type of film or plate | K | $\gamma_\infty$ | Approx. $D_{max.}$ | a | b |
|---|---|---|---|---|---|
| Process A (lantern slide) | 0.354 | 4.05 | 7.5 | 0 to 0.05 | 0 to −0.27 |
| Process B | 0.429 | 4.95 | 6.2 | $\bar{1}.90$ | −0.35 |
| Process C* | 0.262 | 4.87 | 7.3 | $\bar{2}.91$ to $\bar{1}.05$ | −0.25 to −0.31 |
| Positive emulsion | 0.384 | 4.82 | 5.1 | $\bar{1}.82$ to $.\bar{1}92$ | 0 to −0.18 |
| Medium speed A | 0.398 | 1.39 | 5.5 | $\bar{3}.63$ | −0.32 |
| Medium speed B | 0.352 | 1.23 | 4.2 | $\bar{3}.78$ | −0.15 |
| Medium speed C | 0.323 | 1.62 | 5.7 | $\bar{2}.00$ | 0 |
| High speed A | 0.421 | 1.09 | 5.2 | $\bar{3}.58$ to $\bar{3}.82$ | −0.03 to −0.06 |
| High speed B | 0.321 | 0.932 | 3.7 | $\bar{3}.15$ | −0.05 |
| Exper. emuls. No. 1 | 0.254 | 2.42 | — | — | — |
| Exper. emuls. No. 2 | 0.152 | 2.81 | — | — | — |

TABLE XIII (*Continued*)
Sensitometric Characteristics

| Type of film or plate | Relative H. & D. Speed | | | Latitude | | |
|---|---|---|---|---|---|---|
| | 1 min. | 3 min. | 10 min. | 1 min. | 3 min. | 10 min. |
| Process A (lantern slide) | 6 | 6 | 7 | 7 | 9 | 3 |
| Process B | 6 | 7 | 8 | 2.3 | 3.6 | 2.0 |
| Process C* | 27 | 47 | 76 | 9 | 3.0 | 3.0 |
| Positive emulsion | 8 | 9 | 10 | 4 | 7 | 3.2 |
| Medium speed A | 366 | 729 | 918 | 316 | 316 | 316 |
| Medium speed B | 439 | 763 | 856 | 282 | 200 | 200 |
| Medium speed C | 680 | 680 | 680 | 251 | 100 | 45 |
| High speed A | 1236 | 1488 | 1560 | 178 | 159 | 71 |
| High speed B | 2585 | 3820 | 4278 | 2510 | 794 | 398 |
| Exper. emuls. No. 1 | — | — | — | — | — | — |
| Exper. emuls. No. 2 | — | — | — | — | — | — |

* This is a panchromchromatic emulsion.

sions showing regression, i. e., a convergence point below the axis.

The original wedge was calibrated as follows: A plate or film was placed behind the wedge but half covered in the lengthwise direction, and exposed at 0.5 m for 20 seconds to 500 C. M. light intensity (corrected for reflections). That half was then covered and the other half exposed to the same light source but at 1 m. The plate was developed as above in negative developer. A second plate was exposed at 0.5 and 1.5 m, a third at 0.5 and 2 m, and a fourth at 05 and 2.5

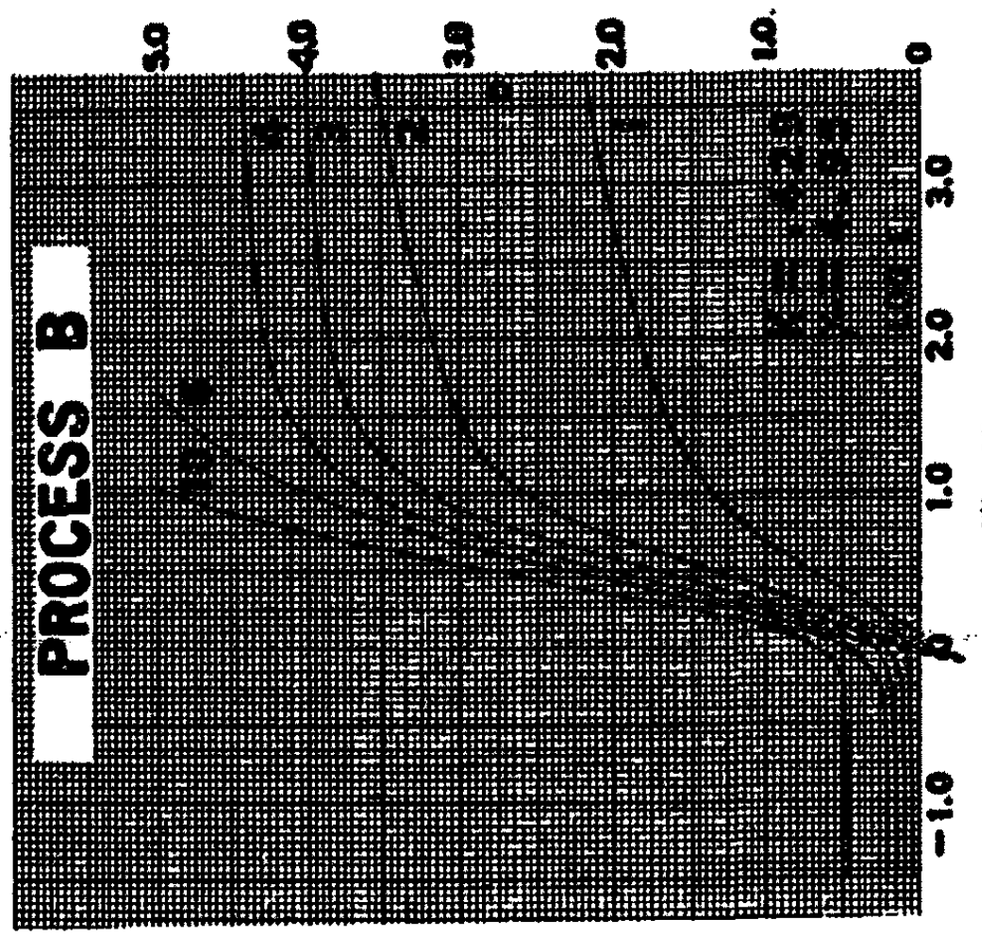

PROCESS B
5.0
4.0
3.0
2.0
1.0
0
3.0
2.0
1.0
−1.0
D

Fig. 15

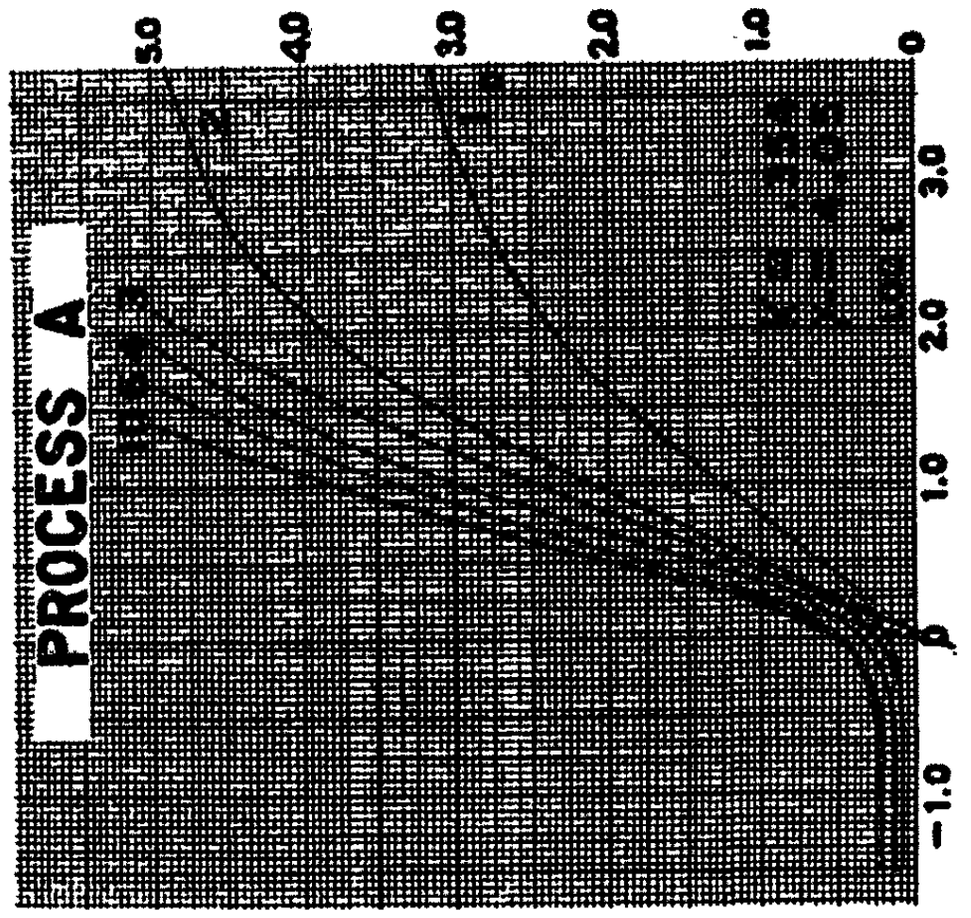

PROCESS A
5.0
4.0
3.0
2.0
1.0
0
3.0
2.0
1.0
−1.0
D

Fig. 14

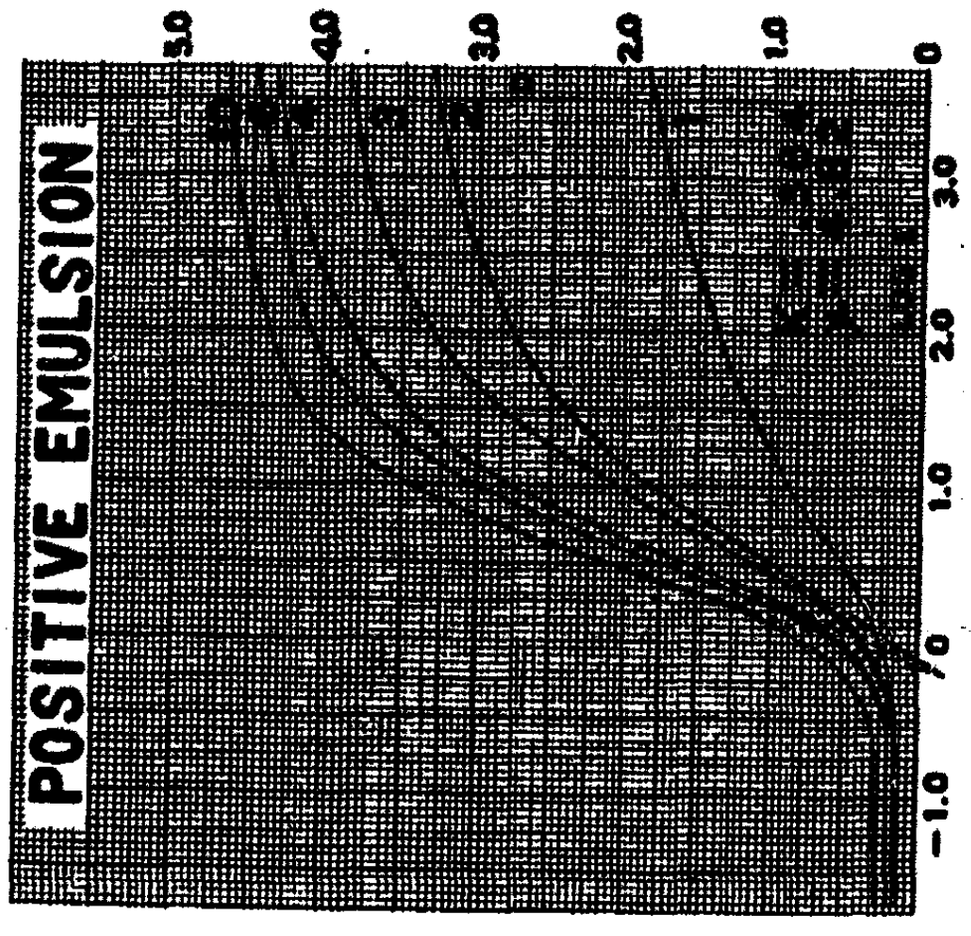

POSITIVE EMULSION
5.0
4.0
3.0
2.0
1.0
0
3.0
2.0
1.0
0
-1.0

Fig. 17

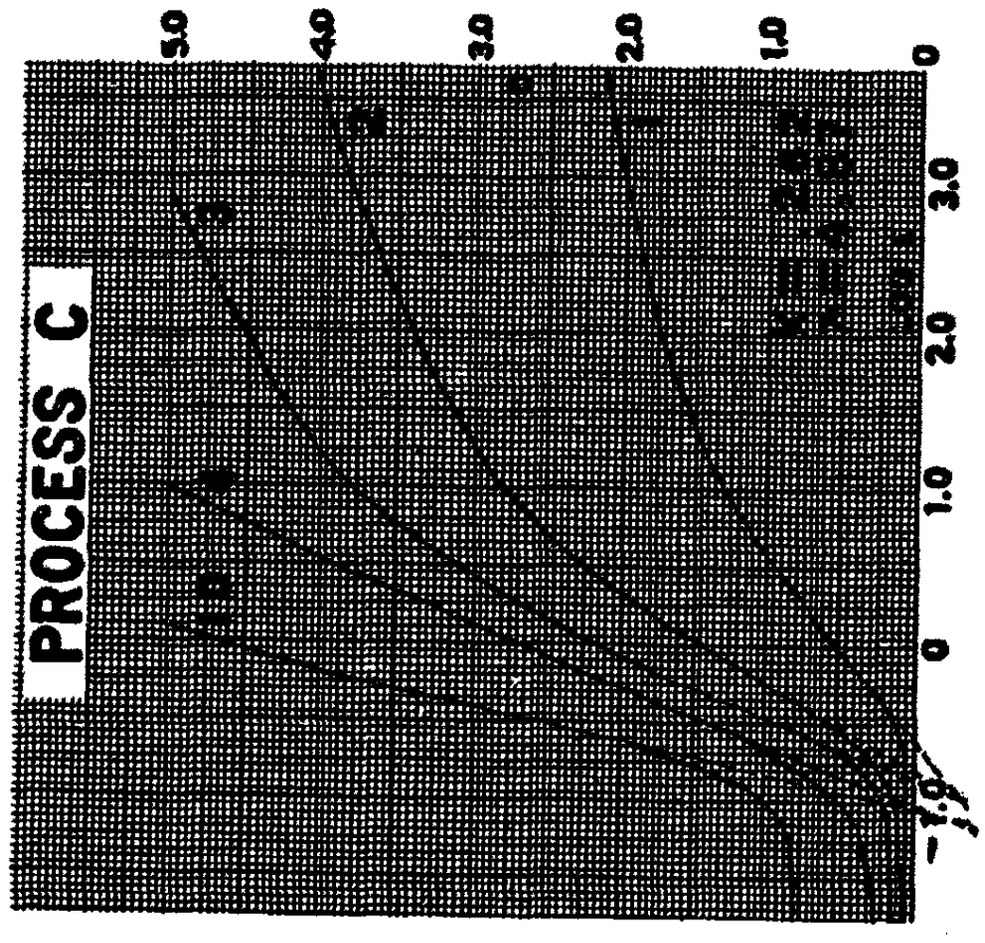

PROCESS C
5.0
4.0
3.0
2.0
1.0
0
3.0
2.0
1.0
0
-0.1

Fig. 16

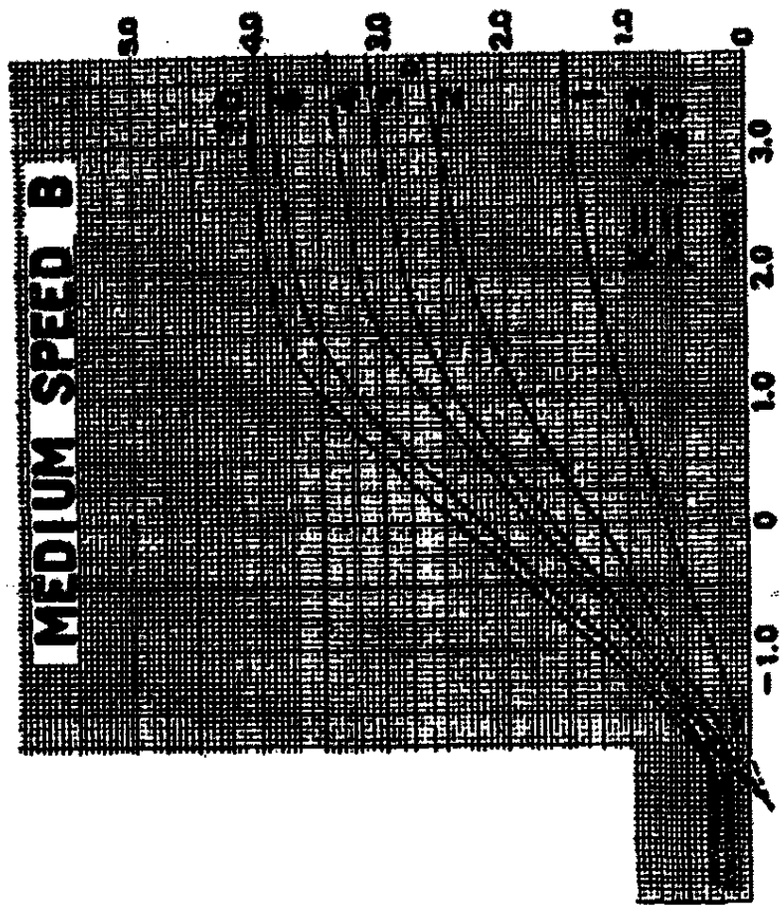

MEDIUM SPEED B
3.0
4.0
3.0
2.0
1.0
0
1.0
2.0
3.0
−1.0

Fig. 19

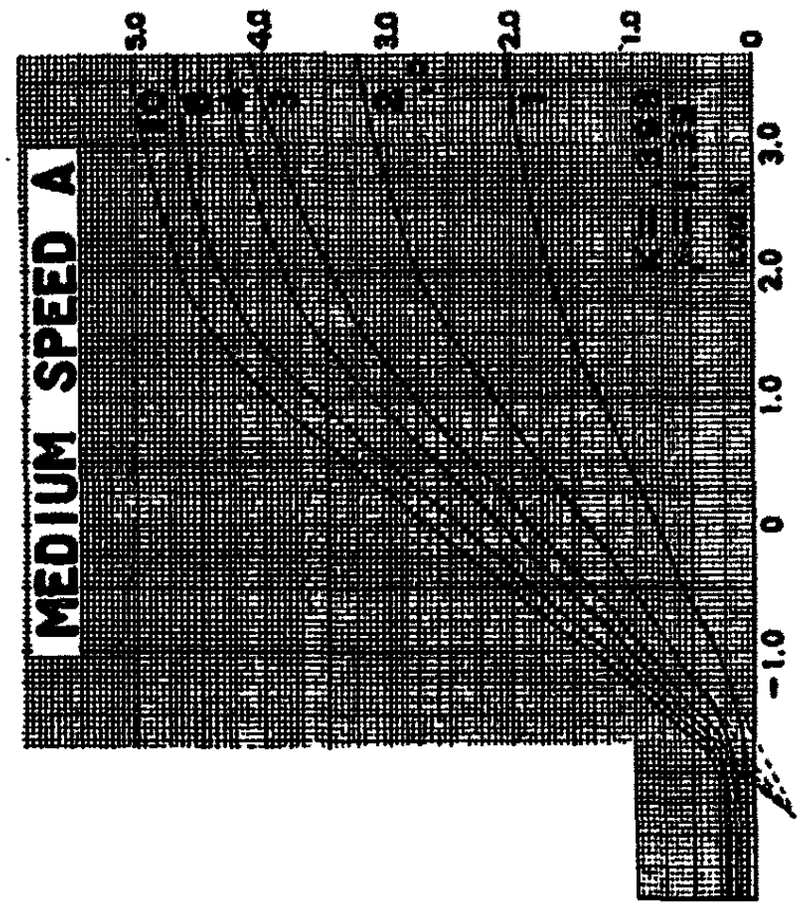

MEDIUM SPEED A
3.0
4.0
3.0
2.0
1.0
0
1.0
2.0
3.0
−1.0

Fig. 18

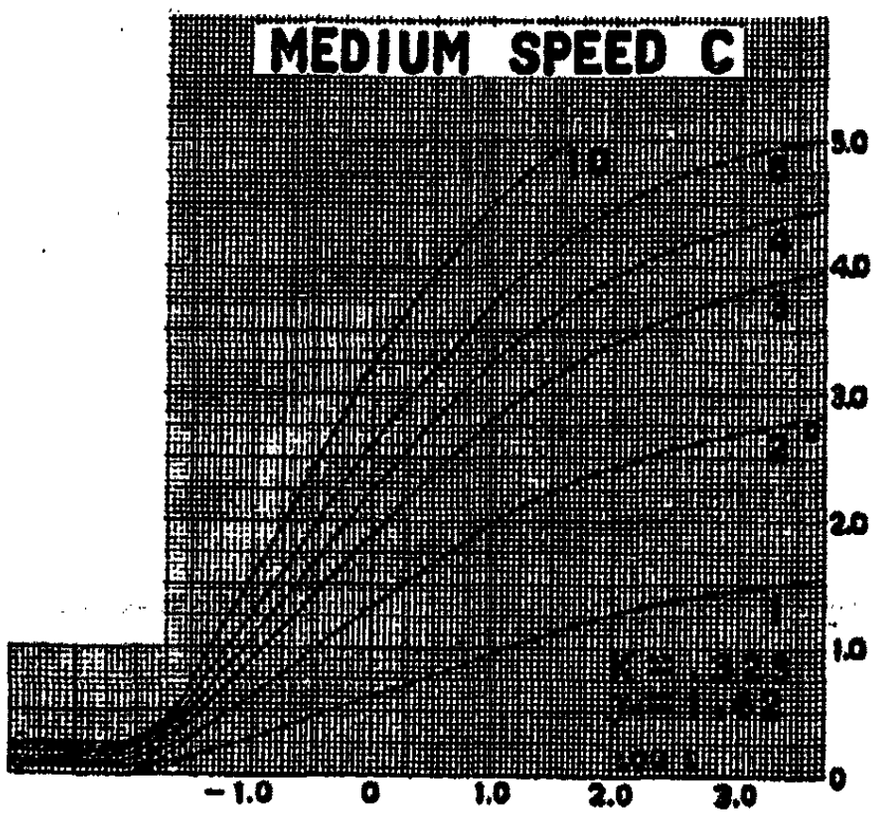

MEDIUM SPEED C
5.0
4.0
3.0
2.0
1.0
0
−1.0
0
1.0
2.0
3.0

Fig. 20

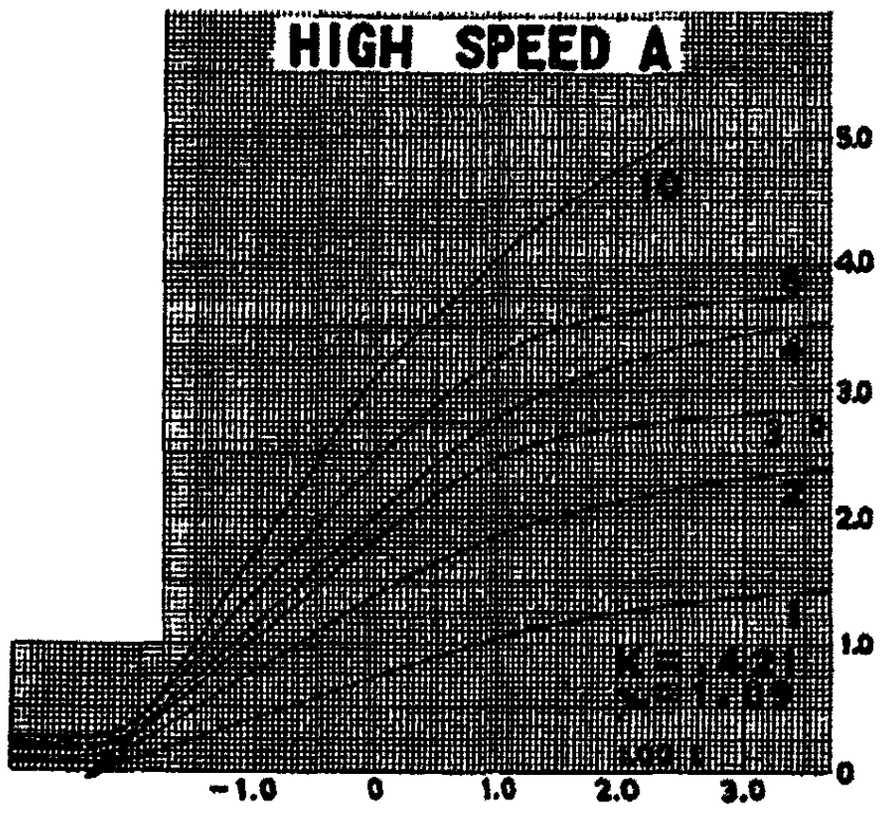

HIGH SPEED A
5.0
4.0
3.0
2.0
1.0
0
−1.0
0
1.0
2.0
3.0

Fig. 21

m in the same way. The intensities at 1, 1.5, 2, 2.5 m were calculated from the inverse square law. Duplicates were also run on each plate.

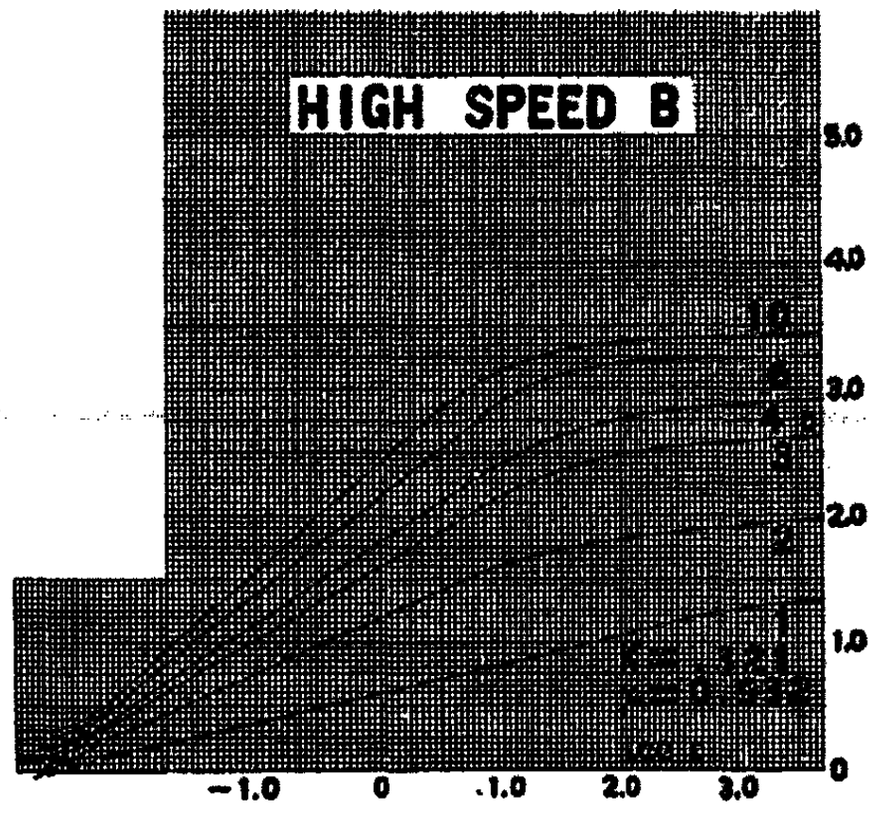



Fig. 22

Each plate now showed two wedges with a central line of demarcation and was cut along parallel lines 1 cm from this central line. The two new edges were then placed side by side with the gradation of the wedges in the same direction and one was displaced along the other until the wedges were perfectly matched. By taking readings all along the line in a Capstaff densitometer[1] this displacement could be measured very accurately. From the displacements and the intensities which had fallen on the two wedges (as calculated above and corrected for reflections) it was very easy to find the intensity transmitted by one of the wedges at the distance of the displacement from the end of the other wedge exposed at the known intensity. From the series of distances of exposure a series of transmissions along the wedge were obtained and

[1] A modified bar photometer of similar design to the Renwick-Ferguson-Benson photometer.

these transmissions of the wedge represented the exposure of the film or plate studied. When plotted against corresponding distances from the end of the wedge they should, and do form a straight line (when the wedge has a uniform gradation).

3. *Determination of the Sensitometric Characteristics by a Time Scale.*—In the present paper, only two, the experimental emulsions were exposed on a time scale. The sensitometric data in this case were obtained in the usual way by Mr. Emery

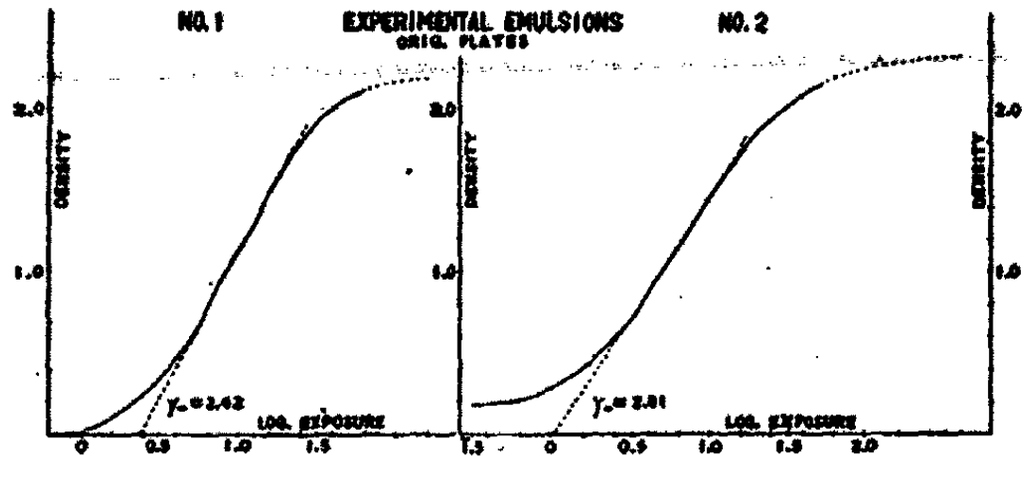



Fig. 23

Hughes of the Physics Department of this Laboratory, whom we wish to thank. They are included in Table XIII and the sensitometric curves for 3 min. development are shown in Fig. 23.

## Summary

1. An improved method of studying microscopically the size-frequency distribution of silver halide grains in a photographic emulsion is given in detail, together with an estimate of the principal sources of error in the method.

2. Frequency curves and data are given for a number of typical emulsions ranging from the slowest to the fastest.

It has been found that if frequencies (per 1000 grains) are plotted against sizes of grains an equation of the form

$$y = y_0 e^{-kx}$$

fits some of the data very closely, while for other data an equation of the form

$$y = y_0 e^{-k(x-\alpha)^2}$$

can be used to express the distribution of size variation. In these equations $y$ represents frequency (per 1000 grains) and $x$ the size of the grains

The distribution of total area of grains in each class (per unit area of the photographic plate) with the variation in class-size is of more importance photographically than the simple frequency distribution, and is obtained by multiplying each side of the above equations by the factor $\frac{N}{1000}x$, in which N represents the total number of grains per cm² of the plate.

3. Empirical sensitometric characteristics for these emulsions were also determined and are summarized in tabular form for comparison with the size-frequency data.

4. The data show definitely that the relative speed of the emulsions increases rapidly with the increase of average size and range of size of the particles contained therein.

5. Of the other characteristics, no definite statement can be made since these depend much more on the variation of other factors in the preparation and coating of the emulsions.

Acknowledgment is made here to Dr. L. Silberstein and Mr. A. C. Hardy for assistance and helpful suggestions in the mathematical treatment of the frequency data. Also we wish to express our thanks to Mr. F. L. Righter, Mr. M. R. Priddis, Mr. W. H. Davis and Miss B. M. LaBar for painstaking assistance in the experimental and statistical work.

The theoretical discussion of the results given in this paper is reserved for Part IV.

*Rochester, N. Y.*
*May 1, 1922.*

# CATALYTIC PREPARATION OF ORTHO-TOLUIDINE

BY C. O. HENKE AND O. W. BROWN



## Introduction

In several previous papers we have given the results of some studies on the catalytic reduction of nitrobenzene to aniline.[1] In this paper we shall give the results of some studies on the reduction of ortho-nitro-toluene to ortho-toluidine. The chemical reactions involved are very similar and one would expect the catalytic preparation of the two amines to be likewise very similar. Although similar in many ways the catalytic preparation of the ortho-toluidine has brought out many interesting differences from the catalytic preparation of aniline.

## Experimental Details

The apparatus used was the same as that used in our previous work on aniline In all the experiments in this paper the catalyst tube was a $^1/_2$ inch iron pipe. The ortho-nitro-toluene used was purified by shaking with sodium carbonate solution, distilling with steam and then subjecting it to two simple distillations. The method of work was the same as in our previous papers. The 2 cc pipette, under the conditions under which it was used, delivered 2.243 grams of ortho-nitro-toluene. The analysis of the product was likewise the same except that, after washing the product into the graduated flask, 25 cc concentrated HCl were added before diluting to the mark in order to make sure of the complete solution of the ortho-toluidine.

## Nickel as Catalyst

The nickel nitrate used was "Baker's Analyzed" c.p. material. According to the maker it contained 0.75% Co, 0.002% Fe, 0.001% Cl and 0.002% $SO_3$. The nitrate after

[1] Brown and Henke: Jour. Phys. Chem., **26**, 161, 272, 715 (1922).

the addition of nitric acid was ignited in a small porcelain evaporating dish in an electrically heated muffle. The temperature was raised to 450° C. Seventeen grams of the resulting oxide were put in the furnace and reduced and heated in hydrogen to 384° C. In the first experiment which was carried out at 190° C, with the hydrogen flow at 14 liters per hour and the ortho-nitro-toluene flow at 14.5 grams per hour the material yield of ortho-toluidine was 68.4% of theory. This low yield was not due to incomplete reduction but to the fact that the reduction was carried too far. The product was colorless and the odor of ammonia was pronounced. After using this catalyst in five experiments with different rates of flow of hydrogen the seventh experiment, which was carried out under the same conditions as the first experiment, gave an 85.3% material yield of ortho-toluidine. The increase in material yield of ortho-toluidine from 68.4 to 85.3% was not due to an increase in activity of the catalyst but rather to a decrease in its activity. The product in all experiments was colorless and ammonia was present as shown by the odor. The nickel was too active and reduced a part of the nitrobenzene too far yielding cyclo compounds and ammonia. After this initial decrease in activity, resulting in an increase in material yield

TABLE I

Catalyst—nickel

Temperature of catalyst—190° C
Rate of flow of ortho-nitro-toluene—13.5 grams per hour

| Hydrogen in liters per hour | Excess of hydrogen in % | Material yield of ortho-toluidine in % of theory |
|---|---|---|
| 5 | −24[1] | 79.0 |
| 9.5 | 50 | 83.5 |
| 14 | 110 | 85.3 |
| 28 | 325 | 82.3 |
| 47 | 610 | 78.2 |
| 63 | 850 | 72.9 |

[1] In this experiment the rate of flow of hydrogen was 24% below the amount theoretically required.

the activity of the catalyst remained fairly constant. Thus in the 21st experiment, which was carried out under the same conditions as the first and seventh experiments, the material yield of ortho-toluidine was 84.6%, which checks well with the seventh experiment.

In Table I are given the results of experiments with different rates of flow of hydrogen. All of these experiments were carried out after the catalyst had been giving constant results.

From the results of Table I the best rate of flow of hydrogen is seen to be 14 litres per hour.

The effect of rate of flow of ortho-nitro-toluene with the best rate of flow of hydrogen as found in Table I is given in Table II.

TABLE II

Catalyst—nickel

Temperature of catalyst—190° C
Rate of flow of hydrogen—14 liters per hour

| Ortho-nitro-toluene in gms per hour | Excess of hydrogen in % | Material yield of ortho-toluidine in % of theory |
|---|---|---|
| 27 | 10 | 86.8 |
| 13.5 | 110 | 85.3 |
| 4 | 600 | 84.6 |

From the results of Table II it will be seen that within the limits studied the lower the rates of flow of ortho-nitro-toluene the lower the yield of ortho-toluidine. However the difference in material yield within these limits is small. At the slow rates the product was colorless, while at the highest rate (27 grams per hour) the product was slightly colored indicating that a part of the ortho-nitro-toluene was incompletely reduced.

In our first paper on the catalytic preparation of aniline we have shown that the oxidation and reduction of the nickel catalyst decreased its activity. An attempt was made to increase the yield of ortho-toluidine by decreasing to a certain

extent the activity of the nickel catalyst so that it would not carry the reduction too far. The nickel was oxidized in a current of air and heated to 500° C. It was then reduced and heated in hydrogen to 438° C. The average of four experiments carried out at 190° C, with a hydrogen flow of 14 liters per hour and the flow of ortho-nitro-toluene at 13.5 grams per hour, was 86.5% compared with 85.3% when used under the same conditions previous to the oxidation and reduction. The catalyst was oxidized again, heated in a current of air to 515° C and reduced and heated in hydrogen to 450° C. Two experiments carried out under the same conditions as after the previous oxidation and reduction gave 86.1% and 85.8% yields of ortho-toluidine, which are in good agreement with the previous experiments. The product, after oxidation and reduction of the catalyst, was slightly colored.

In our previous work we secured over 95% material yields of aniline. These experiments on ortho-toluidine were carried out at the same temperature where the highest yields of aniline were secured. Also the catalyst was prepared under conditions which would give the best yields of aniline. However the yields of ortho-toluidine with the best rates of flow of hydrogen and ortho-nitro-toluene, are about 8% lower than the best yields of aniline secured. The low yields of ortho-toluidine are due to the reduction being carried too far, the product being but slightly colored only in a few experiments. This would seem to indicate that ortho-nitro-toluene is more easily reduced than nitrobenzene and that the reduction of the ortho-nitro-toluene is not so easily stopped at the amine stage.

### Lead as Catalyst

A lead catalyst was prepared by reducing 20 grams of orange mineral (orange mineral is a red lead having an apparent density of 7.8 and made from sublimed litharge). During the reduction the temperature did not rise above 315° C. The results obtained with this catalyst are given in Table III.

The experiments of Table III are given in the order in which they were carried out. The first three are under the

TABLE III

Catalyst—lead from orange mineral

| Temperature of catalyst degrees C | Hydrogen in liters per hour | Ortho-nitro-toluene in gms per hour | Excess of hydrogen in % | Material yield of ortho-toluidine in % of theory |
|---|---|---|---|---|
| 310 | 14 | 3.8 | 640 | 80.1 |
| 310 | 14 | 3.8 | 640 | 90.2 |
| 310 | 14 | 3.8 | 640 | 93.2 |
| 327 | 7 | 3.0 | 300 | 93.2 |
| 327 | 14 | 3.8 | 640 | 91.0 |

same conditions. The results show that the catalyst increases in activity with use. In the third experiment the yield of ortho-toluidine is 93.2%. A catalyst prepared from this same red lead was found in a previous paper[1] to give a 92.7% yield of aniline when used under practically the same conditions. Thus the yield of the ortho-toluidine is slightly higher than the yield of aniline. When the temperature was increased to 327° C the yield decreased to 91% in the fifth experiment, indicating that about 310° C is the best temperature for the reduction with this catalyst.

Another catalyst was prepared from an amorphous red lead having an apparent density of 23.0. Forty-nine grams of this red lead were put in the furnace and reduced at 310° C for $1^1/_4$ hours. It was then used at 310° C with nitrobenzene until the yields became constant. With 14 litres hydrogen and 3.8 grams nitrobenzene per hour the yield of aniline at 310° C was 93.4%. When ortho-nitro-toluene was used instead of nitrobenzene with the same rates of flow and the same temperature the yield of ortho-toluidine with this same catalyst was 94.6%. With this catalyst as with the previous lead catalyst the ortho-toluidine yield is slightly higher than the aniline yield indicating that ortho-nitro-toluene is more easily reduced than nitrobenzene. In our previous paper we found that (with an iron catalyst tube) a catalyst from an amorphous red lead, of an apparent density of 16.5, was the best of the

[1] Henke and Brown: Jour. Phys. Chem., 26, 325 (1922).

lead catalysts for producing aniline, over 96% material yields of aniline being secured. We would expect a catalyst from this red lead to give still higher yields of ortho-toluidine, but unfortunately we had no more of this material and could not try it.

In our previous paper a catalyst prepared from an amorphous white lead gave very low yields of aniline when used in an iron tube, the yield decreasing after a few experiments to 59%. However in a glass tube this catalyst gave over 94% total material yields of azobenzene and aniline. A catalyst was prepared from 24 grams of this same amorphous white lead which had been prepared by electrolysis as described in our previous paper. The white lead was reduced and heated in hydrogen to 327° C. Experiments carried out with this catalyst at 327° C and with the hydrogen flow at 14 litres per hour and the ortho-nitro-toluene flow at 3.8 grams per hour gave yields of but 65 to 50%. This catalyst then, when used in an iron catalyst tube, is as poor a catalyst for the preparation of ortho-toluidine as for the preparation of aniline.

A mixture of 1 gram $Fe_2O_3$ and 40 grams of the amorphous red lead when reduced and used as a catalyst gave practically same yields of ortho-toluidine as the amorphous red lead alone.

### Discussion of Results with Lead and Nickel Catalysts

Low material yields were secured with both of these catalysts, the highest yields being secured with lead. The nickel however can be used at a very much greater rate than the lead. The reason for the low yields is not the same in the two cases. Nickel is too active and carries the reduction too far while the lead although it gives a higher yield than the nickel, produces azotoluene along with the toluidine, the azotoluene formation cutting down the yield of the toluidine. The azotoluene is only slightly volatile and condensed for the most part in the end of the catalyst tube where it solidified to a glassy red solid.

In our studies on the catalytic preparation of aniline

we found that nickel carried the reduction of a part of the nitrobenzene too far while the lead would reduce a part of the nitrobenzene only to the azobenzene stage. However the nickel did not reduce as much of the nitrobenzene too far as it did of the ortho-nitro-toluene. Thus with nickel over 95% yields of aniline were secured while only about 87% yields of ortho-toluidine were secured. The ortho-nitro-toluene is more easily reduced than the nitrobenzene. This same thing is indicated by lead, the ortho-toluidine yields being slightly higher than the aniline yields with the same catalyst.

### Silver as Catalyst

Silver falls between nickel and lead in that it does not carry the reduction past the amine stage and likewise does not produce azo compounds. It then should be an excellent catalyst for the reduction of the ortho-nitro-toluene to ortho-toluidine.

The silver catalyst was prepared from the carbonate. The carbonate was prepared by dissolving 34 grams $AgNO_3$ in 200 cc water and precipitating with 140 cc of ammonium carbonate solution containing 14 grams of the solid salt. The precipitated silver carbonate was washed, filtered and then dried at about 100° C. Twenty-two grams of the dried carbonate were put in the furnace and reduced and heated in hydrogen to 312° C. It was then used in the experiments listed in Table IV. The temperature used was the best temperature for the production of aniline.

The experiments of Table IV are listed in the order in which they were carried out. The yield at first is excellent, being almost quantitative. The product also had a good appearance being practically colorless. The yield however, after use of the catalyst at higher rates of ortho-nitro-toluene, in the last experiment, in which the rate of ortho-nitro-toluene was only a little higher than in the first, decreased to 76.7%.

Another silver catalyst was then prepared like the catalyst used in Table IV. The results with this catalyst are given in Table V.

TABLE IV

Catalyst—silver
Temperature of catalyst—300° C
Rate of flow of hydrogen—14 litres per hour

| Ortho-nitro-toluene in grams per hour | Excess of hydrogen in % | Material yield of ortho-toluidine in % of theory |
|---|---|---|
| 3.4 | 720 | 99.3 |
| 3.4 | 720 | 99.3 |
| 4.5 | 540 | 98.9 |
| 4.5 | 540 | 97.7 |
| 12 | 130 | 79.0 |
| 8 | 260 | 78.6 |
| 5.4 | 440 | 74.8 |
| 3.8 | 640 | 76.7 |

TABLE V

Catalyst—silver
Rate of flow of hydrogen—14 litres per hour

| Experiment number | Temperature of catalyst degrees C | Ortho-nitro-toluene gms per hour | Excess of hydrogen in % | Material yield of ortho-toluidine in % of theory |
|---|---|---|---|---|
| 38d5 to 44d5 inc. | 300 | 3.8 | 640 | 98.5 |
| 45d5 | 300 | 3.0 | 830 | 98.5 |
| 46d5 | 300 | 4.5 | 540 | 97.0 |
| 47d5 | 300 | 4.8 | 480 | 94.7 |
| 48d5 | 300 | 3.8 | 640 | 95.1 |
| 49d5 | 300 | 3.2 | 780 | 97.0 |
| 50d5 | 300 | 4.5 | 540 | 97.4 |
| 51d5 | 300 | 3.2 | 780 | 97.0 |
| 52d5 | 320 | 4.8 | 480 | 97.0 |
| 53d5 | 320 | 6.4 | 350 | 95.9 |
| 54d5 | 320 | 7.5 | 300 | 91.7 |
| 55d5 | 320 | 13.4 | 110 | 75.6 |
| 56d5 | 320 | 4.5 | 540 | 90.2 |
| 57d5 | 320 | 3.2 | 780 | 92.5 |
| 58d5 | 340 | 3.2 | 780 | 91.0 |
| 59d5 | 320 | 3.2 | 780 | 85.0 |

Experiments 38d5 to 44d5 inclusive were all carried out under duplicate conditions and gave a yield of 98.5%. Likewise the eighth experiment gave a yield of 98.5%. Thus during these first eight experiments the activity of the silver catalyst remained fairly constant. Referring back to Table IV we see that the eighth experiment which was carried out under nearly the same conditions, gave only a 76.7% yield of ortho-toluidine. The only difference between the first eight experiments of Table V and the first eight of Table IV is that in some of the first eight experiments of Table IV, a higher rate of ortho-nitro-toluene was used than in any of the first eight of Table V. This indicated that a high rate of flow of ortho-nitro-toluene tends to decrease the activity of the silver catalyst. This same behavior is indicated by experiments 46d5 to 51d5. Experiments 46d5 and 47d5 were carried out at slightly higher rates of ortho-nitro-toluene than experiments 38d5 to 45d5. After use at these slightly higher rates the yield did not reach 98% at 300° C. Upon increasing the temperature to 320° Ca 98.1% yield was secured in experiment 52d5. However, after being used at the higher rates at 320° C the yield decreased as is shown by experiment 57d5 in which the yield was 92.5%. An increase in temperature to 340° C in experiment 58d5 was not beneficial. This higher temperature seemed to cause a still further decrease in activity for in experiment 59d5 the yield was only 85% compared to 92.5% in experiment 57d5 which was carried out under the same conditions just prior to use at 340° C.

Several attempts were made to secure a silver catalyst in such a condition that its activity would not decrease with use, when used at the higher rates. Powdered $Al_2O_3$ mixed with $Ag_2CO_3$ was not so good a catalyst as $Ag_2CO_3$ alone. Likewise a mixture of $CaCO_3$ and $Ag_2CO_3$ made by precipitating the two together from a solution of the mixed nitrates by $Na_2CO_3$ was no better. Asbestos was soaked in a silver nitrate solution and dropped into a solution of sodium carbonate, but gave poorer results than the silver carbonate alone. Silver on pumice was much worse.

All the attempts at increasing the life of the silver catalyst gave negative results. As a result, although nearly theoretical yields of ortho-toluidine can be secured with silver as catalyst, the process would not be feasible due to the short life of the silver catalyst.

### Copper as Catalyst

The catalytic activity of copper is very similar to that of silver. Copper produces very little if any azobenzene and likewise reduces none or practically none of the nitrobenzene farther than the aniline stage. Copper then should, like silver, give high yields of ortho-toluidine. In our previous papers we have given the results of many experiments with copper as catalyst and have pointed out many things affecting its activity. For producing aniline, copper reduced from the precipitated oxide is much better than that from the oxide obtained by ignition of the nitrate.

In Table VI are given the results of some experiments with a copper catalyst prepared by reducing the precipitated oxide.

The catalyst is the same catalyst that was used in our study of its activity in the reduction of nitrobenzene, the results of which have been given in a previous paper.[1] It had been prepared by precipitation with NaOH from the pure nitrate. The pure nitrate had been prepared by refining copper twice by electrolysis as described in our previous paper. Before being used in the experiments listed in the table it had been used in 40 experiments under various conditions with nitrobenzene. One of these conditions (higher temperatures) is detrimental to the activity of the catalyst. As a result, its activity is a little less than it would have been had it not been used at the higher temperatures (300° C). The experiments are listed in the table in the order in which they were carried out. In three of the experiments listed nitrobenzene was used instead of ortho-nitro-toluene so that the aniline yield may be compared with the ortho-toluidine yield.

[1] Brown and Henke: Jour. Phys. Chem., 26, 715 (1922).

TABLE VI

Catalyst—copper from precipitated oxide
Temperature of catalyst—260° C

| Nitro compound in grams per hour | Hydrogen in litres per hour | Excess of hydrogen in % | Material yield of amine in % of theory |
|---|---|---|---|
| 6.6 | 3.5 | −3[1] | 85.6 aniline |
| 5.8 | 3.5 | 20 | 96.4 ortho-toluidine |
| 5.8 | 7 | 140 | 97.2 ortho-toluidine |
| 5.8 | 7 | 140 | 97.5 ortho-toluidine |
| 5.4 | 14 | 380 | 95.6 aniline |
| 8.7 | 7 | 50 | 92.6 aniline |
| 9.0 | 7 | 50 | 94.1 ortho-toluidine |
| 10.2 | 7 | 40 | 79.0 ortho-toluidine |
| 5.8 | 14 | 390 | 94.3 ortho-toluidine |
| 5.8 | 3.5 | 20 | 96.7 ortho-toluidine |

[1] In this experiment the rate of flow of hydrogen was 3% less than the theoretical amount needed.

The results of the second and tenth experiments are in good agreement and show that the activity of the catalyst did not change appreciably during this period of time. On comparing the tenth, second, third, fourth and ninth experiments it will be seen that the lower rates of hydrogen are better than the higher rate, 7 litres per hour being best, as shown by the third and fourth experiments. The third, fourth, seventh and eighth experiments show that the lower the rate of ortho-nitrotoluene the higher the yield of ortho-toluidine. Comparing the ortho-toluidine yields with the aniline yields it will be noted that with the rate of hydrogen at 14 liters per hour in the fifth and ninth experiments the aniline yield was higher than the ortho-toluidine yield. However in all the other experiments (under nearly comparative conditions) the ortho-toluidine yield was higher than the aniline yield. From this one would expect that with a copper catalyst, whose activity had not been decreased by use at too high a temperature, the ortho-toluidine yield would at least be equal to if not higher than the aniline yield. The yields of aniline under different conditions have been given in the paper preferred to above.

The catalyst used for the experiments listed in Table VII was prepared by ignition of copper nitrate at 415° C. Prior to ignition of the copper nitrate an amount of ferric nitrate was added equivalent to 0.005% Fe in $Cu(NO_3)_2.6H_2O$. This would make the iron content of the reduced copper catalyst 0.023%. Prior to use in the experiments listed in the table it had been used in nine experiments with nitrobenzene, and its activity had become constant. The second and last experiments of the table were carried out using nitrobenzene instead of ortho-nitro-toluene and hence the yields of ortho-toluidine may be directly compared with the aniline yields.

TABLE VII

Catalyst—copper containing 0.023% Fe, prepared from ignited nitrate
Temperature of catalyst—260° C
Rate of flow of nitro-compound—3.8 grams per hour

| Hydrogen in litres per hour | Excess of hydrogen in % | Material yield of amine in % of theory |
|---|---|---|
| 14 | 640 | 97.2 ortho-toluidine |
| 14 | 580 | 90.6 aniline |
| 3.5 | 85 | 98.3 ortho-toluidine |
| 7 | 270 | 97.9 ortho-toluidine |
| 14 | 640 | 96.4 ortho-toluidine |
| 14 | 580 | 91.9 aniline |

Upon examining the results of Table VII it will be noted that the yields of ortho-toluidine are much higher than the yields of aniline. The yields of aniline are low, only 90.6% and 91.9% while the yields of ortho-toluidine are high, even up to 98.3%.

The fact that the catalyst for the ignited nitrate gives low aniline yields and good ortho-toluidine yields, the difference between the yields secured and the theoretical not being due to intermediate products or to the carrying of the reduction too far, indicates that the ortho-nitro-toluene is more easily reduced than the nitrobenzene. Nickel gave low yields of ortho-toluidine, not because of incomplete reduction, but

because it carried the reduction too far, so that not only is the ortho-nitro-toluene more easily reduced to the amine stage but also it is more easily reduced past the amine stage than the nitrobenzene. Likewise with lead as catalyst slightly higher yields of ortho-toluidine than of aniline are secured with the same lead catalyst.

## Summary

1. Nickel is too active and reduces a large part of the ortho-nitro-toluene farther than the toluidine stage. Attempts to decrease the amount reduced too far were for the most part unsuccessful. The highest yield secured with nickel as catalyst was 86.8%.

2. Lead catalysts give slightly higher yields of ortho-toluidine than of aniline. Thus a lead catalyst from an amorphous red lead gave a 94.6% yield of ortho-toluidine while the aniline yield with the same catalyst under the same conditions was only 93.4%.

3. Silver, when first used, gives 99% material yields of ortho-toluidine, but its activity decreases with use especially at the higher rates of ortho-nitro-toluene. Attempts to prepare a silver catalyst with such properties that its activity would not decrease were unsuccessful.

4. Copper gives higher yields of ortho-toluidine than nickel over 97% yields being secured with a catalyst whose activity had been decreased by use at too high a temperature. A copper catalyst prepared from an ignited nitrate gives higher ortho-toluidine yields than aniline yields. The activity of the copper catalyst does not decrease with use, as a silver catalyst does. For producing ortho-toluidine copper is superior to nickel because a much higher yield of the toluidine can be obtained.

5. Ortho-nitro-toluene is more easily reduced than nitrobenzene.

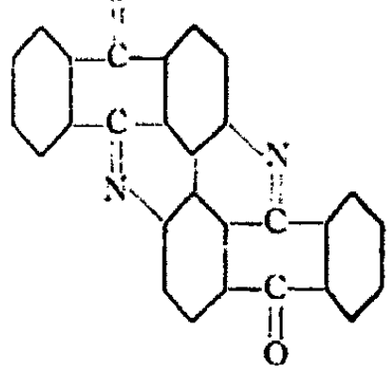
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# THE REDUCTION OF AN INDANTHRENE DYE BY MEANS OF SODIUM HYDROSULFITE

BY JOHN H. YOE AND GRAHAM EDGAR[1]

## I. Introduction

Dyes of the indanthrene series are usually applied to the fabric in the reduced condition, reduction being effected by an alkaline solution of sodium hydrosulfite. Although the most favorable conditions for practical use of these dyes are very well known, relatively little seems to have been established as to the mechanism by which the reduction occurs, and the influence of different factors upon the rate of the reaction. The experiments discussed below were carried out with the object of throwing some light upon this problem. The dyestuff chosen for the investigation was an oxyindanthrene of the formula



furnished by the Du Pont Company, and known by them as Ponsol Yellow G. The sample was of high purity.

## II. Experimental

Some preliminary experiments were carried out under the microscope by mixing a little of the dye with a drop of NaOH solution, and then allowing a solution of $NaHSO_2$ to diffuse into the mixture. When the $NaHSO_2$ reached the dye crystals a growth of small dark blue needles began to cover them

[1] Contribution from the Cobb Chemical Laboratory of the University of Virginia.

and these began slowly to go into solution giving to the mixture the characteristic dark blue color of the reduced dye. These experiments indicated that the actual reduction of the dye is a rapid reaction, but the rate of solution of the reduced dye is much less rapid.

More exact experiments were then designed to measure the rate of reduction and solution of the dye. Since the rate of a heterogeneous reaction is in general largely dependent upon the surface, it was decided to compress the dye into disks having an approximately constant surface. The apparatus finally developed for the work is illustrated in Figure I. The disk of compressed dye was formed by forcing a steel plunger into a steel cylinder of 9.5 mm diameter, containing a sufficient quantity of the dye crystals. The disk was then fitted into a flat container, so adjusted that 0.5 mm of dye projected above the edge of the container. The container was placed in the bottom of a liter beaker, being adjusted so as to take up a position half way between the center and wall of the beaker.

The beaker was fitted with a wooden cover provided with holes through which the stirrer and thermometer passed, and others through which hydrogen gas could be introduced and samples for analysis withdrawn. The stirrer was adjusted so that the arms were exactly 1 cm above the disk, and its speed was kept constant at 500 r.p.m. The beaker was immersed in a thermostat at 25° C (± 0.02).

The procedure observed in carrying out a determination was as follows: the disk of dye was placed in the beaker and the complete apparatus set up. The air in the beaker was then replaced by hydrogen, the stirrer was set in motion, and 500 cc of alkaline $NaHSO_2$ solution, previously warmed to 25° C was then added. At frequent intervals the amount of reduced dye in solution was determined by withdrawing a 10 cc sample of the solution, diluting it with a solution containing NaOH and $NaHSO_2$ and comparing its color with that produced by reducing completely a known weight of the dye. A Sargent colorimeter was used. Experiment showed that

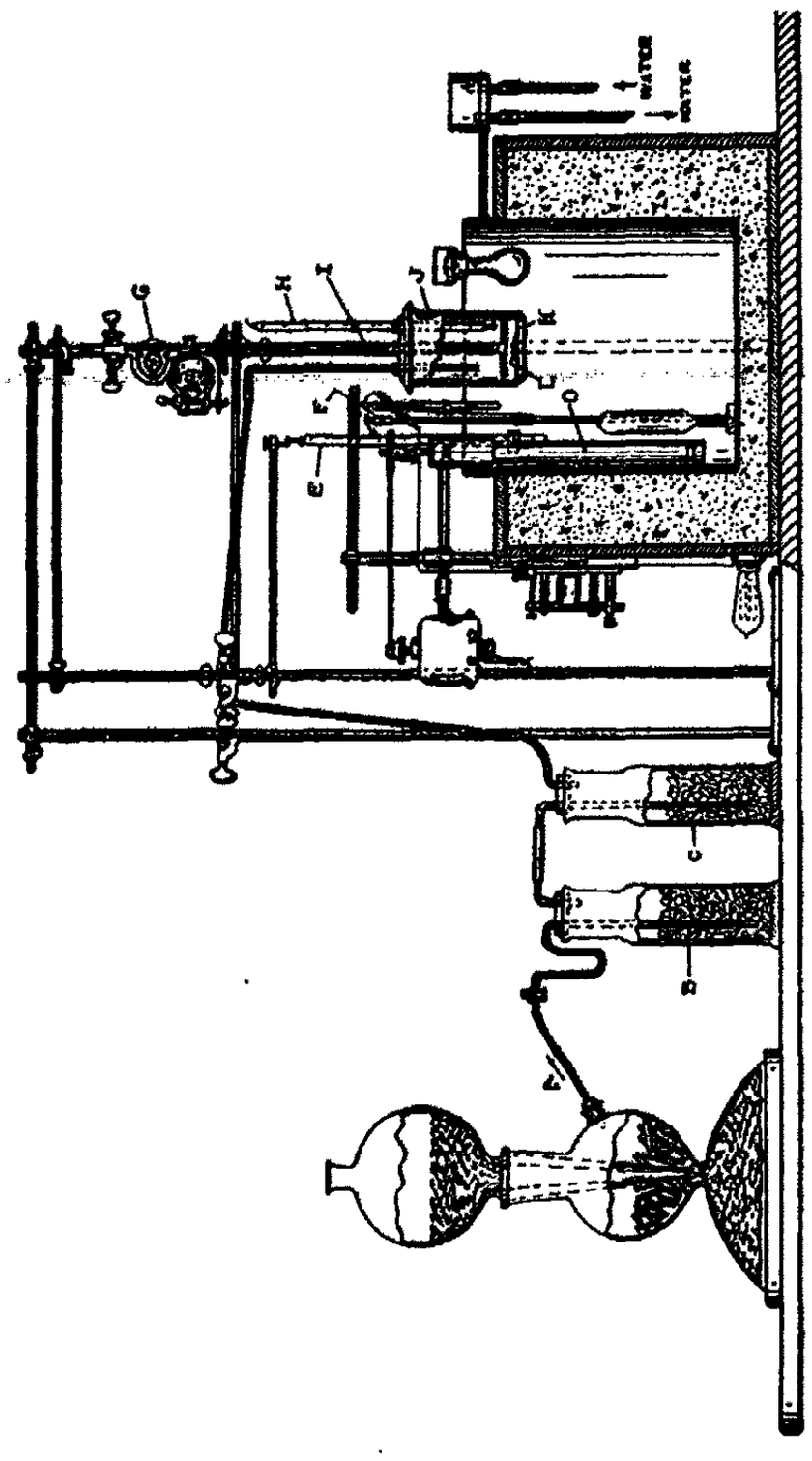


Fig. 1

E = Bath Thermometer
F = Thermo-regulator
G = Speed Indicator
H = Vat Thermometer
I = Vat Stirrer
J = Reduction-Vat
K = Dye Tablet Holder
L = Dye Tablet

A = Hydrogen
B = Sodium Hydroxide Solution
C = Alkaline Pyrogallol Solution
D = Bath Stirrer

the color of the solution was exactly matched to the eye by cobalt glass, and in many cases plates of this glass, calibrated against weighed amounts of the dye, were used as standards. The dye solutions were covered, while in the colorimeter, with a thin layer of oil, to prevent atmospheric oxidation.

The experiments were usually continued until the rate of reaction became very slow. In some cases irregularities were caused by partial disintegration of the dyestuff disk, but these experiments were discarded from consideration. Examination of the disk at the end of an experiment always showed it to be covered by a layer of blue solid, confirming the preliminary indications that the rate of *solution* is the slow factor in the reaction.

The concentrations of NaOH and $NaHSO_2$ were varied separately, and in one experiment NaCl was added.

Characteristic experimental data are given in Table I, and are expressed graphically in Figures 2 and 3.

TABLE I

Reduced Dye in Solution, mg per litre
(Temp. = 25° C; Stirrer = 500 r.p.m.; 5 gm $NaHSO_2$)

| Conc. NaOH | 0.18 N | 0.36 N | 0.72 N | 1.08 N | 1.44 N | 2.88 N |
|---|---|---|---|---|---|---|
| Time (min.) | Concentration of Reduced Dye (mg per liter) | | | | | |
| 10 | — | 70 | 48 | — | 18 | — |
| 20 | — | 91 | 82 | 36 | 25 | — |
| 30 | 28 | 108 | 99 | 54 | 31 | 11 |
| 40 | 30 | 121 | 109 | 67 | 36 | — |
| 50 | 31 | 130 | 122 | 77 | 42 | — |
| 60 | 32 | 135 | 126 | 85 | 48 | 20 |
| 70 | 33 | 136 | 127 | 91 | 53 | 22 |
| 80 | 34 | 137 | 128 | 96 | 59 | 23 |
| 90 | 35 | 137 | 129 | 99 | 63 | 24 |
| 100 | 36 | 137 | 129 | 103 | 68 | 25 |
| 110 | 37 | 137 | — | 106 | 71 | 26 |
| 120 | 38 | 137 | — | 109 | 74 | 26 |
| 130 | 39 | — | — | 110 | 75 | 27 |
| 140 | 40 | — | — | 111 | 76 | 28 |
| 150 | 40 | — | — | 111 | 76 | 29 |
| 160 | 41 | — | — | 112 | 76 | 29 |

On attempting to duplicate the experiments under any given conditions it was found that whereas results of the same general character were invariably obtained, the rate of solution and the final maximum amount of dye going into solution varied considerably in individual experiments. In the light of final conclusions discussed below, it seems probable that these variations are largely determined by unavoidable differences in the degree of compression of the dye disk. It is felt that these variations are not sufficient to affect the general conclusions drawn. The data given have been selected as typical.

## III. Discussion of Experimental Data

(*a*) General Nature of the Reaction Velocity Curves.

Examination of the curves of Figure 2 shows that they all consist of the same general type,—a fairly rapid initial rate of solution, followed by a gradual slowing up of the rate, until finally the reaction practically ceases. In fact, it would at first appear that the process represented the simple solution of a solid, the rate of which is in general determined by the rate of diffusion of the dissolved solid, [1,2] and follows the expression[3]

$$K = \frac{V}{t_2 - t_1} \quad \ln \frac{S - c_1}{S - c_2}$$

where V represents the total volume; $t_2$ and $t_1$, time intervals; $c_2$ and $c_1$ corresponding concentrations, and S the concentration of the saturated solution.

Further consideration, however, makes it apparent that we are not dealing with a simple solution phenomenon, determined by the rate of diffusion. In the first place the great effect of the concentration of sodium hydroxide on the rate (see further below) cannot be accounted for on the diffusion hypothesis, as a relatively small increase in the concentration

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[1] Noyes and Whitney: Zeit. phys. Chem., 23, 689 (1897).
[2] Nernst and Brunner: ibid., 47, 52 and 56 (1904).
[3] Van Name and Edgar: Am. Jour. Sci., 29, 237 (1910).

of NaOH can hardly be expected to double the rate of diffusion of the dissolved dye. In the second place experiments showed that the apparent limit reached by the reaction does not represent a true solubility of the reduced dye, for after the *disk* had practically stopped dissolving, the apparently saturated solution would dissolve considerable quantities of *finely divided dye*. We can therefore dismiss the idea that the reaction

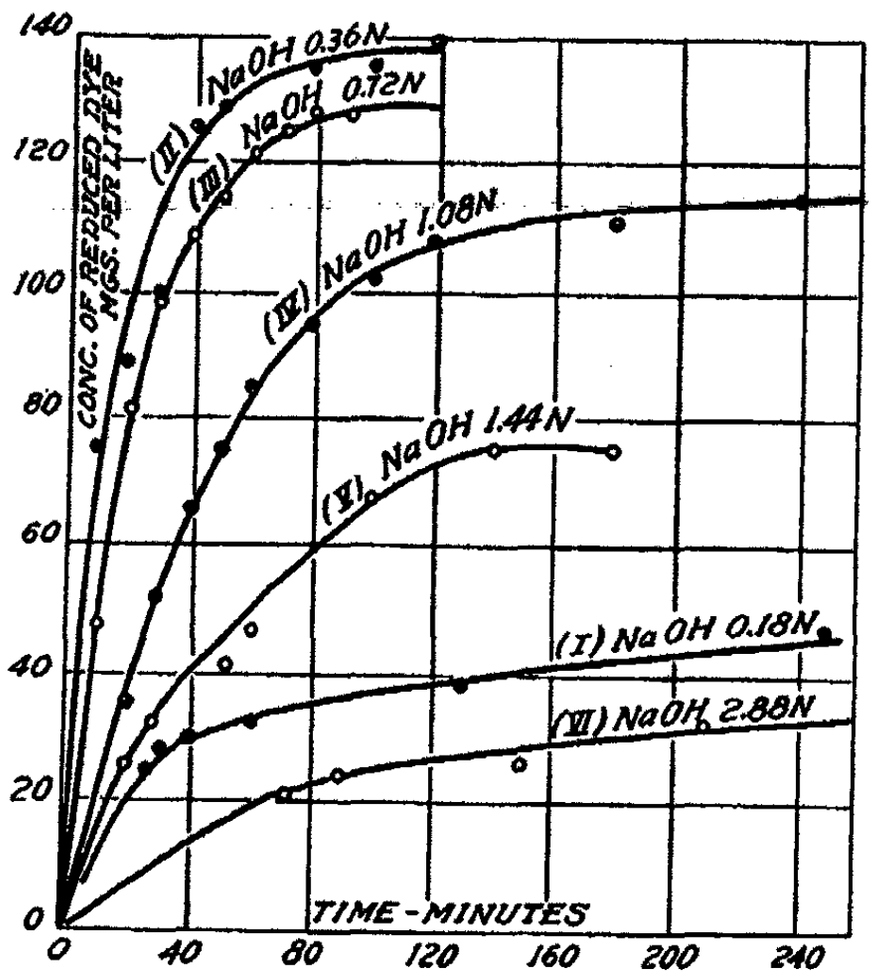



Fig. 2
Effect of Alkali Ion

consists merely of a rapid reduction of the dye, followed by simple solution of the reduced dye.

(*b*) The Effect of Sodium Hydroxide.

The effect of sodium hydroxide on the rate of reaction is most marked. In the curves of Fig. 3 the concentrations of reduced dye have been plotted as ordinates, and concentrations of alkali as abscissas, separate curves being drawn for

the different time intervals. It will be noted that a pronounced maximum occurs between normalities of 0.24 and 0.72, apparently in the neighborhood of 0.5N. In an experiment with 5 normal NaOH the rate was so slow as to preclude measurement. The character of the curves of Fig. 3 suggests that

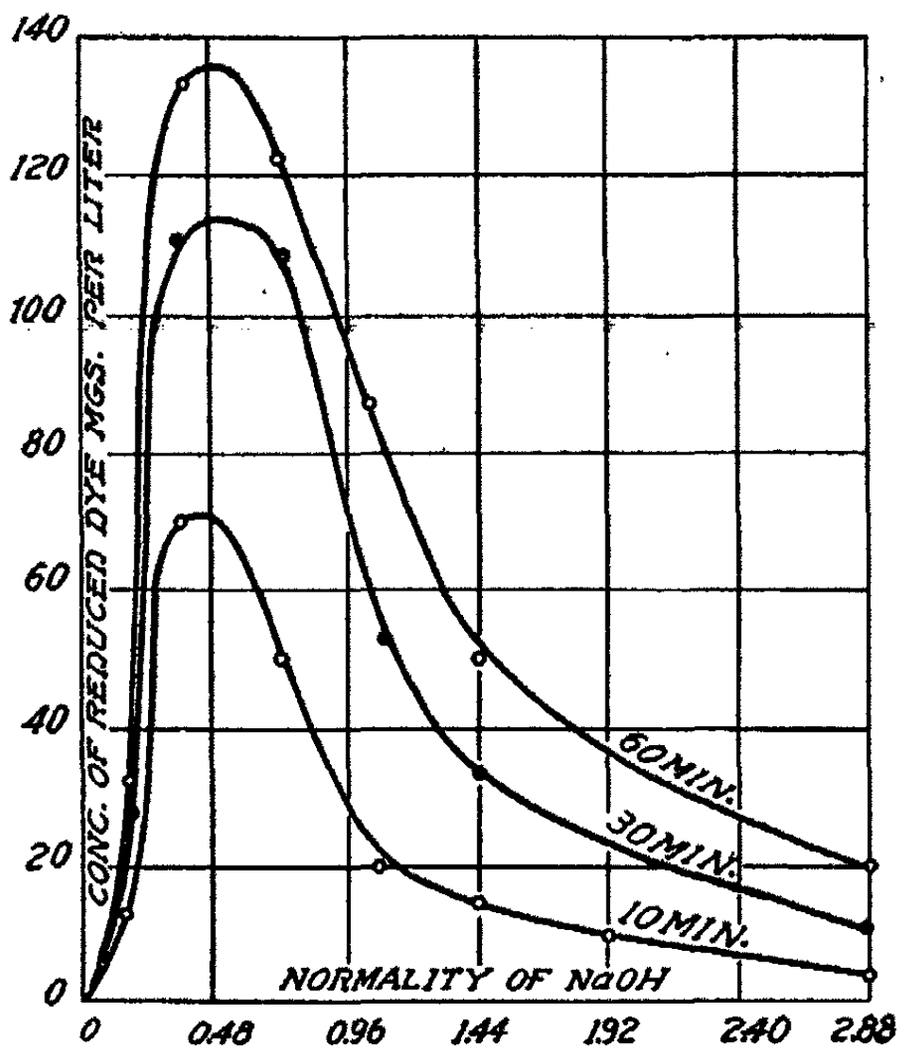



Fig. 3
Effect of Alkali Ion
Conc. Dye vs. Normality of NaOH at Constant Time

hydroxyl ion may favor the rate of solution while sodium ion retards it. Additional data on this point were secured by carrying out an experiment similar to those of Table I, except that the solution was 0.36N in NaOH and 2.52 in NaCl. The rate of reaction was even lower than that in which 2.88N NaOH was employed, although the normality of the NaOH was approximately that giving the maximum rate when pres-

ent alone. The bearing of these facts on the probable mechanism of the reaction is discussed below.

(*c*) The Influence of $NaHSO_2$.

A series of experiments was carried out in which the concentration of NaOH was kept constant at 0.72N, and the amount of $NaHSO_2$ varied between 1 and 30 grams per 500 cc of solution. The results show a very slow rate of reaction when only 1 gm was present but relatively little difference between the rates in solutions containing 5, 20 and 30 grams. Provided a considerable excess is present, therefore, it does not seem that the $NaHSO_2$ materially affects the rate of reaction.

(*d*) Effect of Rate of Stirring.

Two parallel experiments were carried out in which the rate of stirring was 400 and 500 r.p.m., respectively. The result indicated an increase in the rate or solution of about 10% when the rate of stirring was increased from 400 to 500 r.p.m.

(*e*) Indications of the Colloidal Nature of the Reduced Dye.

The experiments outlined above suggested the probability that the reduced dye is really in colloidal suspension rather than in true solution, and that we are dealing with a peptization phenomenon. A few additional facts tend to support this theory. Filtration of the alkaline reduced solution through several layers of hardened filter paper gave a filtrate at first water-clear and colorless, while a layer of the blue reduced dye was found adhering to the filter paper.

The reduced dye solution is readily precipitated (coagulated) by various inorganic salts.

In the field of an improvised ultramicroscope large numbers of ultramicrons were observed. It was, however, found impossible to prepare an optically void solution of the alkaline hydrosulfite, so that this result cannot be taken as conclusive.

## IV. Conclusions

Considering all of the data discussed above we are led to the conclusion that the reduction and solution of the dyestuff in question (and probably others of the same type) in-

volve (*a*) the rather rapid reaction of the dye with the alkaline hydrosulfite to form an insoluble crystalline reduced dye; and (*b*) peptization of the reduced dye through the agency of the hydroxyl ions, the resulting solution being colloidal in nature. The rate of solution and the *amount* of *dyestuff* which will be peptized by a given solution, depends upon the state of subdivision of the dye. Positive ions tend to coagulate the solution, and to retard the peptization of the reduced dye.

It is realized that these conclusions are based on data perhaps in themselves not entirely conclusive, but it has not been possible to make any other explanation account for the observed facts.

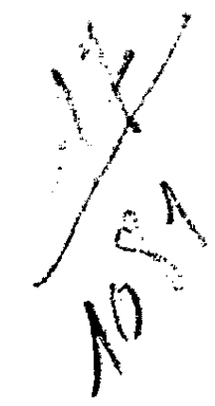
## V. Summary

(1) Measurements have been made of the rate of reduction of an indanthrene dye by alkaline hydrosulfite solutions.

(2) The influence of various factors has been determined.

(3) The results indicate that the rate of reduction of the dye is rapid, but the "solution" of the reduced dye is in reality a peptization by alkali.

*University, Virginia*



# ACTIVE CHLORINE

BY Y. VENKATARAMAIAH

## Introduction

In the year 1897, W. A. Shenstone[1] made some researches on the activation of chlorine by the ozonising discharge and came to the conclusion that, highly purified chlorine is uneffected by it. In the year 1902, Kellner[2] and Vernon[3] made contributions to the effect that chlorine is affected by the silent electric discharge. Again, in the year 1905, F. Russ[4] studied the activation of chlorine by the silent electric discharge and by light.

Much valuable work on the subject of active chlorine was done by Mellor,[5] Burgess and Chapman,[6] Chapman[7] and other chemists. In any case little work was done by all the abovementioned scientists, on active chlorine in regard to its chemical properties. There was also little work done to elucidate the molecular complexity of the active gas. With these in view the author has undertaken this piece of work.

In the present research, the active chlorine was prepared in several ways. Although, the gas is formed in relatively small quantities, yet it is a more powerful chlorinating agent than ordinary chlorine. It is comparatively not a stable gas.

## Preparation of Pure Chlorine

The pure chlorine needed in the experiments was prepared from gold chloride. The method of preparing pure gold chloride is described below. Pure gold obtained from the market was dissolved in aqua regia prepared from pure ni-

[1] Jour. Chem. Soc., **71**, 471 (1897).
[2] Zeit. Elektrochemie, **8**, 500 (1902); cf. also Wiener Anz., **12**, 15 Mai.
[3] Öst. Pat. 11180, Oct. 15 (1902).
[4] Sitzungsber. Akad. Wiss., Wien, **114**, IIb, 194.
[5] Proc. Chem. Soc., **20**, 140 (1904).
[6] Ibid., **20**, 164 (1904); Jour. Chem. Soc., **89**, 1399 (1906).
[7] Proc. Chem. Soc., **29**, 75 (1913).

tric and hydrochloric acids of Kahlbaum. Gold was precipitated from the pure chlorine of gold solution prepared from the above crude solution by means of Kahlbaum's pure oxalic acid. The solutions of gold chloride and oxalic acid were kept at a temperature of 80° C in order to get a good precipitate of gold. The gold so precipitated was washed free from impurities with distilled water and was subsequently dissolved in aqua regia again. The crystallised gold chloride, after it was rendered free from impurities, was dried for a few days at a temperature of 110° C.

Finally, a number of glass bulbs attached to the main apparatus as shown in Fig. 1, were charged with the pure chloride of gold (about 15 gms) ready for use. When pure chlorine was required, these bulbs were heated one by one. As the bulbs were used, they were sealed off the main apparatus.

### Apparatus and Working

The apparatus consisted of a series of gold chloride bulbs fused to the main apparatus at A as shown in Fig. 1. A number of stop-cocks at $S_1$, $S_2$ . . . . were used with phosphoric

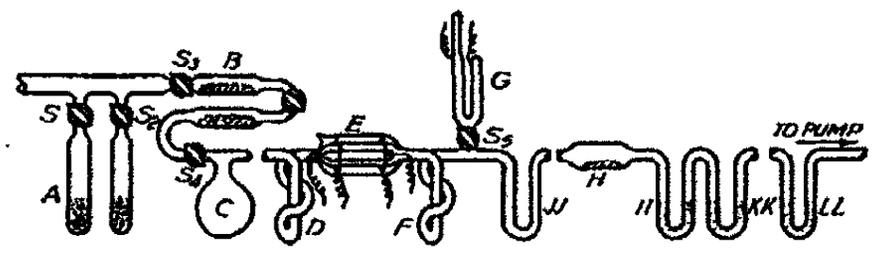



Fig. 1

acid. B were a set phosphorus pentoxide tubes to dry the chlorine. At C were fused four one-litre flasks. The flasks could be heated to 200° C by means of an electrical heater. D was a spiral of glass-tube kept cool by a freezing mixture. E was a vacuum-type ozoniser about 50 cms in length. The diameter of the inner tube of the ozoniser was 2.5 cms, while the ozonising space between the tubes was 3 mm in width. The ozoniser was worked by a powerful induction coil whose

primary could be fed up to 25 amperes with a Wehnelt interrupter as a make-and-break arrangement.

Sometimes, Leyden jars with a spark-gap were used in parallel with the ozoniser with little success. F was another short coil of glass tube kept in ice-water to cool the gas from the ozoniser. G was a small tin-foil ozoniser which could be worked with a two-inch induction coil, in which ozone could be prepared. H was a small test-chamber. JJ were U-tubes kept in freezing mixture at — 25° C II, KK, LL were phosphorus pentoxide, caustic potash, and calcium chloride tubes. A slow current of chlorine was sent through the apparatus either by using vacuum pumps or by making use of the electrical heater.

Chlorine was generated by heating the gold chloride bulbs one by one as necessity demanded. The whole apparatus was swept with dry chlorine for a number of hours preliminarily exhausting the whole apparatus. Finally, before the chlorine gas was stored, the whole apparatus was exhausted and filled with chlorine a number of times. The hot gas from the storing vessels was passed for a long time to rid the apparatus of its moisture and then the gas was stored.

When the activation of chlorine was going on a number of reagents were used to test its activity.

### Properties of Activated Chlorine

(1). Active chlorine combines directly with ozone[1] to form $Cl_2O$. As the active gas was passing through the apparatus, the tin-foil ozoniser was set in action, which supplied a good stream of ozone. The $Cl_2O$ which was formed by the interaction of active chlorine with ozone, condensed as reddish brown droplets in the U-tubes in the freezing mixture. At this stage the primary of the induction coil was consuming 20 amperes. Decrease in the secondary current meant, only a decrease in the production of $Cl_2O$ which meant a decrease in the amount of the active gas formed.

[1] Rendiconti Akad. Sci. Fis. Mat. Napoli, 15, 15 (1909).

The author could not confirm the result of E. Comanducci who says that the compound produced by the interaction of ozone and active chlorine is $ClO_2$. In the present researches it was found that the reddish brown droplets dissolved in water forming a yellowish solution. In order to get big droplets a run of nearly 40 hours was also made.

(2) The active gas when passed over cold powdered sulphur attacks it directly with the formation of $S_2Cl_2$. Sulphur was put in the test tube. $S_2Cl_2$ condensed in the U tubes as yellow oily drops. The drops dissolved in water giving rise to S, $SO_2$ and HCl. A run of nearly 20 hours was made.

(3) Active chlorine combines with fine tellurium powder at a slightly elevated temperature giving rise to tellurium dichloride which can be decomposed by water with the separation of tellurium and the formation of HCl and $H_2TeO_3$. A run of 32 hours was made.

(4) Bright metallic sodium and silver were attacked by the active chlorine.

(5) Carbon in no less than six varieties was presented to the action of the active gas but with no reaction.

(6) Active chlorine attacks benzene and acetic acid even in the dark with the formation of benzene hexachloride and chloro-acetic acid. In both these cases such reactions are possible only in the sun-light.

## II. Activation of Chlorine by the Electrical Discharge

Activation of chlorine by the electrical discharge was carried on in an ordinary type of vacuum tube with aluminium electrodes. The capillary tube was 5 mm in diameter and the length of the vacuum tube was 50 cm. The chlorine gas was passed through the tube at 20 mm pressure. It was found that an increase in secondary current resulted in the increased production of the active gas. The maximum secondary current that was utilized was 40 milli-amperes. In this case also the presence of active chlorine was detected by the above-mentioned tests. The production of the active

gas appeared to take place in a shorter time than in the above silent-electric-discharge method, as in no case was a run made of more than 30 hours.

### III. Activation of Chlorine by Ultra-violet Light

The activation of chlorine was carried on in a quartz tube placed between two parallel rows of iron arcs three inches apart. Each row contained five automatically adjusted arcs three inches apart, connected in parallel, and each supplied with a current of 6 amp. The whole system was enclosed in a brightly polished nickel-plated iron box, kept in a cooling bath of ice-cold water continuously running in and out. A rapid current of cold air was continuously drawn through the box. Occasionally the arcs were rendered free from any coating of iron oxide. The quartz tube was $^3/_4$ in. in diameter and about 16 inches in length. Through the tube a slow current of pure dry chlorine was passed. The presence of active chlorine was tested as before. Here also a very long time elapsed before the presence of the active gas was detected. Runs covering a period of 32 hours were made.

### (IV). The Thermal Production of Active Chlorine

Since it is known that even active chlorine has no action on carbon, it was found convenient to establish an arc between two carbon electrodes in an atmosphere of chlorine. For this purpose an arc was maintained in a glass globe between two carbon electrodes. One of the electrodes (negative) was bored through and a current of chlorine was led into the arc. The chlorine was drawn off through a side tube attached to the globe, through a coil kept in ice-cold water, and to the reagents. By this method also chlorine could be rendered active. No doubt this is not purely a thermal effect.

### Activity of Chlorine

The question now remains whether, the activity of the new chlorine is due to an allotropic modification of the element or to ions. The view that the activity of the gas is

due to ions, produced by the various modes of energy, is precluded by the fact that the gas remained as active as ever whether it was made to pass through a strong electrostatic field or not.

The activity could not have been due to any complex compound formed in the process of the activation of chlorine as suggested by Mellor and others, because the gas was dried thoroughly by phosphorus pentoxide before activation and consequently was free from moisture.

The activity of the gas might be due to atoms (nascent chlorine) or to some complex molecules. If the activity is due to atomic chlorine one should expect an expansion in volume when ordinary chlorine is activated, but on the other hand if any complex molecules are formed during the course of activation, a contraction in volume is to be expected. The experimental results described below appear to lend support to the latter rather than to the former view.

## Contraction in Volume

In order to measure the contraction in volume, the author had recourse to the silent-electric-discharge method as it is liable to less errors than the other methods. For this purpose an ozoniser with a side tube as shown in Fig. 2 was adopted.

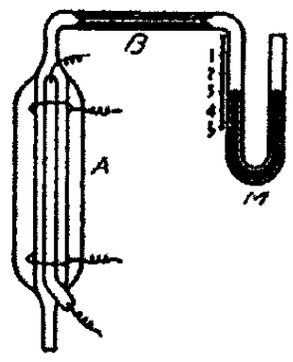


Fig. 2

A was a vacuum type of ozoniser. B was a capillary tube attached to it, which in its turn was attached to another capillary manometer M graduated to tenths of a millimeter. B is 0.5 mm bore while M was 5 mm in diameter. The manometer contained pure dry mercury. It was shown by Shenstone that pure dry chlorine has no action on pure dry mercury. In the present arrangement there is little chance for the active gas to come in contact with the dry mercury through the capillary tube B.

Keeping the chlorine, in the ozoniser at atmospheric pressure, it was found that in 10 hours a contraction of nearly 8

mm in the manometer had occurred. The temperature of the ozoniser was kept at constant temperature, by means of a thermostat. After the ozoniser was stopped from working the mercury regained its original position in the manometer. This clearly shows that when chlorine is activated, a complex molecule is formed, and that the activity of the new gas may safely be traced to it. The nature of the complex body is yet to be determined.

We do not know at present how the different forms of energy—electric, actinic and thermal—act to produce this complex active gas. It seems certain, at any rate, that there exists an allotropic modification of chlorine.

## Summary

1. It is shown by the author that chlorine is rendered active by the silent electric discharge, electric discharge, ultra-violet light and by heat.

2. In chemical properties this new gas is shown to be much more active than the ordinary chlorine. It combines with ozone to form $Cl_2O$, with S to form $S_2Cl_2$, with tellurium to form $TeCl_2$, with bright sodium and silver to form NaCl, and AgCl, with benzene in the dark to form $C_6H_6Cl_6$.

3. It is unstable and is decomposed above 50° C.

4. Chlorine contracts in volume when it is activated.

5. It is clear from the above researches that there is an allotropic modification of chlorine.

Further work on the subject is now being carried on by my friend Mr. M. V. N. Swami. My best thanks are due to Prof. Y. Narasinhan, M.A., for the kind interest he has taken in the work.

*Calcutta*
*July 2, 1922*

# DYEING OF CHLORINATED WOOL

BY J. R. ADAMS

Since 1848 it has been a well known fact, that the treatment of wool with bleaching powder and hydrochloric acid[1] has a marked effect on the dyeing qualities of the wool. John Mercer noticed that wool thus treated was much more receptive to colour. He concluded that this increase in the adsorbing power of the wool arose from the presence of some deoxidizing agent in the fibre. Although this fact is made use of to a large extent in the industries for certain classes of dyeing, very little actual work has been done to clear up the subject. The following investigation has been carried out in order to give some light on the subject, by means of quantitative experiments on the dyeing of both chlorinated and untreated wool with characteristic acid dyes.

The wool used in these experiments was ordinary white sweater yarn as obtained on the market. In order to have the wool as clean as possible it was first washed in a weak soap solution, after which it was rinsed several times in boiling water. It was hung in the air to dry and, after drying, it was kept in an atmosphere of constant humidity.

The chlorination process was carried out in the following manner. Sixty grams of yarn were taken and allowed to stand in a cold hydrochloric acid bath for twenty-five minutes. This bath contained 19.38 cc of hydrochloric acid, sp. gr. 1.2, in two litres of distilled water. The wool was removed from this bath and allowed to drain, after which it was treated in a cold clear solution, containing eight grams of bleaching powder to one litre of water, for twenty minutes. The wool was again drained and immediately allowed to sour for forty minutes in the hydrochloric acid bath. After this treatment

[1] Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 56, 151 (1910); Matthews: "Application of Dyestuffs," 55 (1920).

the wool was dried thoroughly and was then ready for use. At this point the wool had a glossy appearance and was decidedly acid.

The typical acid baths used, were Orange II (duPont) and Lake Scarlet R (National Aniline and Chemical Co.). The following factors were kept constant throughout the runs: Volume of bath = 250 cc; milligrams of dye used = 75; amount of wool dyed = 1 gram; time of dyeing = 45 min.

In each case the bath was prepared and brought to a boil. The wool was then added, allowed to remain for the forty-five minutes, and then removed while the bath was still boiling. The final dye concentration of the bath was determined by the direct titration with titanium chloride as described by Knecht.[1] The pH values of the bath were determined in accordance with the method of Lewis, Brighton, and Sebastian,[2] using a hydrogen electrode.

The data obtained on the adsorption of the dyes by the chlorinated wool have all been compared with the adsorption isotherms for untreated wool. These latter curves were worked out by A. W. Bull in this laboratory.

TABLE I

Dyeing of Chlorinated Wool with Orange II

| Cc of N/10 electrolyte | pH end | Mgs dye adsorbed | Mgs dye left in bath |
|---|---|---|---|
| 5 HCl | 2.55 | 62.51 | 12.49 |
| 3 | 2.72 | 61.04 | 13.96 |
| 2 | 2.78 | 59.2 | 15.8 |
| 1 | 2.94 | 57.36 | 17.64 |
| 0.5 | 2.98 | 55.95 | 19.05 |
| 0 | 3.2 | 54.42 | 20.58 |
| 1.5 NaOH | 3.85 | 40.69 | 34.31 |
| 2.5 | 4.74 | 24.29 | 50.71 |
| 3 | 5.03 | 15.1 | 59.9 |
| 4 | 6.43 | 0.77 | 74.23 |

[1] Ber. deutsch. chem. Ges., **36**, 1552 (1903); **40**, 3819 (1907).

[2] Jour. Am. Chem. Soc., **39**, 2250 (1917).

**Stripping Action of Sodium Sulphate**

| Cc N/10 $H_2SO_4$ | Cc N/10 $Na_2SO_4$ | pH end | Mgs dye adsorbed | Mgs dye left in bath |
|---|---|---|---|---|
| 1 | 24 | 3.05 | 39.72 | 35.28 |
| 10 | 15 | 2.45 | 50.75 | 24.25 |

TABLE II

Dyeing of Chlorinated Wool with Lake Scarlet R

| Cc of N/10 electrolyte | pH end | Mgs dye adsorbed | Mgs dye left in bath |
|---|---|---|---|
| 5 HCl | 2.73 | 71.25 | 3.75 |
| 3 | 2.91 | 67.9 | 7.1 |
| 2 | 3.05 | 64.38 | 10.62 |
| 1 | 3.23 | 62.5 | 12.5 |
| 0.5 | 3.3 | 59.38 | 15.62 |
| 0 | 3.5 | 58.13 | 16.87 |
| 1.5 NaOH | 3.96 | 47.5 | 27.5 |
| 2.5 | 4.3 | 15.63 | 59.37 |
| 3 | 4.62 | 12.5 | 62.5 |
| 4 | 5.76 | 1.3 | 73.7 |

Stripping Action of Sodium Sulphate

| Cc N/10 $H_2SO_4$ | Cc N/10 $Na_2SO_4$ | pH end | Mgs dye adsorbed | Mgs dye left in bath |
|---|---|---|---|---|
| 1 | 24 | 3.27 | 51.63 | 23.37 |
| 10 | 15 | 2.55 | 60.0 | 15.0 |

**Summary**

Curves have been drawn, plotting milligrams of dye adsorbed against pH values. On comparing the adsorption curves of chlorinated with ordinary wool, we find that they lie very close together, any difference being within the experimental error. It appears from these results that the chlorination has no marked effect on the adsorption of dye. It is probable that the reason for the brightness of the dyed sample,

which some have observed, was the increased glossiness of the wool after chlorination, and possibly the presence of acid in the wool.

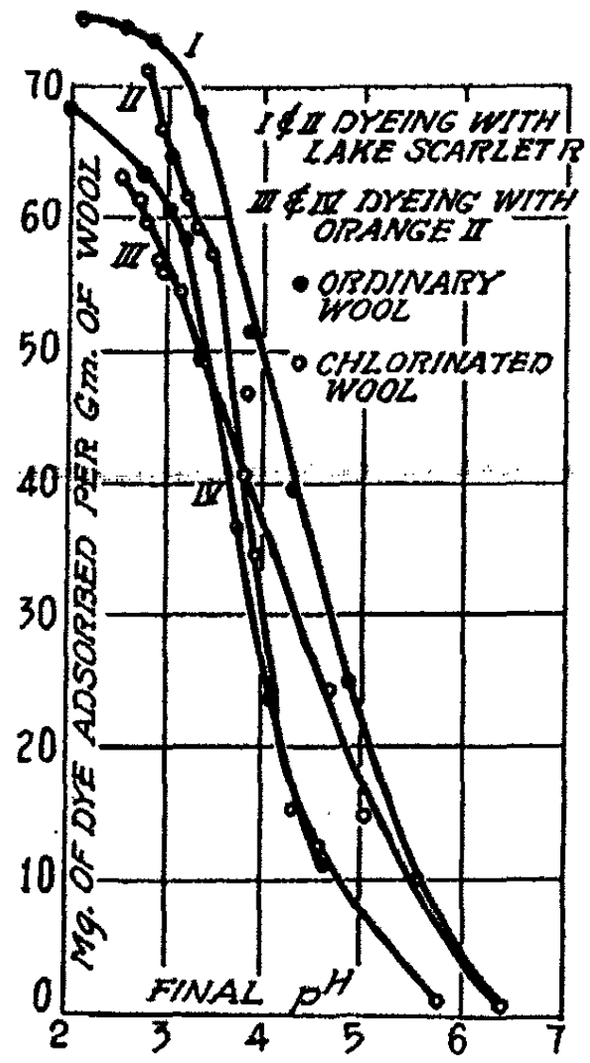



Fig. 1

This work has been carried out under the direction of Professor Bancroft, and was made possible by a grant from the Chemical Foundation.

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# NEW BOOKS

**A Dictionary of Applied Chemistry.** *By Sir Edward Thorpe. Vol. III, Revised edition. 22 × 16 cm: pp. viii + 735. New York and London: Longmans, Green and Co., 1922. Price: $20.00 per vol.*—The third volume includes such topics as: explosives; extraction apparatus; feeding stuffs; feldspars; fermentation; fertilizers; filtration; fire extinction; flame; flash lights; flint; fluorine; formaldehyde; fritts; fuels; furnaces; fusel oil; gadolinium; gallium; gas; gems; glass; glucinum; glucosides; glue; glycerin; gold; granite; graphite; guanidine; gums; gutta percha; hardened oils; helium; hydrazine; hydrogen; hydrogen peroxide; hydrolysis; indanthrene; indigo; iodine; iridium; iron; kermes; ketones; krypton.

On p. 5 it is stated that "an electrical charge causes sulphur to ball together and interferes with the grinding." This seems very improbable. Electrification should act in the opposite way. The statement here made is not confirmed by American practice. On p. 64 is the statement that collodion cotton, or soluble nitrocotton, "is looked upon at the present time as a mixture, in varying proportions, of the di-, tri-, tetra-, and penta-nitrocelluloses of Eder's classification." This is a true statement; but it is a sad commentary on our scientific methods that after all these years we do not know how many nitrocelluloses there are and have no means of determining the constituents of any nitrocotton.

Under explosives, p. 83, is an interesting paragraph on the theory of detonators. "The property of detonating another explosive does not depend merely on the violence of an explosive, for Abel found that 0.32 gram of mercury fulminate would detonate guncotton, whereas ten times the weight of the more violent nitrogen chloride was required. To explain the value of an explosive in initiating detonation in other explosives, Abel advanced his theory of wave synchronism or sympathetic vibration. Wöhler and Matter in the case of mercury fulminate, attributed its value as a detonant to the pressure produced by the kinetic energy of the molecules, that is, that it is due primarily to the rate of detonation and density of the fulminate, and secondarily to the gas volume and heat evolved. Nobel attributed this property of fulminate to the very intense shock or pressure instantaneously set up on its explosion, and Berthelot, as mentioned when considering the properties of mercury fulminate, adopted the same view, but also called attention to the contributing fact that the products of explosion undergo little, if any, dissociation. It is certain that velocity of detonation and power, or total energy, alone do not determine the value of an explosive as a detonant, otherwise nitroglycerin and blasting gelatin would have greater, instead of far less, detonating value than mercury fulminate, and mercury fulminate would have greater value than its admixtures with an oxidizing salt. It is probable that all these factors are contributory to the property of initiating detonation, and considering the high value of this property of silver, mercury, and lead compounds, fulminates, azides, picrates, and acetylides, it still seems that Abel's original theory, or something analogous to it, is not entirely to be neglected."

On p. 119 we read that "bodies of the cellulose type, which resist the solvent treatments referred to, are to a variable extent partially digestible, especially by ruminants. This digestion is probably mainly effected by the action of bacteria in the large intestine. A ruminant can digest much more cellulose than a horse, and a horse much more than a pig. The very thorough mastication of the ruminant prepares the fibre better for such digestion as is possible than does the imperfect mastication of the horse or the still more imperfect mastication of the pig, apart from the anatomical differences in the digestive tracts of the respective animals and the relative abundance of bacteria capable of effecting cellulose digestion."

On p. 153 there is a statement in regard to the chemical changes involved in alcoholic fermentation. "Many theories have been advanced as to the stages which may be supposed to intervene between glucose and the final products of its decomposition—alcohol and carbon dioxide. Baeyer, in 1870, pointed out that the alternate removal and readdition of the elements of water might lead to an accumulation of oxygen on certain of the carbon atoms, and thus render the rupture of the carbon chain possible. Wohl has proposed a modification of this idea, which leads to the supposition that loss of water and intramolecular change result in the formation of a ketoaldehyde which undergoes hydrolysis to methylglyoxal and glyceraldehyde; the latter of which by a similar series of changes, also forms methylglyoxal $CH_3COCHO$. This then passes into lactic acid, and this into carbon dioxide and alcohol. This theory received a certain amount of experimental support from the fact that small quantities of lactic acid appear to be fermented by yeast juice (Buchner and Meisenheimer). The idea of the occurrence of lactic acid as a true intermediate product of alcoholic fermentation has, however, now been abandoned, largely owing to the criticisms of Slator, who pointed out that this substance should be fermented at least as quickly as glucose, and that this is not the case. The same criticism is valid against many of the 3-carbon compounds which have been proposed as intermediate products, including glyceraldehyde and dihydroxyacetone, both of which are slowly attacked by yeast, while dihydroxyacetone is also readily fermented by yeast juice prepared by maceration (Lebedev).

"The universal presence of carboxylase in yeasts capable of producing alcoholic fermentation creates a strong presumption that the decomposition of pyruvic acid actually forms a stage in the alcoholic fermentation of sugars. The fact that the evolution of carbon dioxide from pyruvic acid commences instantly, whereas there is a considerable delay in the case of glucose is interpreted to mean that the glucose undergoes a preliminary change which requires some time and results in the formation of pyruvic acid capable of immediate decomposition. Other explanations of this delay, which is by no means invariable, can, however, be given. A number of observations have also been made by Euler and his school which have led him to the same conclusion, that some intermediate product is formed before the production of alcohol and carbon dioxide."

Under fire extinction there is no mention of Foamite and the article on flames might have been written fifteen years ago. On the other hand, Argo's work on fluorine is cited. In view of the importance of fluor-spar for apochromatic lenses, p. 234, one wonders why suitable material could not be made synthetically.

As an instance of adsorption we may cite the removal of fusel oil from spirit,

p. 291. "The most approved method of separation, however, is by well-burnt granulated vegetable charcoal or bone-black. The charcoal is placed upon perforated trays in a vessel surrounded by a cooling jacket, and the spirit, usually diluted to about 160° Tr., is caused to pass through several layers. The operation should not be performed above the ordinary temperature, as the fusel oil is again dissolved from the charcoal near the boiling temperature. From 3 to 5 vols. of charcoal are required for the successful treatment of 100 vols. of brandy. The whole of the fusel oil is evolved from the charcoal on treatment by superheated steam, and the charcoal may be repeatedly used after heating to redness to drive off the occluded gases, etc. It is noticeable that the fusel oil obtained by steaming the charcoal does not represent the whole of that removed from the spirit, nor are sufficient compounds which might be produced by the decomposition of the fusel oils found to account for this loss."

It is rather staggering to read, p. 374, that the principal flavoring ingredients used for gin besides juniper are "angelica root, almond cake, calamus root, cardamon seeds, cassia buds, coriander seeds, creosote, liquorice powder, orris root, sweet fennel, and turpentine.....Plymouth gin is a special variety of gin made in Plymouth, and used extensively in the West of England. It has a characteristic flavor, said to be due to ether resulting from the addition of a little sulphuric acid to the spirit to be rectified." After this it is comforting to learn that the adulteration of gin, except by dilution with water is not common, though alum and salts of lead and zinc have sometimes been found.

On p. 402 we read that "the frequent association of phosphatic nodules with glauconite deposits has some bearing on the origin of glauconite. The terrigenous deposits of green mud and sand formed on the floor of the ocean at depths of about 200 to 1000 fathoms, and found by the Challenger Expedition to be of wide distribution, particularly off continental coast lines composed of igneous rocks, contain this mineral in considerable amount. The potash set free by the weathering of the feldspars and micas of these rocks and carried into the sea is conserved by the formation of glauconite, but apparently only through organic agencies, which at the same time gave origin to the phosphatic nodules. Grains of glauconite are frequently found filling the chambers of foraminifera and other organisms; and in the artificial production of the mineral the presence of an organic acid seems to be essential." *Wilder D. Bancroft*

**The Chemistry and Technology of Gelatin and Glue.** *By R. H. Bogue. 23 × 16 cm; pp. xi + 641. New York: McGraw-Hill Book Company, 1922. Price: $6.00.*—There is an introductory chapter on historical and statistical considerations, after which come five chapters on the theoretical aspects, entitled respectively: the constitution of the proteins; the chemistry of gelatin and its congeners; the physico-chemical properties and structure of gelatin; gelatin as a lyophilic colloid; gelatin as an amphoteric colloids. The second part of the book deals with the technological aspects, the sub-heads being: the manufacture of glue and gelatin (written by Ralph C. Shuey); water-resistant glue and glues of marine origin; the testing of glue and gelatin; the chemical analysis, detection, and estimation of gelatin and glue; the evaluation of glue and gelatin; the uses and applications of glue; the uses and applications of gelatin.

It will perhaps be well to discuss some of the weak points of the book

first and then we can take up the really interesting things. Perrin worked with gamboge and not with gutta percha, p. 105. Under foamite, p. 554, the aluminum sulphate has been forgotten. So far as the reviewer is concerned, a semipermeable membrane is not an ultra-filter, p. 141. The fact that the swelling of gelatine in water is accompanied by an evolution of heat, p. 164, is scarcely a conclusive proof of the existence of solvates, p. 193. On p. 223 we read that acids combine with deaminized gelatine to nearly the same degree as with untreated gelatine. The author draws the conclusion that "as there can be no terminal amino groups in the deaminized product, it is obvious that the acid reacts with some internal groups." This conclusion is necessary and obvious only in case one insists on postulating a definite compound.

The reviewer noted with pleasure the fact that the adsorption of gelatine by glass is made use of technically, p. 538. "Frosted glass is a form of glass that is much used in the doors and partitioning windows of offices where privacy is desired. It is made by allowing a glue or gelatin to dry out rapidly upon a plate of ordinary rather thick glass. As the glue loses its moisture it contracts, and the power of the gelatin is so great it tears away the surface of the glass itself, chipping it into characteristic fern-like patterns. The general appearance of the design can be modified by varying the properties of the glue used; i. e., a brittle glue will give a different pattern from a tough glue, and the addition of salts also modifies the patterns. A strong gelatin solution containing six percent of alum gives exceptionally fine designs."

The following passages interested the reviewer, pp. 49, 90, 355, 288, 466, 499, 491, 518.

"In plant physiology the principal structural material producing turgor and rigidity is cellulose, a highly polymerized carbohydrate. In the animal a protein, often fortified by inorganic salts, serves in this capacity. Among the invertebrates the hard shell-like coverings are composed largely of a protein called chitin. In the vertebrates the protein material of the bones and of the several connective tissues is a mixture of several proteins, the most important of which is collagen. The organic material of the bones, the tendons, the cartilage and the skin, is to a great extent comprised of collagen. When this collagen is obtained from different tissues it is found to vary slightly in its composition and this has led some writers to regard it not as a definite chemical compound, but rather as a mixture the composition of which is variable within certain limits. When collagen is heated in water to 80° or 90° C, it is converted slowly into the protein gelatin. This conversion would be greatly accelerated if the temperature of the water were raised to or above the boiling point (under pressure) or by the use of dilute acids, but such a procedure would in turn, result in a further hydrolysis of the gelatin, as soon as it was produced, and so greatly lessen the yield and quality of the product."

"The sounds, or air bladders, or swimming bladders, as they are variously called, consist almost entirely of collagen, and have the additional advantage of being exceptionally free from other impurities which might be dissolved out upon heating with water. They also differ from other varieties of collagen in being more readily soluble in warm water than any other type. On account of this unusual purity and the consequent very high quality of the gelatin obtained from them, they have been used for a great many years in the preparation of what

is known as isinglass. Many varieties of fish have been used in the preparation of isinglass. The most notable of these is the sturgeon, it being the first fish to be used extensively for commercial isinglass, and its product is still the standard upon which all others are based. It is made up in several ways, which will be described later, and large amounts are still exported from Russia. Catfish and carp also contribute to the Russian product. Many other countries produce sounds, usually of somewhat inferior quality to the Russian. Cod and ling sounds are obtained from Iceland, cod sounds from Norway, miscellaneous types from Venezuela, Brazil, Penang and Bombay. In America, especially in the Canadian waters, sounds are obtained mainly from the hake, cod, squeteague, and more recently the tilefish."

"One of the oldest and best established uses of isinglass is as a clarifying agent for various beverages, as wine, cider and malt liquors. The efficacy of the isinglass for this service lies in the purely mechanical property it possesses of maintaining a fibrous structure in the solution, and as this settles slowly to the bottom it entangles in its net-like meshes the colloidal bodies that produce the undesirable turbidity. For clarifying wine the isinglass is first swollen in water and then in the wine until it is completely swollen and transparent. It is then thoroughly beaten into a small amount of the wine, strained through a linen cloth, and stirred into the rest of the wine. The temperature is kept low and the isinglass does not go into solution, but only into a very finely divided suspension. Thus the original fibrous structure of the sounds has at no time since it came from the fish been lost. In this lies the difference in the action of isinglass and gelatin for fining. If isinglass were heated and made into a true gelatin it would then have lost the properties which make it so valuable for this service. A single ounce of isinglass will clarify, under the optimum conditions, 500 gallons of wine in 10 days. In the manufacture of beer and ale the starch granules, bacteria, and protein matter, which do not settle in the tanks after the primary fermentation are gotten out by either filtration, adsorption upon wood chips, or fining. In the latter procedure the isinglass is treated with sour beer and, after swelling, macerated as in the fining of wine. After straining it is mixed thoroughly with the rest of the beer. One pound of isinglass will fine from 100 to 500 barrels of beer."

"The mucinous impurities carry nearly the same electrical charge on their colloid particles that gelatin particles carry. On this account the protective action of the gelatin narrows very greatly the limits within which good filtration can be accomplished. The substances to be filtered out appear all to be negative, and the use of fuller's earth which is strongly negative does not improve appreciably the appearance of the glue. On the other hand, if alumina, a strongly positive substance, is used, the liquor will run clear but the filter will block almost immediately. Charcoal is almost neutral and will produce successful filtration for a considerable time. However, the filtering substance preëminent for this purpose is cellulose. Being very slightly negative it holds the particles without holding the glue, and although the actual surface per unit volume is probably much less than with charcoal, the filters are so constituted that they will hold a maximum amount of precipitate before blocking. A convenient form of cellulose is a good grade of cotton paper pulp. Many different forms of filters for holding such pulp are obtainable, but those allowing for a loose packing of the pulp on the

intake surface will provide a matte of considerably longer life than if the filter matte is required to be densely packed throughout.

"Although certain liquors can be filtered perfectly bright, many of them will cloud on cooling and practically all of them cloud on concentrating. To remove this precipitated or precipitable material and thus obtain a brilliant gelatin it is necessary either to produce a colloidal coagulation or to cause the formation of a precipitate or aggregate which will collect and hold by forces allied to adsorption the objectionable substances."

"A study of the gelatin-tannin reaction was made by Trunkel in 1910. He found that 1 gram of gelatin required 0.7 gram of tannin for compiete precipitation when used in a freshly prepared condition, but after the gelatin solution had stood for 24 hours only 0.4 gram of tannin was required. If the latter solution is warmed, however, it regains its former power to precipitate tannin. Where the gelatin and the tannin are both precipitated quantitatively, the precipitate resists decomposition by water, but with an excess of tannin a precipitate may be obtained, containing 3 tannin to 1 gelatin which, however, yields up tannin on treatment with water. By repeated extraction of the precipitate with alcohol, up to 96 percent of the tannin may be removed, but in no case can the precipitate be entirely resolved into its constituents. Only about 6 percent of unaltered gelatinizable gelatin may be extracted from the residue. The action of alcohol leads Trunkel to believe that the precipitation of gelatin by tannin is an adsorption process."

"Our discussion has shown, therefore, that both the gelatin content of a glue or gelatin, and also the joint strength of a glue, may be correctly indicated by a melting point determination, while neither may be correctly assumed to be, in all cases, proportional to either the jelly consistency or the viscosity at 60° C alone. Inasmuch as the primary evaluation of the material should be based upon some fundamental and scientifically selected property or properties, it seems that gelatin content and joint strength should be chosen. It is especially happy that these two properties are parallel. Since the melting point has been shown to indicate the gelatin content and the joint strength, it seems that this determination, either directly or indirectly made, should be selected as a measure of the fundamental constitution and properties of the material. The measurement of the viscosity of an 18 percent solution, dry basis, at 35° C, by means of the MacMichael viscosimeter has been shown to be especially well adapted as an indirect estimation of the differentiation of glues and gelatins in the order of their melting points, and is accordingly recommended as the basis for the primary evaluation of these products."

"The secondary basis for glue or gelatin evaluation lies in many or few other tests which are employed to determine the application of the material for any special service. For example, where the glue is to be used in mechanical spreaders, the tendency to foam is undesirable, and the foam test indicates this tendency. If the glue be applied by hand, the foam test is of little or no significance. If the glue is for use on paper as a size or wall paper as a binder for the clay filler, grease should not be present in large amount, as otherwise little droplets of this substance form, making elliptical 'eyes' or spots on the paper. In admixture with certain dyes the presence of acid or of alkali is not permissible as the dye would be affected in one way or another. Suitable tests must accordingly

be made upon glues designed for such purposes. Gelatin for use in photographic films or in printing rollers must have high jelly strength; if used for food or medicinal purposes it must be free from harmful impurities; if used in making marshmallows or other emulsions, a high viscosity and foam are desirable. Such a list could be extended greatly, and the adaptability of any glue or gelatin for its several uses is determined largely by such secondary tests."

"Among the factors which have been found to influence the strength obtainable in a glued joint, made with any given glue, are the following: the concentration of the glue solution; the time occupied and temperature employed in heating the glue; the temperature of the glue when applied; the species, density, porosity, and moisture content of the wood used; the trueness of the joint; the amount and method of application of the glue in the joint; the temperature of the wood when glue is applied; the rapidity of handling; the pressure applied to the joint, and its uniformity of distribution; the time under pressure, and time of curing; the temperature and humidity during curing; the method of breaking the joint; the hydrogen-ion concentration of the solution."

People have claimed that too much pressure must not be used in gluing surfaced wood, as the glue may be pressed out too completely from the joint, producing a so-called starved joint; but the author concludes, p. 524, that "as the layer of glue between the wood pieces is made vanishingly small, the strength of the joint will approach its maximum value. The bond between the two pieces of wood should consist only of the vertical and interlaced threads of glue passing from the pores in one piece to the pores in the other. If this is the case, and we seem justified in making that conclusion, then it must follow that, provided the glue is properly applied, and in a condition such that a fair degree of penetration results, there can be no such an effect as a 'starving' of a joint, and no such thing as too much pressure, as far as the glue is concerned. The advantageous results realized by high pressures can be explained only upon the assumption that such pressures are necessary to squeeze out the maximum amount of excess glue in the joint, and to minimize any slight inequalities in the perfection of the joint."

*Wilder D. Bancroft*

**Catalysis in Organic Chemistry.** *By Paul Sabatier. Translated by E. Emmet Reid. 23 × 16 cm; pp. xxiv + 406. New York: D. Van Nostrand Company, 1922. Price: $5.00.*—The German translation of the first French edition was reviewed eight years ago (**19**, 78). We now have what purports to be the English translation of the second French edition; but which is really a good deal more than that, because Professor Reid has added a number of valuable footnotes which bring the book more up-to-date. These additions are the more valuable because they refer in great part to work done in this country.

The headings of the chapters are: catalysis in general; on catalysts; mechanism of catalysis; isomerization, polymerization; depolymerization, and condensations by addition; oxidations; various substitutions in molecules; hydration; hydrogenation (5); various eliminations; dehydrogenation; dehydration (3); decomposition of acids; decomposition of the esters of organic acids; elimination of halogen acids or similar molecules; decomposition and condensation of hydrocarbons; hydrogenation of liquid fats.

The book is a store-house of facts and problems. In the following para-

graph, p. 114, one would like to know whether there is any relation between the amounts of iodine converted into hydriodic acid and to nickel iodide.

"In an apparatus in which the hydrogenation of benzene was progressing regularly over nickel at 180°, the benzene was replaced by benzene containing 0.5% iodine. The hydrogenation continued for several hours with an excellent yield. The escaping hydrogen, after the condensation of the cyclohexane, disengaged abundant fumes of hydriodic acid showing that the iodine had been hydrogenated by the catalyst. The operation was interrupted after 130 g of cyclohexane had been collected and it was found that the nickel had combined with iodine in the first half only of the tube. This half was incapable of carrying on the hydrogenation but the other half was unhurt. The poisoning of the metal by the iodine had taken place only slowly and step by step; the hydriodic acid had had on its own account, no harmful effect and had not converted into the iodide the metal the surface of which was covered with an unstable hydride which produced the hydrogenation. Doubtless the fixation of the hydrogen on the iodine and the benzene in contact with the nickel is much more rapid than the reaction of the nickel with the iodine or with the hydriodic acid. As in the direct hydrogenation of unsaturated hydrocarbons, the metal protects itself, by its own action, against the permanent alteration which would render it inactive."

On p. 126 there is an interesting paragraph on regeneration. "Metallic catalysts poisoned by vapors of chlorine, bromine, iodine, sulphur, etc., are difficult to revivify except by dissolving in a suitable acid and working over completely. Calcination does not remove chlorine from slightly chlorinated nickel. The action of hydrogen reduces the chloride to the metallic state below 400°, but the resulting metal is in a peculiar fibrous state and is incapable of reducing benzene to cyclohexane. Even after oxidation and a second reduction it is a poor catalyst. It can be restored slowly to complete activity by employing it for some time in the reduction of nitrobenzene to aniline, work which poisoned nickel is still capable of doing. The aniline which is produced contains increasing amounts of cyclohexylamine. After some hours of this treatment the power of the metal to produce cyclohexane from benzene is restored completely. On the other hand, poisoning by bromine or iodine seems to resist this treatment."

On p. 341 we read that in the action of alcohols on esters, "sodium alcoholate is an even better catalyst than hydrochloric acid. In the transformation of methyl benzoate into the ethyl ester, sodium ethylate was found to be about four thousand times as efficient as an equivalent amount of hydrochloric acid."

It does not appear, p. 596, why vigorous stirring should be essential to hydrogenation. "Very extensive use has been made of the common metals, particularly nickel, for hydrogenation in liquid medium in the case of liquid fats the molecules of which contain ethylene bonds. The description of the methods followed and the results obtained is the special object of the last chapter but the same process can be generalized and extended to a large number of cases. The fundamental condition of success is a sufficiently energetic agitation in the hydrogen. A pressure of several atmospheres is useful but not indispensable, the hydrogenation being capable of being carried out even with reduced pressure. Simply bubbling the hydrogen through the liquid is not sufficient."

Sabatier distinguishes three reactions with esters, p. 861:

$CH_3CO_2C_2H_5 = CH_3CO_2H + C_2H_4$,

$2\ CH_3CO_2C_2H_5 = CH_3COCH_3 + CO_2 + C_2H_4 + C_2H_5OH$,

$2\ CH_3CO_2C_2H_5 = CH_3COCH_3 + CO_2 + 2C_2H_4 + H_2O$.

The reviewer has followed Sabatier's lead in this respect in the past; but he now thinks that it would be more profitable to consider these as different stages of the same reaction. The first stage would then be in all cases the formation of acid:

$CH_3CO_2C_2H_5 = CH_3CO_2H + C_2H_4$

The next stage would be

$CH_3CO_2H + CH_3CO_2C_2H_5 + C_2H_4 = CH_3COCH_3 + CO_2 + C_2H_5OH + C_2H_4$,

and the final stage would be

$CH_3CO_2H + CH_3CO_2C_2H_5 + C_2H_4 = CH_3COCH_3 + CO_2 + 2C_2H_4 + H_2O$.

The action of nickel on acetylene at 180° is apparently a triple one, p. 918.

1. Rapid decomposition into carbon and hydrogen with polymerization to aromatic hydrocarbons.

2. Slow condensation into a solid hydrocarbon doubtless identical with cuprene.

3. Hydrogenation of the acetylene and of the aromatic hydrocarbons with production of aliphatic, unsaturated and cyclo-aliphatic hydrocarbons.

All readers will be grateful to the translator for supplying forty-two pages of subject index. *Wilder D. Bancroft*

**The Properties of Electrically Conducting Systems.** *By C. A. Kraus. 23 × 16 cm; pp. 415. New York: The Chemical Catalog Company, 1922. Price:* $4.50.—"The purpose of the present volume is to present the more important of this material [relating to our conceptions of matter in the ionic condition] in a comprehensive and systematic manner, thus enabling the reader to gain a knowledge of the contemporary state of this subject without an undue expenditure of time and effort."

The subject is presented under the following headings: introduction; elementary theory of the conduction process in electrolytes; the conductance of electrolytic solutions in various solvents; form of the conductance function; the conductance of solutions as a function of their viscosities; the conductance of electrolytic solutions as a function of temperature; the conductance of electrolytes in mixed solvents; nature of the carriers in electrolytic solutions; homogeneous ionic equilibria; heterogeneous equilibria in which electrolytes are involved; other properties of electrolytic solutions; theories relating to electrolytic solutions; pure substances, fused salts, and solid electrolytes; systems intermediate between metallic and electrolytic conductors; the properties of metallic substances.

On p. 65 the author points out that "it will be observed that the ion conductance in ammonia and in water do not stand in a fixed ratio. For example, for the silver ion, the ion conductance in ammonia is 2.15 times that in water, whereas for the lithium ion the conductance in ammonia is 3.36 times that in water. Similiarly, the conductance of the bromide ion in ammonia is 2.54 times that in water, while the conductance of the bromate ion is 3.11 times that in

water. We may naturally inquire as to what are the factors upon which depends the conductance of different ions in different solvents.

"If the current is carried through a solution by the translation of charged particles of molecular dimensions, then we should expect the speed of these particles to be a function of the viscosity of the medium through which they move. It might be assumed, for example, that the conductance is proportional to the reciprocal of the viscosity, or to the fluidity of the solvent. This viscosity of water at 18° is $10.63 \times 10^{-3}$ and that of ammonia is $2.558 \times 10^{-3}$ at its boiling point. Consequently the fluidity of ammonia is 4.15 times as great as that of water. If the conductance of the ions were directly proportional to the fluidity of the solvent, then the conductance of all ions in ammonia should be 4.15 times as great as that of the same ions in water. We see, however, that while the conductance of the various ions in ammonia is markedly greater than that in water, nevertheless the ratio of the ion conductance in the two solvents is in all cases smaller than this value. Furthermore, the effect is one specific with respect to the individual ions. For example, for the sodium ion, the value is 3.0, while for the lithium ion it is 3.36. It is noticeable that the ratio for the ions increases in the order: ammonium, potassium, sodium, lithium. In other words, in ammonia the lithium ion possesses a relatively much higher conductance with respect to water than does the ammonium ion. . . .

"It is evident that the conductance of an ion is a function of the constitution of the solvent as well as of that of the ion itself. In this connection it should be observed that a given electrolyte dissolved in two different solvents does not necessarily yield the same ions. In other words, complexes may be formed between the ions and the solvent properties of which will depend upon the nature of the solvent. It is well known that certain ions tend to form complexes with certain solvents. For example, the silver ion forms a complex with ammonia even in aqueous solutions. It may be assumed, therefore, that the silver ion has a great tendency to form complexes with ammonia. The cause for the relatively low value of the conductance of the silver ion in ammonia may be ascribed to the formation of a relatively large complex silver-ammonia ion in ammonia solution. Similarly, those ions whose salts show a marked tendency to form complexes with water, which, for example, give stable crystalline hydrates, show a relatively higher speed in ammonia than in water. Thus, the speed of the lithium ion in ammonia is relatively much greater with respect to its speed in water than is that of the potassium ion. We may therefore conclude that the lithium ion is relatively less complex in ammonia than it is in water."

At higher temperatures the values of all transference numbers tend to approach one half, p. 124. "These results have an important bearing on our conceptions as to the nature of the conducting particles, particularly as regards the effect of temperature on the speed of these particles. As has been shown by means of transference experiments, the ions are hydrated in water. In order to account for the fact that the speeds of the different ions at higher temperatures approach one another, it might be assumed that the hydrates break down at higher temperatures, but this assumption would not be in harmony with certain facts. Since the conductance of the slowly moving ions changes in direct proportion to the fluidity of the solvent as the temperature increases, it is reasonable to assume that the relative dimensions of the ion complex remain practically

constant. If, therefore, the speed of the more rapidly moving ions approaches that of the more slowly moving ions at higher temperatures, it points to a slowing up of the more rapidly moving ions as the temperature increases. This corresponds to a greater relative resistance to their motion, which can only be interpreted as due to an increase in the dimensions of the ion-complex. In other words, as the temperature increases, the hydration of the more rapidly moving ions increases, which tends to reduce their speed relative to that of more slowly moving ions.

"If the hydration of the ions is due primarily to electrical forces acting between the ions, which are charged, and the surrounding solvent molecules, which have an electrical moment, then we should expect that, as the dielectric constant of the medium decreases, the size of the complex will increase since in a dielectric medium the force is inversely proportional to the dielectric constant. For this reason we should expect the relative speeds of ions in non-aqueous solvents of low dielectric constant to approach one another much more nearly than they do in water. This appears to be the case. Moreover, this is also in harmony with the fact that in the case of very large ions, in other words, in the case of ions which have a low conducting power, the conductance in different solvents, as well as different temperatures, is very nearly proportional to the fluidity of the solvent. We may conclude, therefore, that the hydration of the ions increases, or, including non-aqueous solvents, that the solvation of the ions increases with the temperature because of a decrease in the dielectric constant of the medium. It is not to be assumed, however, that the dimensions of the ions in different solvents are controlled entirely by the dielectric constant. The solvent may combine chemically with a given ion to form a complex, which ion in turn may have associated with it additional solvent molecules, due to electrical interaction between this ion and the solvent. We should expect this to be the case with silver ions which form an extremely stable complex with ammonia. Even in aqueous solutions, the silver ion forms a complex $Ag(NH_3)_2+$ with ammonia. This may account for the relatively low conducting power of the silver ion in liquid ammonia solution. Whereas, for example, the conductance of the lithium ion in ammonia is 3.36 times that of the lithium ion in water, that of the silver ion in ammonia is only 2.15 times that in water. So, also, we find that the ammonium ion in ammonia has a conductance of only 2.03 times that of the ammonium ion in water, indicating the formation of relatively large complexes. In this connection it may be pointed out that the ammonium salts form with ammonia saturated solutions whose vapor pressures are extremely low. For example, the vapor pressure of a saturated solution of ammonium nitrate in ammonia is one atmosphere at 26°."

The question of conductance near the critical point is an important one, p. 167. "Data relative to the ionization of solutions in the critical region are entirely lacking, for which reason it is not possible to interpret the results of conductance measurements with any degree of certainty. However, the conductance data indicate that the properties of solutions in the critical region do not differ materially from those of solutions at lower temperatures. Moreover, it appears that the property of forming electrolytic solutions is by no means confined to the liquid state of matter. Fluids above the critical point yield electrolytic solutions and even the solvent vapors themselves, below the

critical point, possess the power of dissolving electrolytes, forming solutions which conduct the current.

"It has already been pointed out that, as the critical point is approached, the conductance of solutions in solvents of low dielectric constant approaches a very low value, and the conductance-temperature curve if extrapolated would intersect the temperature axis at a temperature not far removed from the critical temperature. It is known, however, that, once the critical point has been reached, the conductance falls only very slowly with increasing temperature. In other words, the conductance-temperature curves exhibit a discontinuity in the immediate neighborhood of the critical point. As will be seen below, this behavior is what we should expect when conductance measurements are carried out in sealed tubes, where the total volume of liquid and vapor remains constant. In the immediate neighborhood of the critical point, the density of the solvent decreases very rapidly with increasing temperature, whereas beyond the critical region the density of the solvent medium remains fixed. The rapid decrease in conductance immediately below the critical point is to be ascribed to the rapid decrease in the density of the solvent medium.

"It is to be expected that the ionization and consequently the conductance of solutions in the critical region will be governed largely by the dielectric constant of the medium, and it may be inferred that those liquids, which under ordinary conditions exhibit a very high dielectric constant, will likewise exhibit a relatively high dielectric constant in the critical region. In the case of sulphur dioxide and ammonia the dielectric constant in the critical region is very low, whereas in the case of the lower alcohols and water a relatively larger value of this constant is to be expected. Water would be an ideal substance for the purpose of studying the properties of electrolytic solutions in the critical region, were it not for the difficulties attending conductance measurements in this solvent at high temperatures. These difficulties, however, disappear very largely in the case of the lower alcohols, although it is to be expected that the ionization in the critical region will be markedly lower in these solvents than in water. . . .

"According to the commonly accepted theory of electrolytic solutions, the change in the conductance of solutions as a function of the concentration is due to a change in the relative number of carriers; that is to a change in the ionization of the electrolyte. Because of various difficulties which have arisen in accounting for the properties of strong electrolytes, some writers have suggested that strong electrolytes in solution are completely ionized. The study of the properties of non-aqueous solutions and of solutions at higher temperatures yields no apparent support for such an hypothesis. If the salts in solvents of low dielectric constant are completely ionized, then it becomes exceedingly difficult to account, on the one hand, for the very low value of the conductance of these solutions at certain intermediate and low concentrations and, on the other hand, for the very rapid increase in the conductance of these solutions at higher concentrations. So, in the case of solutions in the neighborhood of the critical point, it is difficult to account for the rapid decrease in the conductance of the solution as the critical point is approached on the basis of this hypothesis. Again, in the case of solutions above the critical point, the large increase in the conductance of the solution as the concentration of the solvent increases is with difficulty accounted for on the assumption that the electrolyte is completely ionized,

unless, at the same time, an hypothesis is introduced according to which the speed of the ions through the solvent medium is enormously increased by an increase in the concentration of the solvent. For such an hypothesis there is an entire lack both of experimental facts and of theoretical support.

"On the other hand, if the fundamental elements of the usual theory of electrolytes are accepted, we are forced to the conclusion that the ionization of electrolytes is a complex function of the concentration and that, at very high concentrations, in the case of solvents of low dielectric constant, the ionization increases with the concentration. While theoretical support is lacking for this assumption, no theoretical principles are contradicted by such an hypothesis. Furthermore, if we assume that the ionization of electrolytes is a function of the concentration and is approximately measured by the conductance ratio $\Lambda/\Lambda_0$, the influence of temperature, of concentration, and of the viscosity of the solvent may be readily accounted for without contradicting known facts and without introducing any further hypotheses for which a theoretical foundation is lacking. In other words, on the basis of the ionization hypothesis, it is necessary to make only a single assumption whose correctness remains uncertain, whereas in the case of other hypotheses a number of assumptions are necessary. Unless other and more conclusive facts can be adduced in support of the hypothesis that the strong electrolytes are completely ionized in solution, this hypothesis is clearly untenable at the present time."

There are some unexpected phenomena in mixed solvents, p. 181. "The effect of adding water to a solution of hydrochloric acid in methyl alcohol is to decrease greatly the conductance of the solution and this effect is relatively independent of the concentration of the solute. It appears, therefore, that the ionization of hydrochloric acid is not materially affected by the addition of water, but that the speed of the hydrogen ion is reduced greatly. It is true that on the addition of water to methyl alcohol the viscosity is increased; but the viscosity change due to the small amounts of water added in the case of these solutions is inconsiderable and cannot account for the large decrease in the conductance of these solutions. Apparently, therefore, the change in conductance is due to a slowing up of the hydrogen ion, since it is known that the chloride ion is normal in its behavior in mixtures of alochol and water. The values given for the limiting value of the equivalent conductance are approximate, since the extrapolation function employed in determining these values is uncertain."

The author believes, p. 206, that "the hydrogen ion in water is, in fact, not a hydrogen ion, but an oxonium ion. Whether the charge is associated with the hydrogen or with the oxygen atom cannot be determined in this case any more than it can in that of the similar ammonium salts. It appears likely, however, that in salts of this type the charge is associated either with the oxygen or nitrogen atom, or with the group as a whole, rather than with one of the hydrogen atoms."

On p. 238 we read that "Nernst has called attention to the fact that, since the law of mass-action in its simple form does not hold for solutions of strong electrolytes, the laws of dilute solutions cannot be applied to these mixtures. As a consequence, if the ionization is determined correctly by the conductance method, the ionization as determined by osmotic methods, assuming the laws of dilute solutions to hold, should differ from that determined by conductance meas-

urements. It appears, however, that in the case of certain electrolytes, such as potassium chloride, osmotic methods and conductance methods lead to the same value of the ionization, and, in the case of other electrolytes, the two methods lead to very nearly the same value at concentrations approaching $10^{-3}$ normal. Yet, in the neighborhood of $10^{-3}$ normal, strong electrolytes do not conform to the simple law of mass-action. Those who would use the results of osmotic methods to substantiate the correctness of the results of conductance methods thus find themselves in a dilemma, for, if the two methods lead to identical values of the ionization, then, if the results of osmotic measurements are looked upon as correct, the interpretation of conductance measurements must be in error, while, if the results of conductance measurements are accepted in their usual sense, the laws of dilute solutions are inapplicable. That the concordance of the ionization values determined by conductance and osmotic methods at low concentrations is an accidental one is very improbable. It appears, rather, that this agreement is the expression of a fundamental property of such solutions. The significance of this agreement, however, remains uncertain."

With solid electrolytes, we may have the transference number for either ion equal to zero, p. 363. "It has been shown that for silver bromide, silver chloride, silver sulphide above its transition point, and copper sulphide ($Cu_2S$), Faraday's Law holds and that in these salts the current is carried entirely by the positive ion. These results are very significant in that they show that one set of ions in these solids forms a fixed framework through which the other ions move with considerable facility. In the above salts, the negative ions form the framework through which the positive ions move. In lead chloride, however, the current is carried by the negative ion; the positive ions form the framework through which the negative ions move. These facts have an important bearing on the theory of the structure of solid salts.

"Silver sulphide has a transition point at 179°. Above the transition temperature, as was shown by actual electrolysis of the salt, Faraday's Law holds and the current is carried entirely by the positive ions. Below the transition temperature, the $\beta$ form of silver sulphide appears to conduct in part metallically. In the $\beta$ form of silver sulphide, Faraday's Law does not hold, only about 80 percent of the current being carried by the silver ion. The negative ion in this case is apparently not involved in the conduction process, the remainder of the current being carried by a metallic process of conduction. Apparently, therefore, solid electrolytes exist in which the current is carried partly metallically and partly electrolytically. As we shall see in a subsequent chapter, solutions of the alkali metals in liquid ammonia likewise conduct the current by a mixed process."

This is a very interesting book. The criticism might be made, especially with reference to the dilution law, that the author's formula receives relatively too much attention. The reviewer would have liked to have seen Schlundt's work on transference numbers referred to. These are details, however, and we are grateful to the author for giving us a clear-cut presentation of the subject. Since our knowledge turns out to be much less than some of us had hoped, the real question is what we are going to do about it. It is quite evident that the physical chemists should get together and try to map out a campaign which will clear up these points.

*Wilder D. Bancroft*

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## *New Books*

**Women in Chemistry;** *a Study of Professional Opportunities. Issued by the Bureau of Vocational Information. 23 × 15 cm; pp. xvi + 272. New York: The Bureau of Vocational Information, 1922.*—This bulletin aims to give the woman who studies chemistry some idea "of the various kinds of positions available in chemistry and the border fields, particularly bacteriology and physiology." The bulk of the volume is devoted to an analysis of positions in chemistry for women in: educational institutions; laboratories for medical and related analysis and research; laboratories for industrial analysis, development and research; government laboratories. There is a short chapter on training and another on further vocational considerations, while, in an appendix, there is given information in regard to: colleges and universities in which women may secure graduate training in chemistry; prizes and grants available for research in chemistry; fellowships and graduate scholarships open to women; scientific, technical, and other periodical publications of interest to chemists, scientific societies for chemists.

The whole thing has been done in very good style and the bulletin will be of value to women and of interest to others. *Wilder D. Bancroft*

**Laboratory Manual of Physical Chemistry.** *By A. W. Davison and H. S. van Klooster. 25 × 15 cm; pp. viii + 198. New York: John Wiley and Sons, 1922. Price: $2.00.*—The laboratory course follows immediately the completion of the theoretical course in physical chemistry at the Rensselaer Polytechnic Institute. Each student is expected to do all the experiments. These include: determination of vapor density; Graham's effusion law; surface tension and association factor of liquids; refractive index density, and molecular refractivity of liquids; lowering of the freezing point by a non-electrolyte and by an electrolyte; molecular weight determination by the boiling-point method; distribution of a substance between two non-miscible liquids; distillation with steam; minimum boiling liquids; boiling-point and vapor composition curves of liquid mixtures; solubility curve for a ternary system of liquids; transition points in the solid state; inversion of cane sugar; sodium thiosulphate reacting with ethyl bromacetate; heat of neutralization; heat of combustion; heat of solution; adsorption of dissolved substances by charcoal; conductivity and degree of ionization; transport numbers; hydrogen ion concentration and electrometric titration; electromotive force measurements and concentration cells.

The authors cover a great deal of ground and seem to do it very well. Such is the perversity of human nature, however, that the one point which the reviewer feels like criticizing is one of which the authors pride themselves particularly, namely that all the experiments are quantitative. The reviewer has a distinct fondness for qualitative experiments. They are always quicker and they are often more interesting than the quantitative ones. A student must be taught to work accurately; but the labor-saving methods have their value even in research, and accuracy to another decimal place is not yet the real goal of the chemist. *Wilder D. Bancroft*

**Grundzüge der angewandten Elektrochemie.** *By Georg Grube. Vol I. 22 × 15 cm; pp. xii + 268. Dresden and Leipzig: Theodor Steinkopff, 1922. Price: paper, $1.68; 2.06 bound.*—This volume deals with the electro-chemistry

of solutions and is to be followed by a second dealing with the electrochemistry of fused baths and gases and with electric furnaces. The chapters in this volume are entitled: the exact relations between the quantity of electricity and the decomposition products formed at the electrodes; the ions as carriers of the current in electrolytes; electrical energy from voltaic cells; electrical phenomena at the surfaces of phases; electrode potentials in electrolytic processes; electrometallurgical processes in aqueous solutions; electrolysis of alkali chloride solutions; applications of electrolytic oxidation; some applications of electrolytic reduction; technical electrolysis of water.

One interesting case under concentration cells, p. 53, is the one with hydrogen electrodes and two lithium chloride solutions which have the same conductivity and therefore the same concentration of ions. The more concentrated solution is at the cathode. On p. 81 is an account of Hofmann's carbon monoxide and oxygen cell, with copper and copper oxide electrodes.

The Anaconda zinc process is given, and the reviewer was interested to learn that the electrolytic oxidation of manganate solutions has replaced the chemical oxidation. The author's method of making sodium plumbate is also interesting. On the other hand the diagram for the Castner soda process goes back to prehistoric days. There is nothing to show how oxidation of the tannin is avoided in electrolytic tanning and the American work on electrical endosmose, over-voltage, and passivity has been ignored. The book is a fairly serviceable one; but it will not do much to enhance the reputation of the author.

*Wilder D. Bancroft*

# THE ANOMALOUS OSMOSE OF SOLUTIONS OF ELECTROLYTES WITH COLLODION MEMBRANES. I. THE ELECTRICAL PROPERTIES OF THE MEMBRANE SYSTEM

BY F. E. BARTELL AND D. C. CARPENTER*

The general problem of anomalous osmose has been under investigation in this laboratory during the past ten years. A large variety of membranes have been studied by Bartell and co-workers; and they range from inorganic, inert, porcelain membranes[1] to organic membranes, such as gold-beaters skin[2] (animal membrane), parchment paper[3] (vegetable membrane), and collodion. Osmotic effects obtained with all types of membranes show strikingly similar results.[4] It has been brought out repeatedly that the effects obtained are closely related to the pore diameter or permeability of the membranes;[5] the most striking effects being obtained with the fairly permeable membranes. The importance of the study of such membranes will be appreciated when it is considered that nearly all the membranes effective in life processes approximate the permeability of the membranes which give the most pronounced anomalous effects.

In this investigation we desired to use membranes, the permeability of which could be made to cover a wide range, accordingly, collodion was selected. The permeability (which is largely dependent upon the pore diameter) of collodion can be varied within wide limits, furthermore, a given degree of permeability can easily be obtained and duplicated.

* This paper represents a part of the material presented by Dwight C. Carpenter to the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1920.

[1] Jour. Am. Chem. Soc., **38**, 1029, 1038 (1916).

[2] Jour. Phys. Chem., **24**, 444, 593 (1921).

[3] Jour. Am. Chem. Soc., **44**, 289 (1922).

[4] Loc. cit.

[5] Jour. Am. Chem. Soc., **31**, 1199 (1909); Jour. Phys. Chem., **16**, 318 (1912).

The usefulness of collodion as a membrane material was recognized in 1855 by Fick[1] who used it in his studies on diffusion. The ease with which dialyzing membranes can be prepared from collodion has resulted in its use by many biologists.

In 1907, Bigelow and Gemberling[2] found that Poiseuille's law for the flow of liquids through capillaries applied to collodion as also to several other osmotic membranes. Mathews[3] made a number of qualitative experiments with collodion as an osmotic membrane, and concluded that it was not a truly semipermeable membrane, he believed that the direction and magnitude of osmose was largely a question of solubility. More recently Loeb[4] has prepared sacs of collodion with which he has studied the influence of electrolytes on the electrification of the walls of the sacs and also has studied the rate of diffusion of water through them. He found that the rate of diffusion of water was influenced not only by the concentration, but also by the electrical forces. In nearly all of his experiments the collodion membrane was impregnated with gelatin and in this respect his membranes differed from those used in this investigation.

The work undertaken in this investigation may be classed under three heads. The first of these is the subject of the present paper.

1. The determination of the relationship between the osmose of a number of electrolytes and the electrical properties of the membrane system when collodion membranes are used.

2. The determination of the relationship between membrane pore size, osmose, and the rate of salt diffusion through the membrane.

3. The determination of the effect of continuous stirring of the solutions on the rate of osmose and also on the rate of salt diffusion.

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[1] Fick: Pogg. Ann., **94**, 59 (1855).
[2] Bigelow and Gemberling: Jour. Am. Chem. Soc., **29**, 1576 (1907).
[3] Mathews: Jour. Phys. Chem., **14**, 281 (1910).
[4] Loeb: Jour. Gen. Physiology, **3**, 557 (1921).

## Preparation of Membrane

The preparation of collodion sacs for dialysis has been undertaken by many investigators, among whom Novy[1] seems to have been the first to have developed a satisfactory and simple technique that yields sacs similar in properties. Loeb[2] has used collodion membranes which were formed on the inside of a 50 cc Erlenmeyer flask, then subsequently removed after drying and wetting with water. It was found by us that this method yielded sacs of varying permeability and thickness, also that different portions of the same sac varied considerably in these respects.

Preliminary work with these sac membranes revealed the fact that to prevent the partial collapse of the sac, when the filled sac with its manometer tube was lowered into a dish of water, the experiments must be started under an hydrostatic head, which in itself is undesirable for the experiment. Even under an hydrostatic head of 20–40 mm, small wrinkles in the sac were not eliminated, and one to five minutes were necessary before the sac was filled sufficiently to register osmose on the manometer. Results obtained by us showed conclusively that a sac the shape of which was not maintained rigidly would stretch badly, and in the case of materials giving a strong osmose, one such sac was found to have stretched so that the initial sac volume was increased by 8 cc which represents approximately 15% change in total volume and an even greater percent error in osmose readings. The first problem then was to prepare uniform membranes of any required permeability and thickness, and of such shape that they could be held rigidly in place in the osmotic cell.

The method of Bigelow and Gemberling[3] for casting uniform flat membranes on a mercury surface was found to yield excellent results. To obtain membranes with similar

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[1] Novy: Jour. Am. Chem. Soc., **29**, 1578 (1907).

[2] Loeb: Jour. Gen. Physiol., **1**, 717; **2**, 87, 173 (1919); **3**, 387, 659, 673 (1920).

[3] Loc. cit.

properties it was found necessary to control the whole casting and drying process within a closed box. This was done in order to avoid uneven air currents and also to keep the temperature constant.

The following procedure was found to give membranes of any desired permeability in sheets 12 x 18 inches and of uniform thickness. 100 cc of 3 percent soluble gun cotton, dissolved in a mixture of 75 percent ether and 25 percent alcohol, was diluted with an equal volume of solvent to reduce its viscosity. This solution was poured evenly over clean mercury in a shallow pan placed within the casting box and allowed to evaporate slowly. At 25° C the casting time was about four hours for a membrane of medium permeability. A shorter drying period yielded more permeable, and a longer drying period or higher temperatures, less permeable membranes. The permeability was also affected by varying the proportion of water in the alcohol-ether diluent. The perfectly clear, colorless membrane was cut away from the sides of the casting dish with a razor blade, and turned the other side up for 15 to 20 minutes. The air was then changed in the casting box and the membrane turned over several times at short intervals. Very permeable membranes at this juncture began to appear opalescent, while the less permeable did not alter in appearance. The membranes were then immersed in water to dissolve out the remaining ether and alcohol.

Bigelow and Gemberling have shown that the permeability of membranes prepared in a somewhat similar manner, increased gradually for about a month, after which the change was slight. With a view to shortening the curing period, the effect of soaking the membrane in varying concentrations of alcohol and water, as suggested by Brown[1] was tried. Such curing weakened the membranes so materially that this method was abandoned, and curing in distilled water which was changed daily for thirty days was adopted as the most satisfactory procedure. All of the membranes were then cut with a cork borer, so as to fit the osmose cell, and stored

[1] Brown: Biochem. Jour., 320, 591 (1915).

under water until used. The marginal inch from the large cast sheet, by which the latter had been handled during the drying and curing periods was discarded.

### Construction and Assembly of Osmose Cell

The double-compartment osmose cell of the type used by Bartell and Hocker,[1] and later by Bartell and Madison,[2] was used and has proved satisfactory. This cell possesses certain desirable points, such as ease of detection of leakage, elimination of evaporation, elimination of alteration of hydrostatic pressure due to temperature fluctuation, negligible capillary corrections, comparative simplicity and general ease of operation.

As the membrane used in this research possessed neither the rigidity of porcelain, which could be wired into place, nor the flexibility of gold-beaters skin, which could be waxed into position, and furthermore, had to be kept moist constantly a different type of holder was of necessity devised.

The cell used in this work (Fig. 1) was constructed of two glass T-tubes of 15 mm diameter, each of which was fitted into a rubber stopper. These were fitted in turn into a threaded brass collar which carried on one end a circular brass plate. The stopper was held in the collar by a washer secured by a threaded sleeve which could be screwed onto the collar. The half-cells were bolted together through the circular brass plates. Paraffined rubber stoppers were used to close the ends of the cell and also as connectors for the osmometer tubes. The assembled cell was made fast to a substantial support.

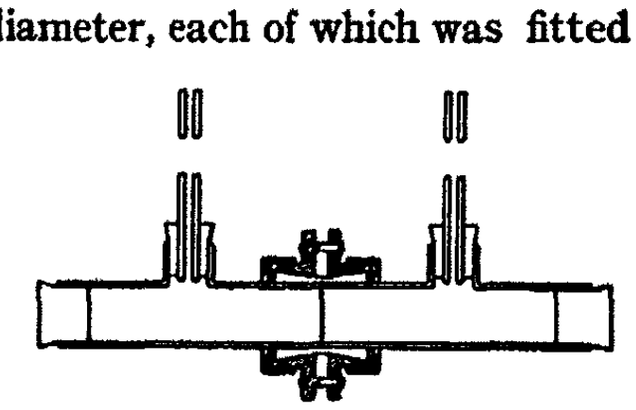


Fig. 1

In assembling the cell, the glass T-tube was adjusted so that the surface of the rubber stopper on which the mem-

[1] Loc. cit.

[2] Ibid.

brane was to be placed, projected slightly beyond the glass so that when the two halves of the cell were bolted together, the glass T-tube would practically touch the membrane. This definitely established the effective membrane area. In order to exclude the possibility of loss of liquid from either compartment of the cell by leakage around the edge of the membrane, the faces of the rubber stoppers were coated with three layers of rubber cement, the first two layers thoroughly dried with the long axis of the cell in a vertical position, and the third coat dried to the "gummy" stage. The membrane which had previously been cut out with a cork borer, was removed by forceps from the water under which it had been stored. It was then dried superficially with filter paper, placed in position on the prepared stopper, and the other half of the cell was bolted on. The bolts were taken up slowly and uniformly so as to avoid buckling of the membrane. The cell was then filled with water and left for at least twenty-four hours before being used. The volume of each compartment was approximately 20 cc.

The osmometer tubes were heavy-walled glass tubing of 2.5 mm internal diameter and were calibrated in the usual manner with mercury. The tubes used in the first part of this work agreed in specific volume to within about five percent, and were of fairly uniform diameter throughout. A given pair of tubes was always used with the same cell.

In setting up a cell for use, the water was first emptied out and the respective compartments rinsed twice with the solutions they were to contain. The compartments were then filled, and the osmometer tubes, previously half filled, were adjusted so that the liquid columns were equal. The rubber stoppers were then immediately waxed into place. In this work, readings of the hydrostatic pressures which developed were taken at two hour intervals over a twelve hour period. At the close of the experiment the cell was emptied, washed with distilled water, and then filled with the water. In order to wash the membrane capillaries free from electrolyte, the cell was put under an hydrostatic head for eight to ten

hours. In this way one membrane could be used a number of times, and still give results comparable with a fresh membrane. Results with the two-compartment cell, when the temperature was accurately controlled, were readily duplicable to within one or two percent.

## Results

What was actually obtained in this work was data showing the rate of flow of solutions through the membrane. In some cases the equilibrium pressure of the solution (expressed in terms of hydrostatic pressure) was determined; that is, readings were recorded when the rate of flow of liquid through the membrane in one direction was just balanced by the rate of flow in the other direction. Such readings will be designated as maximum osmose values. It will be appreciated that the comparison of the rates of flow of different solutions is by no means an exact way of comparing the absolute osmotic activity of the solutions. It does, however, give us a fairly accurate indication of the order of maximum equilibrium pressures obtainable with these solutions.

Results were obtained (1) with chlorides of metals having different valencies, (2) with potassium salts having inorganic acid radicals of different valencies, (3) with potassium salts having organic acid radicals of different valencies and (4) with hydrochloric acid and with potassium hydroxide.

The results obtained are shown in Table I. In this table readings obtained at the end of the two hour, six hour, and twelve hour periods are given. A medium porous membrane (pore diameter = 0.8 to 0.9 micron) was used. The salts were usually recrystallized twice from a good grade of distilled water. The HCl was redistilled as "constant boiling" from C. P. acid. The KOH was a Kahlbaum product and was freed from carbonate by careful precipitation with $Ba(OH)_2$. There was a slight trace of barium left in the solution. Stock solutions of the electrolytes were made up with conductivity water, analyzed, and diluted to the desired concentration.

Conductivity water was used in one compartment of the cell in all experiments. The hydrostatic pressure was recorded in millimeters. The temperature was 25° C ± 0.5° C.

### Osmose of Chloride Solutions of Different Metals

Chlorides of monovalent metals gave a repressed effect at 0.1M concentration. This effect persisted throughout the entire 12 hour period.

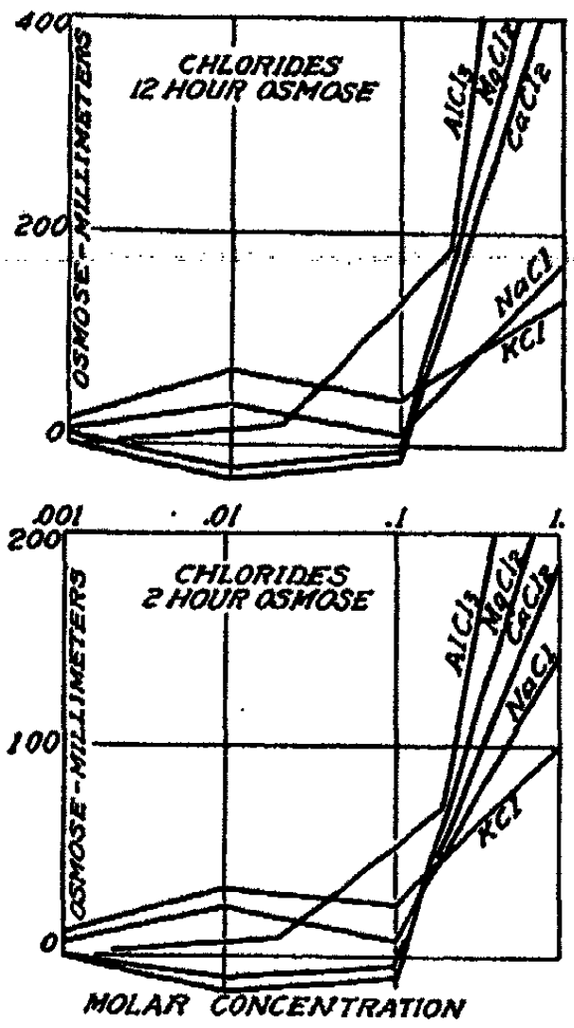



Fig. 2

Solutions of chlorides of bivalent and trivalent metals at low concentrations (0.01 to 0.1M) tended to give either a low positive or negative osmose, while the osmose was strongly positive at higher concentrations (1M).

The general shape of the curve representing initial osmose rate, (i. e., osmose in mm at the end of a two hour period), plotted against the logarithm of molar concentration, is the same in all cases as the maximum osmose curve (12 hour period) plotted in the same manner. These curves are shown in Fig. 2. The data appear in Table I.

### Osmose of Potassium Salts of Inorganic Acids

These experiments were carried out to ascertain the effect of the valence of the anion on osmose. It was found that an increase in valence of anion (with salts which do not hydrolyze greatly) resulted in an increase of the initial osmose rate and also in a higher maximum osmose value.

TABLE I
Osmose of Salt Solutions
(Values are given in millimeters rise)

| | 2 Hr. Period Concentration | | | | 6 Hr. Period Concentration | | | | 12 Hr. Period Concentration | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Salt | 0.001M | 0.01M | 0.1M | 1M | 0.001M | 0.01M | 0.1M | 1M | 0.001M | 0.01M | 0.1M | 1M |
| KCl | 10 | 31 | 24.5 | 100 | 15.5 | 60 | 41.5 | 165 | 20 | 67 | 41.5 | 149 |
| NaCl | 7 | 24.5 | 5 | 146 | 11.5 | 43 | 6.5 | 227 | 13 | 38 | 4.8 | 183 |
| $CaCl_2$ | 2 | − 6.5 | −2.5 | 188 | 4 | −16.5 | − 2.5 | 388 | 3 | −21 | −2 | 477 |
| $MgCl_2$ | 1.5 | −13 | −5.5 | 240 | 3.5 | −28.5 | −14 | 521 | 4 | −36 | −14 | 654 |
| $AlCl_3$* | 0.0 | 10.5 | 73.5 | 367 | 0.0 | 22 | 156 | 805 | 0.0 | 27 | 190 | 1045 |
| $K_2SO_4$ | 37 | 62 | 66 | 196 | 90 | 137 | 132 | 391 | 129 | 165 | 142 | 425** |
| $K_3FeC_6N_6$ | 61 | 103 | 109 | 276 | 146.5 | 228 | 205 | 547 | 220 | 269 | 222 | 590** |
| $K_4FeC_6N_6$ | 83 | 123 | 156 | 405 | 204 | 282 | 322 | 829 | 305 | 350 | 376 | 943** |
| $K_2CO_3$ | 26 | 247 | 375 | 410 | 61 | 590 | 697 | 900 | 81.5 | 760 | 670 | 1036 |
| $K_3PO_4$ | 27.5 | 88 | 98 | 422 | 63.5 | 219 | 209 | 945 | 102 | 291 | 247 | 1045 |
| $KC_2H_3O_2$ | 12 | 57 | 61 | 179 | 21.5 | 127 | 119 | 352 | 31.5 | 198 | 130 | 385 |
| $K_2C_2O_4$ | 21 | 106 | 86 | 362 | 63 | 232 | 174 | 750 | 103 | 291 | 196 | 830 |
| $K_3C_6H_5O_7$ | 37 | 129 | 145 | 465 | 91 | 319 | 317 | 1100 | 151 | 455 | 404 | 1550 |
| HCl | 16 | 13.5 | 29 | 108 | 28 | 36 | 49 | 170 | 28 | 45 | 50 | 154 |
| KOH | 5 | 39 | 6.5 | −11 | 10.5 | 81 | 17 | — | 16 | 92 | 17 | — |

* Concentrations of $AlCl_3$ were 0.002 M, 0.02M, 0.2M and M.

** Solution of 0.5M concentration was used in this case instead of 1M.

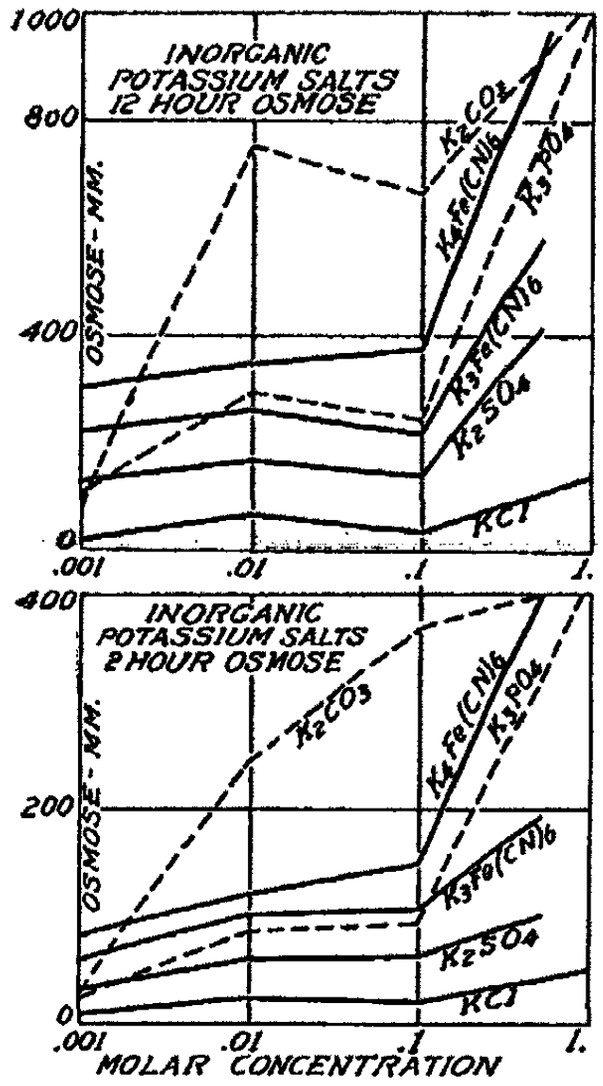



Fig. 3

In concentrated solutions, readily hydrolyzable salts of inorganic acids (i. e., carbonate, phosphate, etc.) when compared with slightly hydrolyzable salts of inorganic acids of equal anion valence, were found to give an abnormally high osmose. In dilute solutions, the readily hydrolyzable salts were found to give a somewhat lesser osmose than the slightly hydrolyzable salts.

When osmose is plotted against logarithm of molar concentration, the shape of the initial osmose curves is shown to be somewhat different from the maximum osmose curves. The initial osmose curve approaches a straight line. When taken over a longer time interval, the osmose curve is found to have developed into the peculiar N shaped curve having a minimum at 0.1M, as shown in Fig. 3.

### Osmose of Potassium Salts of Organic Acids

With increasing valence of anion, the osmose of salts of organic acids was found to increase in the same manner as did the osmose of salts of inorganic scids. (Fig. 4.)

The magnitude of the osmose of potassium salts of organic acids was greater at all concentrations than of the salts of inorganic acids, (i. e., slightly or non-hydrolyzable salts) of corresponding anion valence. (An exception is to be noted

in the case of $K_2C_2O_4$ at 0.001M concentration, which gives lesser osmose but of the same order of magnitude, than the corresponding concentration of $K_2SO_4$.)

The initial osmose curve and the maximum osmose curve for $K_2C_2O_4$ when plotted against log. of concentration are both of the same shape and are of the N type.

The initial osmose curves for both acetate and citrate show but little of the repression tendency; with time, osmose is repressed and these curves change to the N shaped type. In this respect, a close resemblance is noted between the behavior of the potassium salts of organic acids and the salts of inorganic acids.

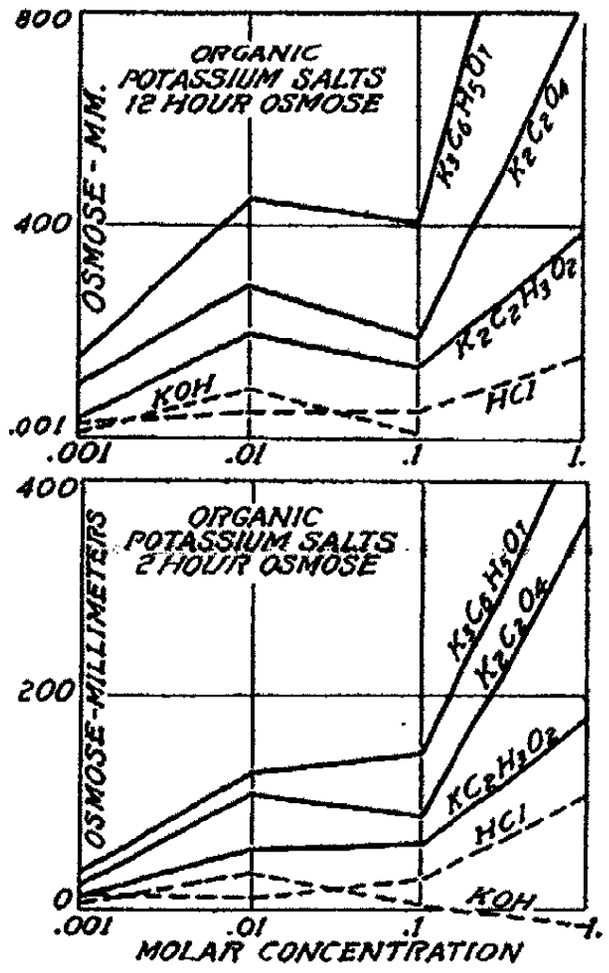



Fig. 4

### Osmose of Hydrochloric Acid and of Sodium Hydroxide

Hydrochloric acid gives a low positive effect which gradually becomes more positive with increase in concentration.

Potassium hydroxide at first gives increased positive osmose with increasing concentration, but in concentration greater than 0.01M, it shows a fairly strong negative tendency. At somewhat higher concentrations, the membrane becomes rapidly disintegrated; were it not for this fact we might, reasoning from our experience with other types of membranes, expect positive osmose with still higher concentrations.

### Cell Potential

It was hoped that measurement of the development and subsequent decline in cell potential might be accomplished

while osmose was actually taking place under the usual conditions. When calomel electrodes are used, in order to have the hydrostatic pressure register in the manometer and not continually leak out around the glass stop-cock on the calomel electrode, a perfectly fitting valve must be used. Unfortunately, there is practically no conduction through such a valve when it is closed. This difficulty terminated temporarily the thought of measuring E.M.F. and osmose on the same experiment.

The potential measurements were made by the compensation method as described in a previous paper,[1] using calomel electrodes, a Leeds and Northrup precision potentiometer and a sensitive galvanometer. The solution side of the membrane is understood to have a higher potential than the water side when the sign is plus and a lower potential when the sign is minus.

TABLE II

Cell Potential

Potential Measured in Volts Temperature 25° C

| Electrolyte | Concentration of Electrolytes | | | |
|---|---|---|---|---|
| | *0.001M* | *0.01M* | 0.1M | 1M |
| KCl | 0 | 0 | −0.005 | −0.003 |
| NaCl | 0.0 | 0.008 | 0.019 | 0.030 |
| $CaCl_2$ | 0.032 | 0.042 | 0.060 | 0.078 |
| $MgCl_2$ | 0.034 | 0.050 | 0.065 | 0.085 |
| $AlCl_3$* | 0.032 | 0.052 | 0.076 | 0.087 |
| $K_2SO_4$ | −0.031 | −0.028 | −0.055 | −0.072** |
| $K_3FeC_6N_6$ | −0.025 | −0.036 | −0.059 | −0.094** |
| $K_4FeC_6N_6$ | −0.037 | −0.050 | −0.069 | −0.097** |
| $K_2CO_3$ | −0.017 | −0.020 | −0.030 | −0.041 |
| $K_3PO_4$ | −0.030 | −0.048 | −0.064 | −0.095 |
| $KC_2H_3O_2$ | −0.008 | −0.029 | −0.044 | −0.052 |
| $K_2C_2O_4$ | −0.026 | −0.040 | −0.051 | −0.078 |
| $K_3C_6H_5O_7$ | −0.042 | −0.053 | −0.075 | −0.104 |
| HCl | −0.035 | −0.062 | −0.109 | −0.157 |
| KOH | −0.010 | 0.032 | 0.068 | 0.081 |

* Concentrations of $AlCl_3$ were 0.002, 0.02, 0.2 and 1M.

** Solution of 0.5M concentration used in this case instead of 1M.

[1] Bartell and Hocker: loc. cit.

The reversal of the electrical orientation of the cell system with increase in concentration of KOH appears to be unique, in these experiments and is the same condition noticed by Bartell and Hocker when using porcelain membranes with NaOH. With collodion, however, this reversal occurs at a greater dilution than with porcelain.

The electrical orientation appears to be controlled largely by the relative migration velocity of the respective ions in the solution, and is a function of the concentration as is demanded by Nernst's formula. So far as data on ionic velocities are available, they are found to agree with the expected direction and magnitude of cell orientation, with the exception of KOH in dilute solution, and with $K_2CO_3$. As the latter is fairly well hydrolyzed, we may expect a counter potential to be set up by the KOH produced, which would account for the low value actually found.

### Sign of the Membrane Charge

It is possible to determine the sign of the membrane charge by either one of two methods, namely by electro-osmose or cataphoresis.

The use of gassing electrodes in electro-osmose experiments was clearly out of the question for any refined work. Electrodes such as those developed by Barratt and Harris[1] (i. e., Cu in saturated $CuSO_4$ solution) eliminate gassing and are excellent, but cannot be used in certain combinations such as ferrocyanides. Although a great deal of work was done with collodion membranes with a modification of Barratt and Harris' apparatus, and also by Briggs' method,[2] the cataphoresis method was found to be more satisfactory, since it was dependable and at the same time more rapid.

A quantity of dried membrane was finely pulverized, after which a fairly stable water suspension of it was made. This suspension was examined under the ultra microscope,

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[1] Barratt and Harris: Zeit. Elektrochemie, **18**, 221 (1912).

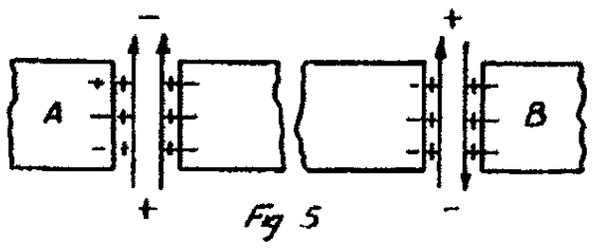
[2] Briggs: Jour. Phys. Chem., **22**, 256 (1918).

and the direction of migration of the collodion particles under an applied potential noted.

The direction of motion of finely divided collodion particles in water was found to be slowly to the anode which indicated that collodion bears a small negative electrical charge with respect to water. In all four dilutions of each of the fifteen electrolytes tried, the collodion was likewise negative. It also appears that no amount of acid up to and including 10M HCl will cause it to become charged positively, nor will any concentration of salts of trivalent cation, such as aluminum, produce this effect. This appears to be an extreme case of an "unprecipitable" suspension. These results confirm those of Loeb and also those of Gyemant,[1] which were obtained by the electro-osmose method. In this respect collodion is different from any other membrane we have used.

## General Discussion and Conclusions

It will be seen from the data already presented that the membrane charge and the orientation of the cell systems for chlorides of Na, Ca, Mg and Al are given according to B of Fig. 5.




The diagram represents one pore through the membrane. The solution side is understood to be above the membrane and the water beneath. The arrow on the left, pointing up toward the solution, represents the normal osmotic tendency while the one on the right represents the imposed electrical effect. Applying this idea we see that the exosmotic tendency opposes the normal osmotic tendency and we should expect a low degree of positive osmose (Na, Al) or even a negative osmose, which is actually realized with the case of Ca and Mg. At high concentrations, the normal osmotic tendency overcomes the imposed exosmotic effect, and positive osmose results.

[1] Gyemant: Kolloid Zeit., 28, 103 (1921).

The condition with HCl (also with KCl) is shown in A of Fig. 5, the orientation being the opposite of that in the above case. The osmotic tendencies should operate in the same direction and a high positive osmose should result. While in dilute solutions of HCl, positive osmose is obtained which is of greater magnitude than with Na, Ca, Mg, and Al, these latter substances in concentrated solutions give an osmose which materially exceeds that with HCl. It might be argued, though admittedly not at all conclusively, that except in the case of NaCl, this is due to the greater number of ionic units furnished by the dissociation of the more complex salts.

The peculiar case of KOH with its reversal of orientation with change of concentration, is an admirable illustration of the applicability of the electrical theory. In dilute solutions, the condition of the system is such that a strong positive tendency should result. (A, of Fig. 5.) The results are in accord with this prediction. In a more concentrated solution, however, the orientation changes and conditions are as in B, giving a weak positive effect; with still higher concentrations, a strong negative effect results.

All the potassium salts studied gave orientations of the cell system corresponding to A, Fig. 5, which would lead us to infer that abnormally positive osmose should result. This has been shown to be true (with the exception of $K_2C_2O_4$) so far as initial osmose rate is concerned. The maximum osmose, however, shows that some factor, of which time is an important element, plays a part in reducing the initial high osmose rate to a considerably lower value.

## Summary and Conclusions

1. A method for preparing flat collodion membranes of uniform thickness and permeability is described. Methods for controlling the permeability to any desired value are given.

2. A non-leaking osmotic cell of two T-shaped glass compartments of equal volume, held together by a machined brass coupling which also holds the membrane firmly between

the two compartments, has been developed and used successfully.

3. The osmose values obtained with thirteen different salts, an acid and a base (chosen to show the relative influence of cation and anion valence, hydrolyzability of salt, and weak and strong acid radical) are given for 0.001, 0.01, 0.1, and 1M concentrations.

4. The maximum potential with each of these osmotic systems was measured and recorded.

5. The sign of the membrane charge has been determined by cataphoresis, using finely ground membrane material in suspension.

6. Consideration of the data obtained shows that the initial osmose rate of practically all the salts examined bears a definite relationship to the electrical properties of the membrane system.

7. The anomalous effects obtained with collodion are very similar to those obtained with membranes of porcelain, of gold beater's skin, of calf's bladder, and of parchment paper. The maximal and minimal values obtained with these different membranes do not come at exactly the same concentrations, but when consideration is given to the exact condition of the electrical orientations of the different membrane systems, the results are closely comparable.

8. It has been shown that anomalous effects are related somewhat to the time factor. For example the data for the osmose of potassium carbonate at the end of a two hour period, when plotted against log of concentration of potassium carbonate gave no N shaped curve while the N shape was pronounced for the curve obtained at the end of a 12 hour osmose period. This fact makes it appear probable that the process of diffusion is in some way responsible for the repressing effects noted at the intermediate concentrations. The development of this idea with substantiating data will be given in an early paper.

# FACTORS AFFECTING SOIL REACTION

## I—THE SOIL-WATER RATIO

BY ROBERT M. SALTER AND M. FRANCIS MORGAN*

Many attempts have been made in recent years to correlate biological processes with reaction. Positive relations have been established between the germination of seeds, the growth of plants, the ecological distribution of plants, the development of both pathogenic and non-pathogenic soil organisms and the reaction of the growth medium.

Both electrometric and colorimetric procedures for measuring reaction are in common use, the former being employed for soil suspensions, the latter more frequently for solution cultures, liquid media, and soil extracts. In the application of most of this work to soil conditions the tacit assumption has been made that the reaction of soils under normal field conditions is not far different from the values obtained in measurements upon soil suspensions and soil extracts. The possible effects of wide differences in moisture content, of drying, or of time of standing in contact with water have in general been neglected in spite of the fact that the value of much of this work depends necessarily upon how accurately it applies to soils under normal growth conditions. The present work is an attempt to discover the nature of any possible relationship between the ratio of soil to water and the hydrogen-ion concentration of the soil suspension.

A review of the literature fails to reveal any consistency of opinion among soils workers as to the effect of variable moisture content upon reaction. Sharp and Hoagland, (18) working with a modification of the hydrogen electrode procedure found no significant differences in hydrogen-ion concentrations of soil suspensions over quite wide ranges of soil-water ratios. They state:

* From the Department of Soils, The Ohio State University.

"An inspection of the data indicates comparatively insignificant changes in the H-ion concentration when widely varying proportions of water to soil are used. Most of these small fluctuations can be ascribed to the limitations of the apparatus. Hence it is reasonable to assume that the H-ion concentration of the soil suspensions approximates those of the soil solutions. This argument is theoretically sound, since, in all the larger proportions of soil employed it is probable that the solution is saturated with respect to the acid-forming constituents."

Gillespie and Hurst (6) in reporting upon the H-ion concentration of two soil types, the Caribou Loam and the Washburn Loam, make the following comment:

"The average difference obtained by varying the ratio from 1:1 to 1:2 was 0.14 in the value of the exponent for nine soils. This indicates that at optimum moisture content the acidity may be more intense, but to what extent cannot be calculated. Only results between the same ratios of water to soil should be compared."

In later work the same investigators obtained a mean value of 0.04 for the difference between the exponent of the H-ion concentration when the dilution was increased for a soil-water ratio of 1:1 to a ratio of 1:2. This positive difference means that the soil extract was less acid when more water was used.

Rice and Osugi[16] measured the inverting power of acid soils for cane sugar at soil-water ratios varying from 1 to 32 grams of soil to 100 cc of water. They found greatly increased hydrolysis with the higher amounts of soil but since they were unable to observe any difference in the reaction of the extracts from such soils, determined colorimetrically, they concluded that the solid phase is the active factor in inverting cane sugar. It should be mentioned however, that, although these investigators were undoubtedly working with acid soils, all determinations of reaction on the extracts from these soils gave results indicating almost exact neutrality. Since this work is so completely at variance with the results of other workers in this respect is seems highly probably that the results of Rice

and Osugi may be in error due to some fault in the technique of the colorimetric procedure employed, and that the greater hydrolysis of sugar at higher soil-water ratios may well have been due to a higher concentration of hydrogen-ions in solution.

Plummer[14] found that the film water obtained by the oil pressure method from soils of approximately optimum moisture contents was more highly acid in the case of acid soils and more highly alkaline in the case of alkaline soils than the soil suspensions determined at a much lower soil-water ratio. Thus the film water from a Porter's loam soil at 25% moisture content (dry basis) showed a H-ion concentration of $0.25 \times 10^{-4}$ as compared to $0.9 \times 10^{-6}$ for a suspension of the same soil containing 10 grams of soil to 100 cc of water. The film water from a Chickamauga limestone soil showed a reaction of $0.8 \times 10^{-11}$ compared with $0.1 \times 10^{-9}$ for the suspension. If such differences as these actually exist between the reaction of soils at normal moisture contents and those commonly employed in H-ion measurements it would appear that a study such as herein reported may be of value.

More recently Hudig and Sturm,[10] working with both soil solutions and soil suspensions found that the H-ion concentration varies with the soil-water ratio.

## Experimental Methods

In measuring the variations in hydrogen-ion concentration under different moisture conditions the following procedures were followed:

1. Electrometric Method, using the Hydrogen-Electrode.—This method has come into very general use in soil acidity investigations. Its high degree of accuracy at any dilution at which the soil is actually in suspension makes it especially applicable to this work. In this respect it is superior to the colorimetric procedure employed by Wherry and others.

A type "K" Leeds and Northrup potentiometer was used, measurements being made against a normal KCl-Calomel electrode. A platinum-coated glass electrode of the Luther

type was used in a hydrogen cell of about 10 cc capacity. Hydrogen was passed over the electrode at the rate of about two small bubbles per second. It was found that with the small quantity of liquid used (1 to 5 cc) the bubbling of the gas made sufficient provision for keeping the soil in suspension. The temperature was kept near 25° C and any unavoidable deviation from this point was corrected for in calculating the results.

As it seemed advisable to cover a rather wide range of dilution, it was decided to vary the ratio of soil to water from 1:1 to almost infinite dilution in steps such that the degree of dilution was each time multiplied by 5. Experimental work developed the need for intermediate ratios in order to more accurately establish the systematic variation observed, hence ratios representing logarithmic means were also included. As finally developed, the following soil-water ratios were used:

| Grams soil per 1000 cc water | In electrode vessel | |
|---|---|---|
| | Cc water | Gram soil |
| 1000.0 | 1 | 1.0000 |
| 447.0 | 2 | .8940 |
| 200.0 | 2 | .4000 |
| 89.4 | 5 | .2000 |
| 40.0 | 5 | .4470 |
| 17.88 | 5 | .0894 |
| 8.0 | 5 | .0400 |
| 3.58 | 5 | .0179 |
| 1.6 | 5 | .0080 |
| .716 | 5 | .0036 |
| .32 | 5 | .0016 |

2. *Sucrose Hydrolysis Method.*—The velocity of sucrose hydrolysis has been quite generally employed as a measure of the H-ion concentration of solutions. Hanley[7] and Rice and Osugi[16] have used the method to indicate soil reaction. It seemed advisable to correlate the H-electrode method with determination of the soil's capacity to produce inversion of cane sugar at varying moisture contents. This method possesses the advantage of indicating reaction with moisture contents

closely approaching those of field soils. On the other hand, it is recognized that no direct measurement of hydrogen-ion concentration can be made by this means, the velocity of sucrose hydrolysis serving only as an index of the relative reaction.

The soil to which varying quantities of 15% sucrose solution had been added was digested in an autoclave steam bath kept at atmospheric pressure for two hours. The soil suspensions were kept in constant agitation since preliminary work indicated that this was necessary to uniformity of results. After digestion the amount of invert sugar was determined by a combination of the Munson and Walker and Bertrand methods in which $Cu_2O$ is finally determined by reduction of ferric iron and titration with standard $KMnO_4$.

Velocity constants were calculated for each dilution from the usual formula for mono-molecular reactions:

$$K = \frac{2.30}{t} \log_{10} \frac{a}{a - x}$$

where "$a$" is initial amount of sugar present, and "$x$" is amount inverted in time "$t$."

Dilutions were made upon the same basis as for hydrogen-ion determinations. In this case successive steps of moisture content approaching normal field conditions could be added.

The following amounts of soil and sucrose solution were used:

| Grams soil per 1000 cc water | Sucrose solution | Soil, gm |
|---|---|---|
| 11180 | 2 | 22.36 |
| 7480 | 4 | 29.92 |
| 5000 | 4 | 20.00 |
| 1000 | 15 | 15.00 |
| 200 | 25 | 5.00 |
| 40 | 25 | 1.00 |
| 8 | 25 | .20 |
| 3.58 | 50 | .179 |
| 1.6 | 50 | .08 |

In the first three cases the amount of liquid was not sufficient to permit of soil suspension. To insure thorough incorporation of sucrose solution at these low moisture contents the air-dry soil was ground in an agate mortar with the required quantity of the liquid. Even with this precaution, results were found to be quite irregular, and as shown later by the tabulated data and graph serve only to show approximate relations. With all other dilutions an accuracy of about one percent was obtained.

In these investigations nine soils were studied by the electrometric method. Four of these were compared as to sucrose hydrolysis. The soils used were acid, showing calcium carbonate requirements of from two to three and one-half tons per 2,000,000 pounds, by both Veitch and Jones methods. With the exception of the one designated 1WS the soils used were taken from the collection of the West Virginia Experiment Station. Their chemical analysis is reported in Bulletin 168 of that station.

The soils studied were as follows:

| Soil | Series | Type | Color |
|---|---|---|---|
| No. 171A | Dekalb | Sandy loam | Yellow-brown |
| No. 357A | Dekalb | Silt loam | Yellowish gray |
| No. 149A | ——— | Sandy loam | Dark gray |
| No. 152A | ——— | Silt loam | Light gray |
| No. 44A | ——— | Silty clay loam | Dark gray |
| No. 1WS | Elk | Silt loam | Medium gray |
| No. 78A | Moshannon | Clay loam | Red |
| No. 154A | Huntington | Sandy clay | Reddish brown |
| No. 59A | Upshur | Clay | Indian-red |

## Experimental Data

For the sake of brevity complete data for the H-ion concentration as determined electrometrically is given for only one soil, No. 357. (See Table I.)

The condensed results of the electrometric measurements for all soils is given in Table II.

Complete data used in calculating the sucrose hydrolysis velocity constants are shown in Table III, for soil No. 171A only. The sucrose hydrolysis velocity constants for all soils studies are given in Table IV.

TABLE I

Complete Hydrogen-ion Data for Soil No. 357A

| Soil, gm per 1000 cc $H_2O$ | Potentiometer reading, m-volts | | | Average | pH | H-ion concentration |
|---|---|---|---|---|---|---|
| | (*a*) | (*b*) | (*c*) | | | |
| 1000 | 518.0 | 518.1 | 517.3 | 518 | 3.983 | .0001040 |
| 447 | 525.0 | 525.3 | 524.9 | 525 | 4.091 | .0000811 |
| 200 | 532.8 | 533.1 | 533.1 | 533 | 4.226 | .0000594 |
| 89.4 | 546.5 | 546.2 | 546.0 | 546 | 4.446 | .0000358 |
| 40.0 | 557.3 | 557.0 | 557.1 | 557 | 4.632 | .0000233 |
| 17.88 | 568.7 | 568.3 | 567.9 | 568 | 4.818 | .0000152 |
| 8.00 | 581.2 | 581.0 | 580.9 | 581 | 5.038 | .0000092 |
| 3.58 | 602.3 | 602.5 | 601.8 | 602 | 5.393 | .0000041 |
| 1.6 | 625.1 | 625.7 | 624.9 | 625 | 5.782 | .0000016 |

## Discussion of Results

From an inspection of the data it is at once apparent that the H-ion concentration increases as the soil-water ratio increases. It is also seen that the increase in H-ion concentration is not a linear function, but increases at a slower rate than the soil-water ratio. The fact that such a variation is observed immediately discredits any theory of soil acidity which assumes that the acid reaction is due to highly insoluble acids, either organic or inorganic which must under conditions of equilibrium form a saturated solution and give an approximately constant H-ion concentration. Reference has already been made to Hoagland's statement suggesting that the constancy of H-ion concentration which he observed at varying soil-water ratios could be taken as supporting such a theory.

The distribution of H-ions between soil and solution at varying soil-water ratios suggests the possibility that we are here dealing with a phenomenon similar to adsorption. To test out the validity of this assumption, it seemed desirable to determine to what extent the data might be made to satisfy

TABLE II

Relation of pH of Soil Suspensions to the Soil-water Ratio

| Soil gm per 1000 cc $H_2O$ | 171A pH | 357A pH | 149A pH | 152A pH | 44A pH | 154A pH | 1WS pH | 59A pH | 78A pH |
|---|---|---|---|---|---|---|---|---|---|
| 1000 | 3.787 | 3.983 | 4.023 | 4.176 | 4.210 | 4.581 | 4.446 | 4.649 | 4.514 |
| 447 | 3.999 | 4.091 | 4.159 | 4.210 | 4.243 | 4.598 | 4.514 | 4.734 | 4.615 |
| 200 | 4.193 | 4.226 | 4.277 | 4.260 | 4.311 | 4.666 | 4.632 | 4.852 | 4.767 |
| 89.4 | 4.446 | 4.446 | 4.429 | 4.412 | 4.412 | 4.767 | 4.801 | 4.987 | 4.953 |
| 40 | 4.734 | 4.632 | 4.598 | 4.548 | 4.548 | 4.920 | 4.936 | 5.156 | 5.122 |
| 17.88 | 4.970 | 4.818 | 4.818 | 4.717 | 4.683 | 5.089 | 5.055 | 5.258 | 5.224 |
| 8 | 5.292 | 5.038 | 5.038 | 4.953 | 4.869 | 5.292 | 5.173 | 5.342 | 5.342 |
| 3.56 | 5.664 | 5.393 | 5.376 | 5.325 | 5.089 | 5.596 | 5.342 | 5.410 | 5.511 |
| 1.6 | 5.917 | 5.782 | 5.697 | 5.697 | 5.444 | 5.866 | 5.596 | 5.495 | 5.697 |
| .716 | —— | —— | —— | 6.340 | 5.765 | —— | 5.985 | 5.596 | 5.968 |
| .32 | —— | —— | —— | —— | 5.985 | —— | 6.272 | 5.697 | —— |

TABLE III
Complete Sucrose Hydrolysis Data for Soil No. 171A

| Soil gm per 1000 cc $H_2O$ | Total mgm sucrose | Aliquot used | $KMnO_4$ titration cc .05 N (a) | (b) | Average titrations | Cu mgm | Sucrose in aliquot mgm | Total sucrose hydrolyzed mgm | Velocity K |
|---|---|---|---|---|---|---|---|---|---|
| 11180 | 300 | .5 | 65.5 | 65.2 | 65.35 | 205.7 | 100.88 | 201.76 | .009316 |
| 7480 | 600 | .2 | 50.3 | 50.3 | 50.30 | 158.4 | 75.9 | 379.5 | .008066 |
| 5000 | 600 | .2 | 51.9 | 51.2 | 51.55 | 162.2 | 78.0 | 390.0 | .008500 |
| 1000 | 2250 | .1 | 69.3 | 69.2 | 69.25 | 218.0 | 107.4 | 1074.0 | .006166 |
| 200 | 3750 | .1 | 79.1 | 79.0 | 79.15 | 249.2 | 123.16 | 1231.16 | .003308 |
| 40 | 3750 | .1 | 48.8 | 49.6 | 49.20 | 156.0 | 74.86 | 748.6 | .001858 |
| 8 | 3750 | .1 | 21.2 | 20.9 | 21.05 | 66.4 | 29.64 | 296.4 | .000683 |
| 3.58 | 15000 | .05 | 25.4 | 25.6 | 25.50 | 80.3 | 36.28 | 725.6 | .000408 |
| 1.6 | 15000 | .05 | 16.8 | 16.7 | 16.75 | 52.9 | 22.40 | 448.0 | .000268 |

TABLE IV
Sucrose Hydrolysis Velocity K

| Soil-grams per 1000 cc $H_2O$ | 171A ($\times 10^{-4}$) | 357A ($\times 10^{-4}$) | 154A ($\times 10^{-4}$) | 1WS ($\times 10^{-4}$) | 78A ($\times 10^{-4}$) |
|---|---|---|---|---|---|
| 11180 | 93.16 | 47.83 | 50.33 | 43.58 | 24.92 |
| 7480 | 80.66 | 37.33 | 38.91 | 35.00 | 21.50 |
| 5000 | 85.00 | 34.19 | 34.50 | 30.33 | 19.75 |
| 1000 | 61.66 | 27.75 | 26.00 | 24.91 | 22.25 |
| 200 | 33.08 | 19.16 | 15.41 | 17.41 | 17.16 |
| 40 | 18.58 | 10.66 | 8.50 | 10.91 | 10.83 |
| 8 | 6.83 | 6.00 | 5.00 | 4.42 | 6.08 |
| 3.58 | 4.08 | 4.33 | 3.75 | 2.25 | 5.08 |
| 1.6 | 2.68 | 3.41 | 2.25 | 1.00 | 3.75 |

the well-known adsorption isotherm of Freundlich. To do this, however, necessitates a somewhat modified statement of Freundlich's equation, since in varying the soil-water ratios, we not only vary the mass of the adsorbent, but at the same time vary the total amount of acidity (H-ions) present.

The following procedure illustrates the development of the modified equation from the usual method of statement.

General formula for adsorption:

(1) $\frac{x}{m} = \beta C^d$ where $x$ = amt. adsorbed

C = concn. in solution
$m$ = mass of adsorbent
$\beta$ and d are constants.

For the purpose of present study, let

C = concn. of H-ions in soln.
$x$ = amt. of H-ions adsorbed
$x + C$ = total H-ions present (adsorbed and free).

Since the total number of H-ions present is presumably a function of the total mass of the soil, m, it follows that

(2) $X + = Km$, where K is a constant.

or

(3) $x = Km - C$

by substituting in (1)

$$(4)\quad \frac{Km - C}{m} = \beta C d$$

from which

$$(5)\quad K - \beta C d - \frac{C}{m}$$

Equation (5) contains three unknowns, viz: the constants K, $\beta$ and d. By selecting from the data for any one soil three known concentrations: $C_1$, $C_2$, $C_3$, corresponding to three known amounts of soil: $m_1$, $m_2$, and $m_3$, it should be possible to calculate mathematically the values of the above constants. The extent to which these same constants may be used in predicting the H-ion concentrations at still other soil-water ratios forms a measure of the degree of conformity of the concentrations observed to the usual adsorption distribution. The details of the mathematical procedure involved in the calculation of the constants is given in the footnote.[1]

[1] Methods of calculating constants *d*, $\beta$ and K.

From the observed values of C at three different soil-water ratios, we have

$$K - \beta C_1 d = \frac{C_1}{m_1} \qquad (1)$$

Similarly

$$K - \beta C_2 d = \frac{C_2}{m_2} \qquad (2)$$

Similarly

$$K - \beta C_3 d = \frac{C_3}{m_3} \qquad (3)$$

Subtracting (2) from (1)

$$(C_2 d - C_1 d) = \frac{C_1}{m_1} - \frac{C_2}{m_2} \qquad (4)$$

Subtracting (2) from (3)

$$(C_2 d - C_3 d) = \frac{C_3}{m_3} - \frac{C_2}{m_2} \qquad (5)$$

Dividing (4) by (5)

$$\frac{C_2 d - C_1 d}{C_2 d - C_3 d} = \frac{\frac{C_1}{m_1} - \frac{C_2}{m_2}}{\frac{C_3}{m_3} - \frac{C_2}{m_2}} \qquad (6)$$

TABLE V

Comparison of Actual with Calculated Soil-water Ratios corresponding to pH Values given in Table II

| Actual quantity soil per 1000 cc water, gm | Calculated quantity of soil per 1000 cc required to give observed H-ion concentrations | | | | | | |
|---|---|---|---|---|---|---|---|
| | Soil Number | | | | | | |
| | 171A gms | 357A gms | 149A gms | 152A gms | 44A gms | 154A gms | 1WS gms |
| 1000 | 1000 | 1000 | 947 | 1015 | 995 | 1120 | 1000 |
| 447 | 424 | 453 | 429 | 426.4 | 449.6 | 630 | 249 |
| 200 | 214 | 207 | 205 | 215.4 | 190.3 | 204 | 86.3 |
| 89.4 | 94.2 | 81.05 | 95.6 | 73.78 | 94.3 | 87.2 | 34 |
| 40 | 40 | 42.15 | 58.74 | 39.99 | 40.1 | 38.1 | 17.6 |
| 17.88 | 19.9 | 23.31 | 20.6 | 21.9 | 21.9 | 19.25 | 12.0 |
| 8 | 8.3 | 12.18 | 9.92 | 10.6 | 10.52 | 9.63 | 8 |
| 3.56 | 3.56 | 4.59 | 3.52 | 4.01 | 3.77 | 4.43 | 4.4 |
| 1.6 | 1.6 | 1.66 | 1.40 | 1.6 | 1.6 | 1.87 | 2.1 |
| .716 | ——— | ——— | ——— | .35 | .626 | ——— | .74 |
| .32 | ——— | ——— | ——— | ——— | .338 | ——— | .32 |

Table V shows a comparison for seven of the soils studied of the grams soil per 1000 cc of water actually employed with the quantities of soil calculated to produce the H-ion concentration observed. It was not possible to give the calculated H-ion concentration for the variable amounts of soil used, since equation (5) does not lend itself readily to the calculation of "C."

The agreement of the calculated amounts of soil per 1000 cc required to produce the observed H-ion concentrations and the amounts actually used are in general very good for work of this nature. For six soils there is an almost exact agreement. Some discrepancies are apparent in the data for soils 154A and 1WS, while for soils 59A and 78A the data did not permit of calculation of the constants of the adsorption isotherm. These apparently abnormal soils will be discussed later.

### Graphic Representation of Results

To facilitate visualization of the variation of reaction with varying soil-water ratios as well as to bring out the degree of conformity of observed and theoretical values, it seemed de-

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Let

$$\frac{C_1}{m_1} - \frac{C_2}{m_2} = a$$

and

$$\frac{C_3}{m_3} - \frac{C_2}{m_2} = b$$

Then

$$b(C_2{}^d - C_1{}^d = a(C_3{}^d - C_2{}^d) \qquad (7)$$

From which

$$(a - b)C_2{}^d = a\ C_3{}^d - b\ C_1{}^d \qquad (8)$$

This equation cannot be solved directly, but $d$ can be calculated by a method of approximation where assumed values for $d$ (between 0 and 1) are substituted until a value is found which satisfies (8).

From (4)

$\beta = \frac{a}{C_2{}^d - C_1{}^d}$ from which $\beta$ can be calculated by substituting the determined value of $d$.

By substituting known values of $d$ and in (1), (2) or (3), K can be calculated.

sirable to express the data in graphic form. Figure 1 shows the direct plotting of H-ion concentration against the soil-water ratio (Curve I) and also the same data plotted against the logarithm of the soil-water ratio (Curve II) for soil 357A. In this and subsequent graphs with the exception of Curve IX and X in Fig. 3, and of Figs. 4 and 5, the curve itself connects values which satisfy the calculated isothermal constants, while the points representing experimentally determined values are enclosed by small circles. It will be observed that by this method of plotting, the curve approaches neutrality with increasing dilution at such a rate as to make significant differences between the logarithmically increasing soil-water ratios employed. The plotting of H-ion concentration against the logarithm of the soil-water ratio overcomes this objection. Data for all soils are shown plotted in this way in Figs. 2–3 inclusive.

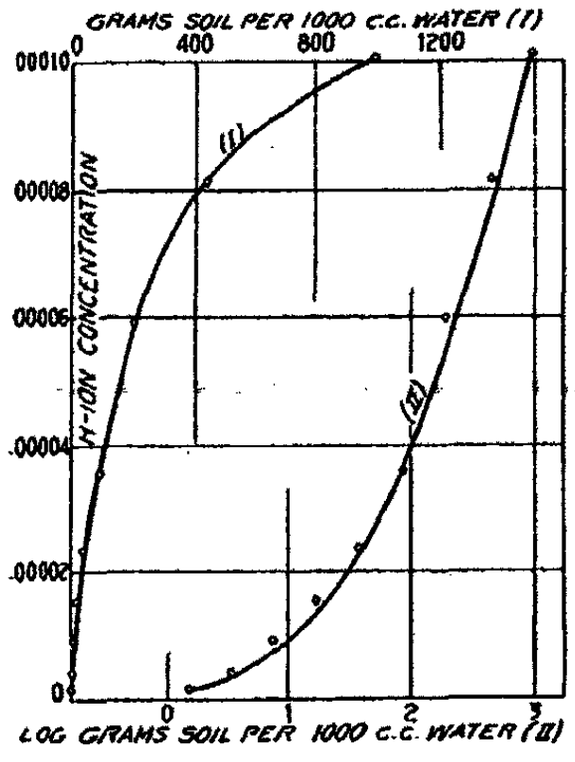



Fig. 1

Soil No. 357 A
$K = 1.319 \times 10^{-5}$
$\beta = 2.322 \times 10^{-4}$
$\delta = 0.32$

Both tabular and graphic representation of the data emphasize the fact that there is a close conformity of the observed values and the theoretical values calculated on the assumption that we are dealing with an adsorption phenomenon. With the soil designated as lWS, data shown graphically Curve VIII in Fig. 3, the observed H-ion concentrations are considerably below calculated values for the range of concentration from 17.88 gm to 1000 gm per liter. With soils 78A and 59A Curves IX and X in Fig. 3, the depression of H-ion concentration values over this same range of dilution is so great that it becomes impossible to calculate an ad-

sorption isotherm which will satisfy any three points on the curve.

The apparent abnormality over this range of dilution is more clearly shown by plotting the logarithm of the soil-water ratio against the logarithm of the pH values as shown in Fig. 5 for soils 78A, 152A, 171A and 1WS. Of these four

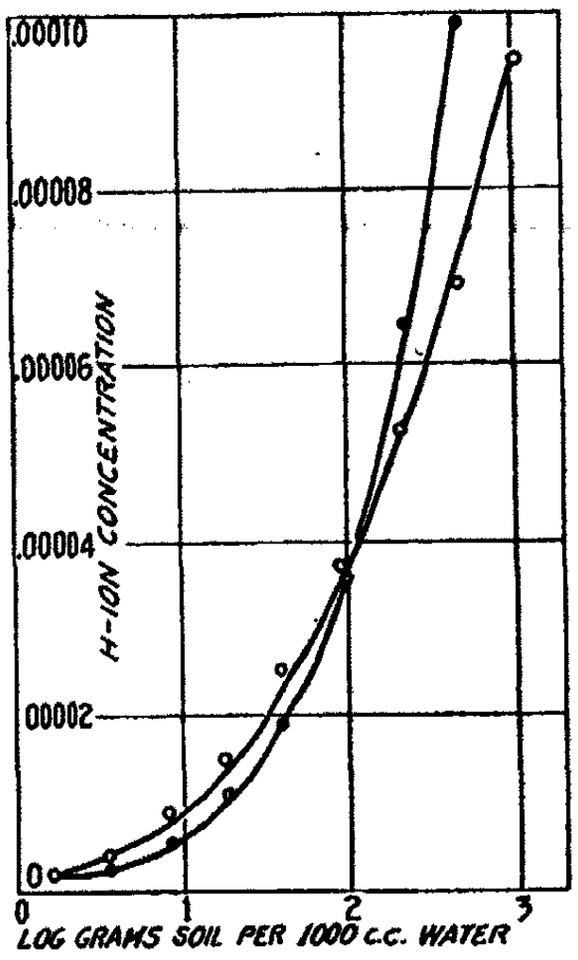



Fig. 2

| Dots | Circles |
|---|---|
| Soil No. 171 A | Soil No. 149 A |
| $K = 1.690 \times 10^{-5}$ | $K = 5.430 \times 10^{-5}$ |
| $\beta = 3.650 \times 10^{-4}$ | $\beta = 1.140 \times 10^{-4}$ |
| $\delta = 0.10$ | $\delta = 0.08$ |

soils, 152A and 171A, while conforming quite closely to the theoretical adsorption isotherm (See Curves V in Fig. 3, and Fig. 2), are seen to show this abnormal tendency to a slight extent at corresponding degrees of dilution. Curve IX in Fig. 3 for 78A and Curve VIII in Fig. 3 for 1WS on the other hand are seen to be decidedly depressed at these ranges as

compared to the former soils. The other five soils studied show similar tendencies, but to avoid complexity were not included in the graph. If we are actually dealing with an adsorption phenomenon it would appear that over the range of dilution noted there is a slight increase in the adsorptive ca-

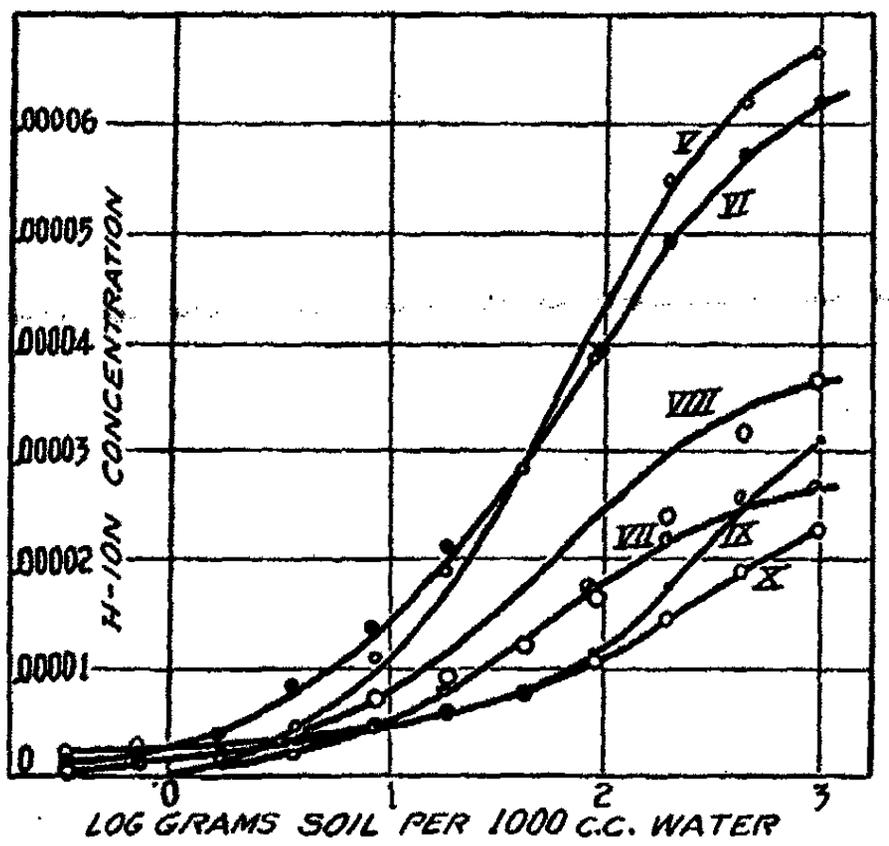



Fig. 3

| V | VI | VII |
|---|---|---|
| Soil No. 152 A | Soil No. 44 A | Soil No. 154 A |
| $K = 1.3257 \times 10^{-5}$ | $K = 1.2177 \times 10^{-4}$ | $K = 9.423 \times 10^{-6}$ |
| $\beta = 3.681 \times 10^{-4}$ | $\beta = 2.388 \times 10^{-4}$ | $\beta = 1.617 \times 10^{-4}$ |
| $\delta = 0.83$ | $\delta = 0.07$ | $\delta = 0.49$ |
| **VIII** | **IX** | **X** |
| Soil No. 1 WS | Soil No. 78 A | Soil No. 59 A |
| $K = 2.8818 \times 10^{-5}$ | | |
| $\beta = 2.206 \times 10^{-4}$ | | |
| $\delta = 0.2$ | | |

pacity of the soil, possibly due to an increased peptization of colloidal materials with increased specific surface. In this connection it is interesting to note that Bradfield[2] found a considerable increase in the relative amounts of colloidal

material present when a highly colloidal subsoil was suspended in increasing amounts of water. This increase was most rapid over a range of soil-water ratios in general similar to that noted above.

The highest soil-water ratio used in the H-ion measurements was 1:1 or a moisture content of 100% on a dry basis. This is of course considerably above moisture conditions for optimum growth relations. It is especially desirable to be able to predict the reaction at lower moisture ranges. Where H-ion concentration is plotted against the logarithm of the soil-water ratio the theoretical adsorption curve is an S-shaped line asymptotically approaching neutrality at infinite dilution on one end and asymptotically approaching some definite H-ion concentration at infinitely high soil-water ratios on the other. Curves V–VIII in Fig. 3 show the S-shape of the typical isotherm. In the two curves of Fig. 2 the bending of the curve at high soil-water ratios is not observed, and by the extrapolation of the theoretical curve it can be shown that this flexing of the curve should appear at soil-water ratios which are considerably higher than can be employed experimentally. Figure 2 shows at the highest soil-water ratio a slight tendency for this flex to appear.

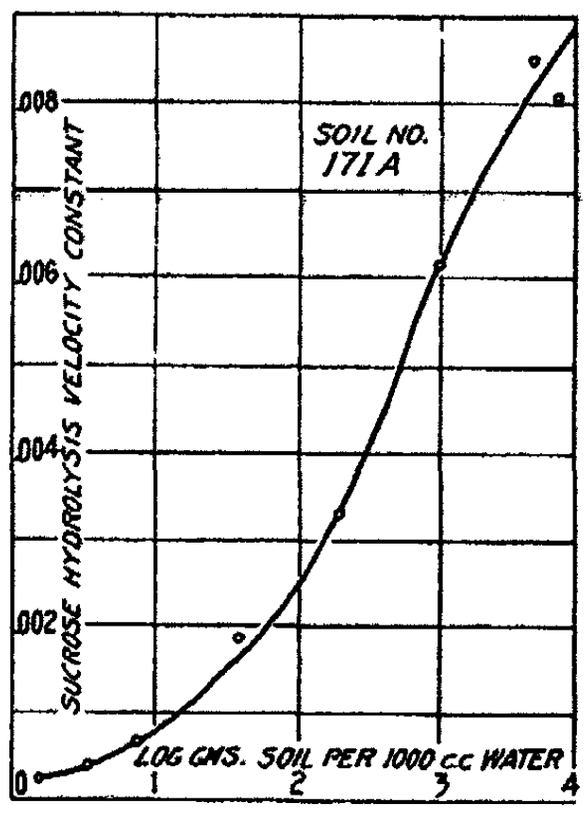



Fig. 4

It was hoped that by the sucrose-hydrolysis method it would be possible to investigate the higher soil-water ratios to better advantage. While over the range of dilution covered by both H-ion and sucrose-hydrolysis methods the two procedures appear to give results showing close correlation, as

shown by Table IV, the experimental error in the sucrose hydrolysis method at moisture contents below a 1 : 1 ratio was found to be so great that only a very general idea of the probable trend of the reaction could be obtained. This is apparent from Fig. 4 which shows graphically the sucrose-

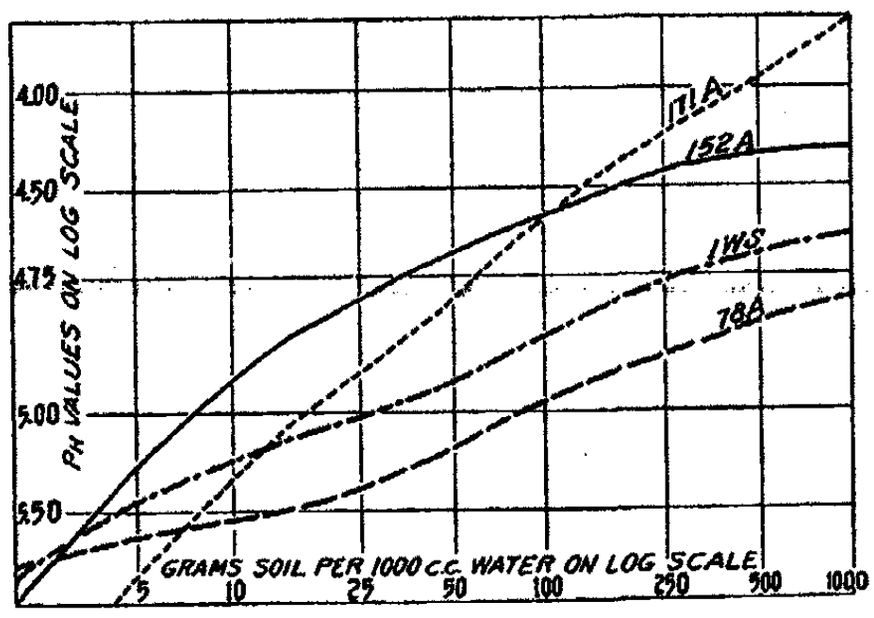



Fig. 5

hydrolysis data for soil 171A. The graph does show, however, that the flexing of the curve actually begins at a point beyond the highest soil-water ratio used in the electrometric H-ion measurements.

## Adsorption and Soil Acidity

Van Bemmelen[1] first suggested that the combination of bases with humus were not true chemical compounds but instead "mixtures of base and of various colloid substances held together by some sort of surface attraction." Later since the general theory of surface adsorption has been developed by Willard Gibbs, J. J. Thomson, Freundlich and Wo. Ostwald, it has been applied to soil processes by Cameron,[3] Parker,[13] Harris,[9] Russell,[17] Prescott,[15,17] Fisher[5] and numerous other workers. The term "adsorption" can at present be most satisfactorily described as the concentration of a solute on a

surface (in the case of soils at the interphase solid-liquid surface), due to interatomic attraction of a truly chemical nature, designated by Irving Langmuir[11] as secondary valence. That such surface concentration is rather definitely related to changes of surface tension and electrical potential has long been known. According to the ideas of Langmuir,[11] Harkins[8] and other workers on surface forces, the question as to whether surface concentration is a physical or chemical phenomenon would seem to be no longer pertinent.

On account of the high specific surface of soils, particularly those of finer types due both to their macroscopic and colloidal components it appears that they should offer unusual opportunity for surface phenomena in general. Under soil conditions the various soil colloids, due to mutual adsorption, probably form adsorption compounds of high complexity. This fact makes any prediction as to their adsorptive capacity, precipitation or physical properties very difficult. Since the colloidal material of most soils when suspended in water migrate in an electrical field to the anode, negative colloids must predominate at the normal reaction of such suspensions.

In general it can be said that a theory of surface concentration of adsorption which supposes the existence of a specific adsorptive relation between the surface of the adsorbent and the individual ions (including H and OH ions) of electrolytes, dependent upon the attraction of secondary valence of the atoms of the adsorbent and of the particular ions, can be made to explain most of the properties of soil acidity, basic exchange and precipitation phenomena in soils. The presence of an electrical charge on the surface of the adsorbent due either to certain production of ions in solution or to adsorption of ions from the solution opposes but does not necessarily prevent the adsorption of ions of like charge. The adsorption of oppositely charged ions neutralizes the electrical charge of a colloidal particle, decreases the electrostatic repulsion between such particles, and increases the interphase surface tension, all tending to decrease the stability of the colloid and favoring flocculation. The adsorption of ions of like charge

increases the charge of the colloid, thereby lowering the interphase surface tension and stabilizing the colloid thus necessitating the adsorption of more of the ion of opposite charge for precipitation. The H and OH ions have much greater adsorbability than most of the common ions, which fact explains the sensitivity of colloidal solutions to changes in reaction, also the fact that the iso-electric point of colloids generally can be stated in terms of pH in spite of the presence of other ions. Judging from the slope of the electrometric titration curve of soils above and below neutral the soil colloids have a stronger preferential adsorption for the OH than for the H ion. Basic exchange in soils can be looked upon as the substitution of one adsorbed cation by another, although Parker's work[13] would indicate that in the action of neutral salts on acid soils the replacement of adsorbed H-ions by the base of the salt is the primary action. Since equivalent quantities of various ions carry equal amounts of electrical energy it is not surprising that replacement of ions should take place in equivalent amounts. According to the adsorption theory the reaction of an acid soil with an alkali is a combination process involving both the neutralization of the H-ions present and the adsorption of the base. This agrees with Fisher's[5] conclusion from his study of the adsorption of CaO from calcium bicarbonate solutions by soils that "there would appear to be little doubt therefore that the lime requirement of a soil is the sum of two quantities: (1) the lime required to neutralize soil acids, and (2) the lime actually adsorbed by the soil complex, and it is impossible at present to differentiate between these." In this connection it should be mentioned that the value of "K" of the adsorption isotherm used in the present work gives a measure of the total amount of acidity in the soil in the form of adsorbed and unadsorbed H ions. The values obtained by this method, however, are so small as to indicate that either a relatively large fraction of the base adsorbed is used up in satisfying the adsorptive capacity of the soil or that the factors of ionization or solubility of unionized

acids are of considerable importance in determining soil reaction.

Loeb[12] has recently applied the theory of "Donnan Equilibrium" to the adsorption of electrolytes from colloidal solutions of the emulsoid colloids, gelatin, egg albumen and casein, and finds that it offers a very satisfactory explanation of the change in physical properties including viscosity, swelling and osmotic pressure with varying concentration of electrolyte, or varying pH. While this theory has never been applied to soils it would appear that a study of soil acidity and the physical properties of soils from the viewpoint of "Donnan Equilibrium" might be highly profitable. Donnan[4] has shown on thermo-dynamic grounds that when a membrane separates ions to some of which it is permeable and to others impermeable an equilibrium is set up between the ions which are free to pass through the membrane whereby they are unequally distributed on either side. Loeb has shown that the ultimate particles in colloidal solutions of gelatin, etc., are true ions and molecules. Since these are unable to penetrate the colloid proper, he assumes that each colloidal particle acts as if it were surrounded by a membrane impermeable to these ions and molecules, resulting in an unequal distribution of any electrolytes present between the solution within and without the colloidal particle. He has shown that the physical properties of such colloidal solutions are very definitely related to the potential difference which arises from such an unequal distribution of electrolyte. This distribution, which is logarithmic over a certain range of concentration, is in certain respects similar to the usual adsorption distribution.

## Summary

1. A study has been made of the H-ion concentration of nine acid soils at soil-water ratios varying from 1 : 1 to 1 : 3125, employing the hydrogen-electrode method.

2. The velocity of sucrose hydrolysis at a range of soil-water ratios from 1 : 0.0894 to 1 : 625 has been determined for five of the same soils.

3. The electrometric and sucrose hydrolysis methods were found to agree in indicating a systematic variation of H-ion concentration with variations in soil-water ratio, the highest H-ion concentration occurring at high soil-water ratios, with a progressive decrease as dilution is increased.

4. In general, the changes in H-ion concentration at varying soil-water ratios agree with the distribution of H-ions between soil and solution which could be expected if controlled by an adsorption mechanism.

5. A slight tendency was noted with all soils to deviate from the theoretical adsorption values over a restricted range of dilution. With two of the nine soils studied, this deviation was sufficient to prevent the determination of a theoretical equation which would describe the variations in H-ion concentration observed.

6. On the basis of the results obtained, it appears that the reaction of a soil is dependent upon: first, the total dissociated acid present; second, the adsorptive capacity of the soil for the H-ion; and third, the soil-water ratio.

## Conclusion

In view of the fact that the effective hydrogen-ion concentration of a soil is not a constant, but varies significantly and systematically when the soil-water ratio is changed, it must be recognized that the reaction of a soil as ordinarily determined by either electrometric or colorimetric procedures is not an exact indication of the reaction of the same soil at normal field moisture contents. For the soils included in the present study, the calculated reaction at a field moisture content of 20% varies from .10 to .85 pH below the reaction at a soil-water ratio of 1:5. Part of the difficulty of interpreting work involving measurements of soil reaction might perhaps be eliminated if workers in this field would agree to accept some standard soil-water ratio for measurements of this kind. The authors would suggest a soil-water ratio of 1:5 as being well suited to both colorimetric and electrometric procedures. Where a more accurate idea of the reaction at low moisture

contents is desired this can be obtained by extrapolation of the graph connecting the H-ion concentration determined at three soil-water ratios, preferably 1:5, 1:25 and 1:125. Plotting the pH values against the logarithm of the soil-water ratios lends itself best to this treatment.

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# THE SIZE-FREQUENCY DISTRIBUTION OF PARTICLES OF SILVER HALIDE IN PHOTOGRAPHIC EMULSIONS AND ITS RELATION TO SENSITOMETRIC CHARACTERISTICS[1]

## PART IV

BY E. P. WIGHTMAN, A. P. H. TRIVELLI, AND S. E. SHEPPARD[2]

### Relation of Size-Frequency to Sensitometric Properties

1. *Theoretical Discussion.*—Before considering the actual correlation of the observed frequency curves and the sensitometric constants derived from the corresponding characteristic curves, let us see what relations may be anticipated from the photochemical theory of the characteristic curves.

These, curves, it is well known, represent the accumulation of the developed silver as a function of exposure, which in turn is a function either of increasing intensity or of increasing time, the other factor being kept constant.

If the so-called reciprocity law

$$E = It \tag{1}$$

held, the two functions would be identical. If the exposure is given by Schwarzschild's law

$$E' = It^p \tag{2}$$

the intensity and time curves will only differ in the silver mass, or *density* ordinate by a common factor $p$, and otherwise will be of the same form.

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[1] Communication No. 148 from the Research Laboratory of the Eastman Kodak Company.

[2] We have given in the preceding paper (Part III of this series) the experimental results of size-frequency measurements of a number of typical photographic emulsions and of the determination of their empirical sensitometric characteristics. In the present paper we shall discuss the theoretical bases for the correlation of this data.

The conclusions of Slade and Higson that intensity enters into the density-exposure function as $I^2$ for small values of I (and large values of $t$) and as I for large values of I (and small values of $t$) do not appear to us conclusively proven. In the first place, if uniformity of sensitivity be conditioned by uniformity of size of grain, then their process emulsion does not appear to us, in defect of statistical data, likely to have been sufficiently uniform. Secondly, if sensitivity variation exists among grains of the *same* size, then their experiments do not really determine "the photochemical law of the (individual) silver halide grain," for statistical variation of sensitivity among the grains would invalidate any such conception.

For the elementary theory it is sufficient, therefore, to assume equation (1) to hold and that either I or $t$ may be held constant while the other is varied.

2. *The Fundamental Reaction.*—Let us first of all assume the simplest case and set up equations for the course of the fundamental photochemical reaction in a homogeneous system, i. e., molecularly disperse; and then let us consider in what way the derived equations will be modified by the introduction of definite statistical variations associated with the dispersity of the reacting materials. The relations thus obtained will then be typical of the relations to be anticipated between the size-frequency curves and the sensitometric curves.

Let $\Delta$ = the thickness of the homogeneous emulsion layer
$a$ = the original concentration of the unaffected silver halide
$x$ = the amount of silver halide altered in time, $t$
$I_0 = I_0'(1 - R)$ = the intensity of light incident per unit area, corrected for reflection
A = the light absorbed per unit volume
K = the absorption coefficient.[1]

We shall assume initially that the light is monochromatic, that the reaction is irreversible, and also that the product is not photo-active, i. e., neither autocatalytic nor absorptive.

[1] R. W. Wood: "Physical Optics."

These may well be questioned as undue simplifications, in view of the complexity of the photochemical change in silver halides. Nevertheless, they are the more justifiable, if we consider only the production of the "latent image," i.e., the photo-product which is produced in quantities below visual perception.

Yet it has to be assumed that the "latent image" production is faithfully revealed by the process of development, or that

$$D = \gamma.\Phi = \gamma x \tag{3}$$

where $\Phi$ is any given mass of latent image, $\gamma$ is the development factor, i. e., a constant depending only upon the development, and D is the photographic density produced by development.

Then according to the Grotthuss-Draper law of photochemical absorption,[1] the rate of change

$$\frac{dx}{dt} = -\frac{d(a-x)}{dt} = kA \tag{4}$$

but

$$A = \frac{I_0}{\Delta} - \frac{I}{\Delta} \tag{5}$$[2]

where I represents the light transmitted and since from Beers' law[3]

$$I = I_0 e^{-K\Delta(a-x)} \tag{6}$$

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[1] Grotthuss: Gilbert's Ann. Phys., **61**, 50 (1819); Draper: Phil. Mag., [3] **19**, 195 (1841); cf. also W. D. Bancroft: Jour. Phys. Chem., **12**, 213 (1908).

[2] If the changed material does absorb then

$$A = \frac{I_0}{\Delta} - \frac{I}{\Delta} + \frac{I'}{\Delta}$$

where I has the same value as above and I′ is the intensity of the light absorbed by the changed material with a corresponding absorption coefficient K′. In a paper by F. Halla and A. Schuller [Zeit. phys. Chem., **93**, 173 (1918)], they assume at the start two different absorption coefficients, but they use a somewhat different argument from our own. They later arrived at a result similar to that of Hurter and Driffield (to be considered later) by assuming then that their two absorption coefficients are equal.

[3] Beers: Pogg. Ann., **86**, 78 (1852).

equation (5) becomes

$$A = \frac{I_0}{\Delta}\left[1 - e^{-K\Delta(a-x)}\right] \tag{7}$$

hence (4) becomes

$$\frac{dx}{dt} = -\frac{d(a-x)}{dt} = \frac{kI_0}{\Delta}\left[1 - e^{-K\Delta(a-x)}\right] \tag{8}$$

Integrating this we have

$$-\int \frac{d(a-x)}{1 - e^{-K\Delta(a-x)}} = \frac{kI_0}{\Delta}\int dt \tag{9}$$

whence

Let $(a - x) = y$, $-K\Delta = b$, and $z = e^{by}$; then $dy = \frac{1}{b} \cdot \frac{dz}{z}$ and

$$-\int \frac{dy}{1 - e^{by}} = -\frac{1}{b}\int \frac{dz}{z(1 - z)} = -\frac{1}{b}\left\{ln\, z - ln(1 - z) + C\right\}$$

whence

$$ln \frac{e^{-K\Delta(a-x)}}{1 - e^{-K\Delta(a-x)}} + C = kKI_0t \tag{10}$$

when $t = 0$, then $x = 0$ and

$$C = -ln \frac{e^{-K\Delta a}}{1 - e^{-K\Delta a}}$$

substituting this in (10) we get

$$ln \frac{e^{K\Delta x} - e^{-K\Delta(a-x)}}{1 - e^{-K\Delta(a-x)}} = kKI_0t \tag{11}$$

which, by multiplying numerator and denominator by $e^{-K\Delta x}$ may be put in the form

$$ln \frac{1 - e^{-K\Delta a}}{e^{-K\Delta x} - e^{-K\Delta a}} = kKI_0t \tag{12}$$

which reduces to

$$e^{-K\Delta x} = e^{-K\Delta a} + (1 - e^{-K\Delta a})e^{-kKI_0t} \qquad (13)^1$$

Now let us consider the three principal cases (*a*) when the absorption coefficient, K, is very large, (*b*) the other limiting case when K is very small, and finally, (*c*) the general case for moderate absorption.

(*a*) When K is very large there is very strong absorption. The larger K, the smaller $e^{-K}$, hence when $e^{-K}$ becomes negligible, $e^{-K\Delta(a-x)}$ is also negligibly small, and equation (11) becomes

$$ln\, e^{K\Delta x} = kKI_0t \qquad (14)$$

which gives

$$\Delta x = kI_0t \qquad (15)$$

i. e.,

$$x = \frac{k}{\Delta} I_0t = k'I_0t$$

or, substituting in (3)

$$D = \gamma.k'I_0t \qquad (16)$$

a linear relation between density and exposure, which is actually true photographically for the first stage of exposure. We should expect this phase to be more prolonged for strongly absorbed (e. g., blue violet) light, and less for slightly absorbed (e. g., red) rays.

(*b*) The alternative extreme case is for very weak absorption, i. e., for K very small—either for very short wave lengths (X-rays) or for very long wave lengths (red, etc., in non-color-sensitized emulsions).

Now the function $e^{-K\Delta a}$ can be expanded thus

$$e^{-K\Delta a} = 1 - K\Delta a + \frac{(K\Delta a)^2}{\lfloor 2} - \frac{(K\Delta a)^3}{\lfloor 3} + \ldots \qquad (17)$$

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[1] J. Plotnikoff's integration [Zeit. wiss. Phot., 19, 238 (1920)] of a similar differential equation leads to a different result and appears to us incorrect.

also $e^{-K\Delta x}$ may be expanded in like manner, and if K is very small, we may neglect all terms above the first two, then putting $D'_{max}$ for $K\Delta a$, and D′ for $K\Delta x$ in these expansions, and substituting them in equation (12), we get

$$ln \frac{D'_{max}}{D'_{max} - D'} = kKI_0t = \kappa' I_0 t \tag{18}$$

which may be written

$$D' = D'_m(1 - e^{-\kappa' I_0 t}) \tag{19}$$

This equation, identical in form with the so-called monomoleeular reaction equation for "dark reactions," is the same as that proposed by Elder[1] for the characteristic curve, although obtained by slightly different premises, viz., from the so-called "intensity" formulation of reaction velocity of light, and the mass law for a monomolecular reaction.

$$\frac{dx}{dt} = KI_0(a - x) \tag{20}$$

It happens that for very low absorption these give the same formula as above. As it stands, however, this does not represent the actual course of the sensitometric curve satisfactorily. We shall see later how this equation has been modified to take care of both stronger absorption and statistical variation.

(*c*) Finally, for the general case we may write equation (13) in the form

$$K\Delta x = - ln[e^{-K\Delta a} + (1 - e^{-K\Delta a})e^{-KkI_0 t}] \tag{21}$$

or

$$D' = - ln[e^{-D_m} + (1 - e^{-D_m})e^{-k' I_0 t}] \tag{22}$$

Hurter and Driffield's formula[2] for the characteristic

[1] Elder: Jour. Camera Club, **7**, 131, 135 (1893).

[2] Hurter and Driffield: Jour. Soc. Chem. Ind., **9**, 455 (1890).

curve is obtained from the equation

$$\frac{dx}{dt} = \frac{I_0}{i}\left[e^{-kx} - e^{-ka}\right] \tag{23}$$

$I_0$ having the same significance as above, $i$ being the inertia of the emulsion, $\frac{I}{i}$ being approximately equivalent to our $K\Delta$; $e^{-kx}$ is the light not absorbed by the changed silver, i. e., the transparency with respect to the changed plate; and $e^{-ka}$ is the light not absorbed by the total silver, i. e., the transparency with respect to the original plate.

When integrated and rearranged (23) gives

$$ln\frac{1 - e^{-ka}}{1 - e^{-k(a-x)}} = \frac{kI_0t}{e^{ka}i} \tag{24}$$

which is the same as

$$kx = ln\left[e^{ka} - (e^{ka} - 1)\, e^{-\frac{1}{e^{ka}}\frac{I_0t}{i}}\right] \tag{25}$$

Hurter and Driffield substituted $\frac{D}{\gamma}$ for $kx$ and O, i. e., the opacity of the unchanged plate, for $e^{ka}$, thus

$$D = \gamma\, ln\left[O - (O-1)\, e^{-\frac{1}{O}\frac{I_0t}{i}}\right] \tag{26}$$

Assuming that O is large with respect to 1, which is similar to our case ($a$) where K was assumed large (26) reduces to

$$D = \gamma\, ln\frac{I_0t}{i} \tag{27}$$

by discarding powers greater than 1.

If O is assumed very small compared to 1 then (26) becomes

$$D = \gamma\frac{1}{O}\frac{I_0t}{i} \tag{28}$$

which, unless $\frac{It}{i}$ has a very small value, is very large. But

this equation is a linear relation, whereas in case (*b*) above we obtain the monomolecular relation.

It does not appear worth while at present to discuss in detail the differences or similarities of these equations.

Ross[1] has pointed out, however, that Hurter and Driffield's assumption that the transparency of the light-affected material is given by $e^{-kx}$, while that of unaffected material is given by $e^{-ka}$, must be incorrect, since it leads to a mathematical inconsistency. The incorrectness appears to lie in the assumption that $k$, the absorption coefficient, is the same for both affected and unaffected halide. The experimental proof Hurter and Driffield give for this is vitiated by the difficulty of determining true absorption coefficients of silver halide from opacities of emulsions.

On the other hand, the assumptions we have made in the general formula, namely, that the photo-product exerts neither a light absorbing nor a catalytic rôle, are not entirely warranted. However, the complications introduced by allowing for these are for the moment not justified by any obvious advantages.[2]

3. *Effect of Heterogeneity of Material on the Fundamental Reaction.*—Before considering any such complications of the fundamental reaction equation, let us rather suppose this to be of simple type, e. g., either like equation (16) or (19), and then consider the effect produced by supposing the material not homogeneous and continuous, but heterogeneous and discrete.

In point of fact, the silver halide emulsion has not the homogeneity really assumed in the Hurter and Driffield and

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[1] Ross: Jour. Opt. Soc. Amer., **4**, 255 (1920).

[2] If the actual photosensitive material be supposed to be dispersed metallic silver, in agreement (to this extent at least) with Renwick's theory of the latent image [Hurter Memorial Lecture, Jour. Soc. Chem. Ind., **39**, 156T (1920)] and with Weigert's recent work [Sitzungsber. Akad. Wiss. Berlin, 39, 641 (1921)], and if we suppose this adds to itself autocatalytically, by action on the silver halide, then the autocatalysis will tend to be opposed by the increased absorption, thus approaching the condition assumed above (so long as we are considering only the latent image).

other theories, which suppose a molecularly disperse system, each molecule of identical reactivity to light. Actually, the material is a suspension of crystalline grains of a variety of sizes—if not varying in other respects.

It may be further considered possible, even probable, that wide variations of "sensitivity" exist among the grains of one and the same emulsion. We may initially define "sensitivity" as the reciprocal of the energy required to make a grain developable by a developer of given reduction potential. It is generally accepted at present that the condition for developability is a *nucleus*, i. e., that the photo-effect, whatever its nature, is localized in the grain. The most concrete development of this is that the nuclei consist of colloid silver, either provided (in part at least) by photolysis of silver halide, or formed by condensation of pre-existent colloid silver amicrons to submicrons. This latter hypothesis is due to F. F. Renwick.[1] His primary contention, that the sensitive substance is not silver halide at all, but colloid (metallic) silver has recently received support from some remarkable experiments of F. Weigert.[2] In formal contrast to this stands the thesis that the photo-effect is not localized in nuclei, but consists in the altered reactivity of the silver halide crystal as a whole, or at least of a whole surface. This increased reactivity may now be conceived as a change of quantum state of the atoms, e. g., in such a form that the ionic pairs $Ag^+Br^-$ in the lattice system $[Ag\ Br_6]\ [Ag_6\ Br]$ possess intermediate stable states intervening in the reaction

$$\begin{array}{ccc} Br^- & \xrightarrow{\ominus} & Ag^+ \\ \downarrow & & \downarrow \\ Br & & Ag \\ \text{(bromine atom)} & & \text{(silver atom)} \end{array}$$

and that these intermediate phases have increased reactivity (e. g., by way of adsorption) toward reducing agents. The

[1] F. F. Renwick: Hurter Memorial Lecture, Jour. Soc. Chem. Ind., 39, 156T (1920).

[2] F. Weigert: Sitzungsber. Akad. Wiss. Berlin, 39, 641 (1921).

behavior of the latent image to oxidizing agents, and its stability when silver bromide is converted to iodide are not satisfactorily accounted for. In either case, if we attribute a definite sensitivity to a grain, this means that a certain finite increment of energy is necessary for developability. In the general problem of chemical reactivity, what has been termed the *critical energy increment*[1] of a molecule is analogous to this "inertia" of the grain, the reciprocal of its sensitivity.

Considering the variable of sensitometry, the *density* D, it must be remembered that to a near approximation grains contribute, on complete development, to density in proportion to their number and size conjointly, or again, to a slightly lower approximation, to their number and projective area. The quotient

$$\frac{\Delta D}{\Delta E} = \frac{\text{density increment}}{\text{energy increment}}$$

reckoned per unit area, would appear *a priori* to be independent of the size of grain, assuming a continuous wave-front. But if conditions permit a local concentration of energy related to the size of grain, the magnitude of the above quotient will depend upon the distribution of grain sizes in unit area.

Supposing a continuous wave-front, that is, *not* a quantum-like or discrete structure of radiation, local condensation of the energy to the critical increment might be effected in the material: (1) by reason of a variable distribution of a photochemical catalyst in the material, or specifically, among the grains. The probability of a grain reaching the critical increment would then depend upon its having a certain amount, and perhaps individual distribution, of the catalyst, the primary function of which would be to increase the energy density of absorbable type.[2] Colloid silver submicrons supply a concrete example. Alternatively, it may be supposed that the silver halide is itself relatively inert, and with Renwick that the colloid silver particles are the true photosensitive material. In either case,

[1] W. Mc C. Lewis: "System of Physical Chemistry," **3**, 140 (1919).
[2] W. Mc C. Lewis: Loc. cit.

the distribution of the "catalyst" could depend on the size of the grains, e. g., the probability of a grain having sufficient catalyst might be proportional to its mass. *In this case, the sensitiveness-variation curve would coincide, to a first approximation, with the size-frequency curve*, for one and the same emulsion. On the other hand, the effective distribution of catalyst might not coincide with the size-frequency. The very ingenious experiment of Toy[1] shows that grains of the *same size and shape* similarly oriented to the light need not have the same sensitiveness but can give a normal characteristic curve. (2) Local condensation and a sensitivity variation might be effected, as suggested in Toy's paper, by optical conditions of refraction, reflection, etc., depending on chance orientations and concentrations of the crystalline grains. Such a hypothesis is difficult to prove or disprove, but the statistical data being accumulated may strengthen or weaken its plausibility.

There remains, by exhaustion, the possibility of local, or granular, concentration of energy not by virtue of inherent factors of the sensitive material, nor by accidental circumstances in its disposition, but as a necessary consequence of a discrete structure of the energy itself.[2]

The mathematical development of this assumption has been dealt with by Dr. L. Silberstein.[3] It may be pointed out here that to a large extent it gives the same relation between effective sensitivity variation and size-frequency distribution as

[1] F. C. Toy: Phot. Jour., **61**, 417 (1921). That such grains can give a characteristic curve indicates either that they vary in sensitiveness inherently from one another by other factors than size and shape, or that the fundamental reaction is governed by none of the premises so far assumed—namely, continuous wave front, etc., and would apparently favor the quantum hypothesis mentioned in the next succeeding paragraph. On the other hand, the fact that there are emulsions of large grain size which are less sensitive than some emulsions with smaller sizes, and also that an emulsion can change its sensitiveness on standing unexposed for a period of time in its original box seem to show that we cannot throw overboard every idea of an inherent variation in sensitiveness. We may note here also, in connection with the data given later, that in *thick* grains the *position* of a photocatalytic center might vary in grains of the same size and shape.

[2] Cf. F. E. Ross: Astrophys. Jour., **52**, 96 (1920).

[3] L. Siberstein: Phil. Mag. in press (1922).

that previously discussed on the hypothesis of a photocatalyst distributed among grains with a probability varying as their masses. On the quantum theory, however, it is the projective area which is fundamental rather than the mass. The very important modifying factor of "clumping," or secondary aggregation of the primary grains will be noted in connection with the results of measurement of size-frequency.

Instead of making any restricted hypothesis concerning sensitivity, we may suppose that a general sensitivity variation exists, without explicit statement as to what determines sensitivity.

The conception of statistical variation among the reacting units—as distinct from difference of chemical species—has not entered much into the general chemical dynamics. Statistical variation of gas molecules as to velocity has been from the first, however, a feature of the kinetic theory of gases. Through statistical mechanics and the radiation theory this has begun to react powerfully on classical chemical kinetics.

Nevertheless, it is not in this field that we may immediately expect to find instances of variation applied to reaction velocity problems, but rather in the field of biochemistry. In problems of the immunochemistry of cells and unicellular organisms, the existence of variation has to be admitted *ex post facto*, without, at present, any satisfactory theory for the origin of variation prevailing.

While we have utilized conceptions developed in this field by W. McC. Lewis, R. C. Tolman and E. K. Rideal, without recitation of the earlier work, we may refer particularly to a valuable review by S. C. Brooks,[1] on "The Mechanism of Disinfection and Haemolysis." In order not to confuse the issue, we shall not refer further to the explicit cases dealt with by this author (haemolysis of blood corpuscles, mortality of spores, etc., under attack of disinfectants), but briefly restate his argument for the general case of a reaction—termed the fundamental reaction—consisting in the transformation of one kind of discrete particles into another—in our own case, the passage of

[1] Brooks: Jour. Gen. Physiol., 1, 61 (1919).

unexposed silver halide grains into developable grains, and thereby, into silver grains, under the influence of light.

So far we have discussed such a change solely in terms of the course of a fundamental reaction—implicitly of identical molecules not varying *inter se*. Brooks points out that the actual course of such a process may be very largely dependent upon the variations in resistance among the different individuals, and only secondarily upon the course of the fundamental reaction.

Now the actual progress of the reaction may be expressed graphically in two ways. First, as the usual accumulation or time-curve, the amount changed being plotted as ordinate against time as abscissa. For dispersed granules or cells, we could plot (number x volume) against time. There is also the rate curve, the ordinates being the amount of substance changed per unit time $\frac{\Delta x}{\Delta t}$, plotted against time. The former is the more usual in reaction kinetics, while the latter is the "mortality curve" of vital statistics. The latter curve is evidently the first derivative of the time curve, and we can pass from the *rate* curve to the *time* curve, either empirically by graphic integration, or algebraically, if the differential equation expressing the rate curve is known and integrable. Conversely we can obtain the rate curve from the time curve by differentiation.

Essential to the present argument is the fact that under certain conditions the *rate* (or mortality) curve may be identical with the variation (or frequency) curve of individual resistivities (inertias, reciprocals of sensitivities). Supposing the time-curve replaced photographically by an exposure curve

$$D = f(E) \tag{29}$$

then with certain restrictions to be discussed, the first derivative of this

$$\frac{dD}{dE} = f'(E) \tag{30}$$

would give the variation curve of inertias of the reacting particles, or correlatively, the sensitivity-frequency curve.

The importance of the first derivative of the characteristic curve was first noticed by Nutting, Jones and Mees[1] for positive emulsions. It was introduced as dependent upon finite groups of grain sensitivities by Ross[2] in a theoretical discussion of the density-exposure function, and attention was a little later drawn to the subject in respect to negative emulsion by F. F. Renwick.[3] The latter's statement of the fundamental property of the derived curve appears to agree to a large extent with the conclusions reached here. "Since every ordinate of the derived curve represents the amount of silver bromide which has just attained the developable condition at the corresponding exposure, it is evident that we might regard each ordinate as a measure of the quantity of silver bromide in the film having that particular true inertia value." It is now evident that if for "quantity" we substitute "number of particles per unit area" that the first derivative becomes the statistical frequency curve of inertias—provided there is no reduction of intensity through the film, as noted by Renwick, but also provided that the relation of grain size to grain sensitiveness is explicit.

Considerable modifications are necessary before these premises can be applied to actual sensitometric curves—obtained normally as

$$D = \phi (\log E) \tag{31}$$

with first derivative

$$\frac{dD}{d \log E} = \phi' (\log E). \tag{32}$$

To facilitate this application we have developed an approximate theory of the density-exposure function for very restricted conditions. The direct theoretical development of a

[1] Phot. Jour., **54**, 342 (1914).
[2] F. E. Ross: Jour. Opt. Soc. Amer., **4**, 255 (1920).
[3] Phot. Jour., **61**, 10 (1921).

function for the characteristic curve is beset with difficulty. Application of the calculus to a system composed of finite discontinuous units, such as silver halide grains, is itself contestable, and the difficulty becomes greater if statistical variation of the grain sensitivities is admitted.

The following device has been adopted for an indirect attack. In the relatively simple photochemical reaction in an ideal homogeneous system, as assumed at the outset, the heterogeneity or variation factor will now be introduced by replacing the reaction-constant of this function by various sensitivity or inertia-variations.

These expressions, on the other hand, are such as have been found experimentally to represent our size-frequency data. A preliminary basis is afforded for comparison of these size-frequency curves en bloc:—

*a.* With graphically determined first derivatives of experimental

$$D = f(E) \text{ curves.}$$

*b.* With algebraically derived first derivatives of theoretical

$$D = f(E) \text{ curves.}$$

We do not propose at this stage to consider the effect of modifying assumptions proper to the homogeneous reaction, e.g., allowing for absorption by the altered silver halide, for limited autocatalysis by the photoproduct, etc.[1] It is indeed quite feasible that actually, for any grain singly, the absorption by altered halide plays a negligible part for the normal latent image formation, since the "latent image" active in normal development will be mainly superficial. It has appeared to us more important to proceed to consideration of sensitivity variation.

Consider the simplest case of sensitivity distribution, viz., negligible deviation from a certain average value. The

[1] The changes in developability of the grain, with different developers, with solarization, with iodide, etc., are not consistent with so simple a view as that adopted, but these are secondary properties.

sensitivity variation curve, corresponding to the rate curve, would be a straight line perpendicular to the abscissa. Its integral, the time curve, would, if the fundamental reaction is supposed uniform (of zero order), follow the axis to this point of intersection, then rise perpendicularly. That is, all grains would become developable at the same exposure.

Apart from inherent and "quantum" sensitivity variations, in thick layers absorption of light in the upper layers involves an apparent gradient of sensitivity through the film. This is partly allowed for in the deduction of a reaction formula, which remains, however, of complicated form except for very high or very low values of the absorption factor. (See previous section.)

Following Ross, we may combine this absorption factor with inherent variation of sensitivity. Before resorting to this artifice it will be simpler to limit consideration at first to one-grain layers. Suppose the photochemical absorption proper to be of such large or such small magnitude as to give the limiting cases obtained for the ideal reaction:

$$(a) \quad x = kE, \text{ Uniform rate} \tag{33}$$

$$(b) \quad x = a\,(1 - e^{-kE}), \text{ Monomolecular rate.} \tag{34}$$

Then let us assume that the material is broken up into "micro-systems," each obeying one or the other of above formulae but in either case having different individual values of $k$—the velocity constant—distributed according to some probability function, e. g., the normal law of error. We must then equate the actual rate to the distribution function of the $k'$ values, i. e., to the sensitivity distribution.[1] For immediate convenience in testing the "size variation" hypothesis of sensitivity, we have selected distribution functions of the type found experimentally to represent our actual size-frequency data. The general progressive increase of "speed" with grain

[1] The equating of $i$ $1/k$ to $E = \phi\,(I, i)$ will appear more obvious if we reflect that $i$ (= resistance or inertia) is effectively the *period* of *existence* of the particle unchanged by light, i. e., is the exposure required to change it.

size shown in our data (Jour. Phys. Chem., **27**, 1 (1923). warrants such an attempt.

In general, if the granular material does not cover the whole of a given area, say 1 sq. cm., for which the reaction is being considered, the available exposure will be that falling on the normal grain surface or projective area, i. e., according to previous considerations.

$$a. \qquad \frac{dx}{dt} = kI.S \qquad x = S.E \tag{35}$$

$$b. \qquad \frac{dx}{dt} = k'I.S(a - x);\ x = a(1 - e^{-k'SE}) \tag{36}$$

provided the grains have the same sensitivities (or inertias), and $S = \sum_{o}^{n} s$, the sum of the areas of $n$ grains per sq. cm. Now we may obviously have two extreme cases for the function $k = f(i)$, the variation of inertia, in relation to size of grain.

These are:

Case (*i*) $k = f(i)$, totally independent of grain-size. Then, if the grains are the *same size*, integration has to be extended only to inertias, if of different sizes, to both inertias and grain sizes.

Case (*ii*) $k = f(i)$ is a function of grain size. For example, the sensitivity may vary directly as the grain-size, or the inertia inversely proportional thereto. This is the simplest possibility, integration over a range of sizes being at the same time integration over sensitivities.

According to the argument developed, either of these cases may be conjoined with the fundamental "molecular" equation (*a*) or (*b*). This procedure is developed to illustrate the modifications, in the following synopsis:

EQUATION TYPE (*a*)

| | Fundamental reaction | Variation function of inertias | Size condition | Integral, or exposure function |
|---|---|---|---|---|
| *i.* | $\frac{dx}{d\mathrm{E}} = k$ | $k = y = y_0$ | S (All same size) | |
| *ii.* | $\frac{d\mathrm{D}}{d\mathrm{E}} = k$ | $f(i) = y = y_0$ | S | $\mathrm{D} = k\mathrm{E}\mathrm{B}s$ |
| | $\frac{dx}{d\mathrm{E}} = k$ | $k = f(i)$ | S | $\mathrm{D} = s\int f(i)di$ |
| | | e. g., $f(i) = \mathrm{B}e^{-ki}$ | S | $\mathrm{D} = \mathrm{B}s\int e^{-ki}\,di$ |
| | | | | $= \mathrm{B}s\int e^{-k\mathrm{E}}\,d\mathrm{E}$ |
| | | | | $= \frac{\mathrm{D}_m}{k}(1-e^{-k\mathrm{E}})$ |

*Note.*—A uniform rate of reaction, combined with an exponential inertia-distribution. gives the same type of density function (for constant grain size), as the "mono-molecular" rate combined with uniform inertia-distribution. If the size of grain *s* varies, integration must be extended over *f* (s) *ds* for the corresponding limits as *f* (*i*) *di*—which are not given unless the relation of *i* to *s* is explicit.

EQUATION TYPE (*b*)

| Fundamental reaction | Variation function of inertias | Size condition | Integral, or exposure function |
|---|---|---|---|
| *i.* $\frac{dx}{dE} = k(a-x)$ | $k$ constant | S (Same size) | $D = D_m(1-e^{-k'E})$ |

*ii.* $\frac{dD}{dE} = k'(D_m - D)$

$\frac{dD}{D_m - D} = k'dE$ $\quad k' = f(i)$ $\quad$ S $\quad \int \frac{dD}{D_m - D} = \int f(i)di$

$k'dE = f(i)di$ $\quad \frac{1}{D_m} ln \frac{D_m}{D_m - D} = (1-e^{-kE})$

or

$\frac{D_m}{(D_m - D)} = e^{\frac{D_m}{k'}(1-e^{-k'E})}$

$D = D_m\,(1-e^{-\mu})$

---

*Note.*—This expression, $D = D_m\,(1-e^{-\mu})$ which may be written

$$D = D_m\left[1-e^{-D_m}\int_0^E e^{-KE}dE\right]$$

has considerable similarity to that obtained by Ross[1] ([1]*Jour. Opt. Soc. Amer.*, 4, 255 (1920)), viz.

$$D = D_m\left[1 = \frac{1}{n}\sum_{p=0}^{p=n-1} e^{-Kr^pE}\right]$$

where $n$ is the finite number of classes in grains of different sensitivities supposed arranged in geometrical progression, $p$ the sensitivity factor, $r$ the ratio of sensitivities of different groups.

**Relation of Size of Grain to Inertia**

On the "quantum" theory, as developed by Dr. L. Silberstein, the relation of "size of grain" to "inertia of grain" is apparently quite explicit. The projective-area of the grain, say $s$, is the measure of its chance of being hit by a quantum, hence, is the effective sensitiveness, statistically. On the other hand, the "size of grain" considered in this is not necessarily the "size" as found by the direct measurements of frequency, nor is the distribution function of sizes thus directly available for the quantum theory but requires some corrections for reasons noted later. We may, without immediate recourse to this theory, test empirically the hypothesis that the effective sensitivity of a grain is its "size"—to a first approximation, its "area." Then, the value of $f(i)$ in the foregoing synopses will be given by the distribution of *reciprocals* of the areas of the grains. On this assumption, the relation of size of grain to inertia is explicit; if the reciprocal area-frequency (= inertia-frequency) per sq. cm. of plate be multiplied at each point by the area itself, the resultant curve should give, to a first approximation, the first derivation of the density-exposure function, when expressed in suitable units. Such curves are given in Fig. 1 as constructed from the original "frequency curve" for the two types of emulsion in question. They are each plotted for two cases,

A. for the original multilayer plate.

B. for a one-grain layer plate.

If now the curves (Fig. 1, No. 1, A and B and No. 2, A and B) are integrated graphically, the resulting curves should be comparable with the D-E curves. This has been done for both concentrated and dilute experimental emulsions and the results are shown in Figs. 2 and 3. (See Table I for data.) It is obvious that for adequate comparison, both abscissae and ordinates should be expressed in the same units in both cases. The scale for the exposures, is obtained from the condition that the maximum density must be reached with exhaustion of all classes of grains. For the density ordinates, the values 2 and 2′ in Figs. 2 and 3 should be multiplied by a factor for con-

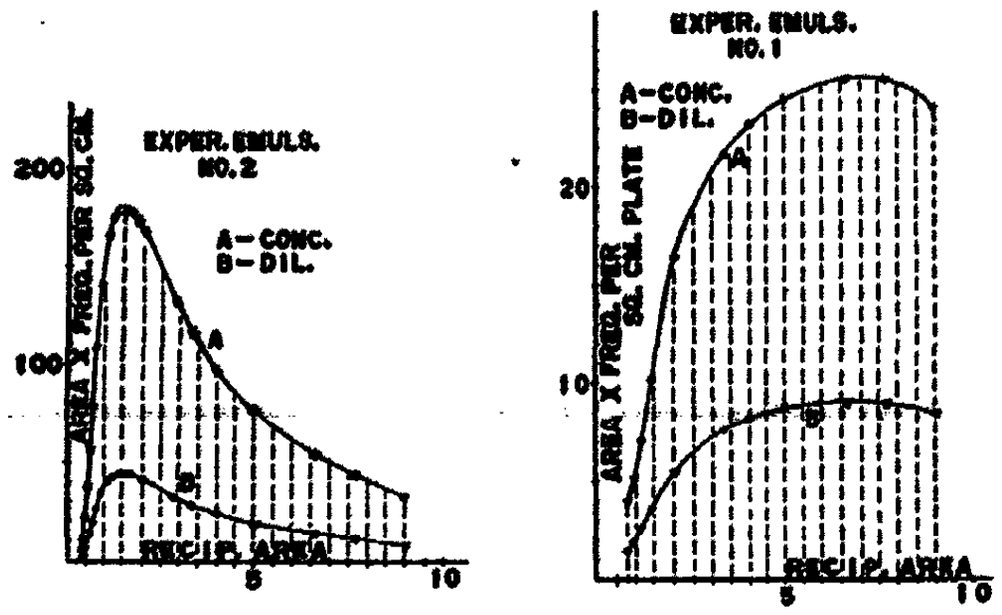

EXPER. EMULS. NO. 2
A—CONC.
B—DIL.
AREA X FREQ. PER SQ. CM.
200
100
A
B
RECIP. AREA
5
10
EXPER. EMULS. NO. 1
A—CONC.
B—DIL.
AREA X FREQ. PER SQ. CM. PLATE
20
10
A
B
RECIP. AREA
5
10

Fig. 1

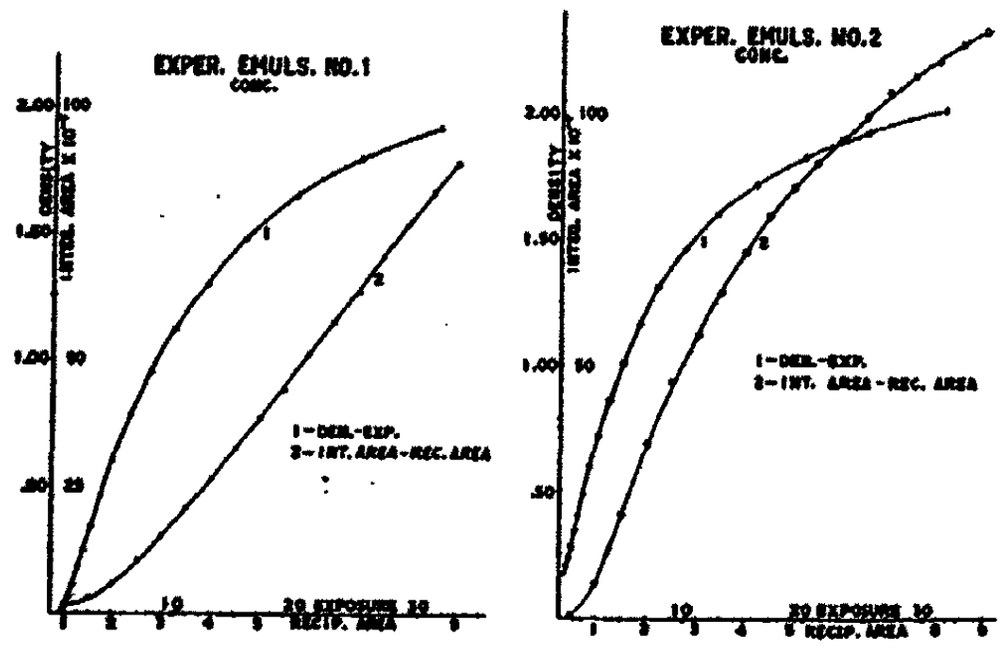

EXPER. EMULS. NO. 1
CONC.
DENSITY
INTEGR. AREA X 10⁻⁴
2.00
1.00
100
50
1
2
1—DEN.-EXP.
2—INT. AREA-REC. AREA
10
20 EXPOSURE 30
RECIP. AREA
EXPER. EMULS. NO. 2
CONC.
DENSITY
INTEGR. AREA X 10⁻⁴
2.00
1.50
1.00
.50
100
50
1
2
1—DEN.-EXP.
2—INT. AREA-REC. AREA
10
20 EXPOSURE 30
RECIP. AREA

Fig. 2

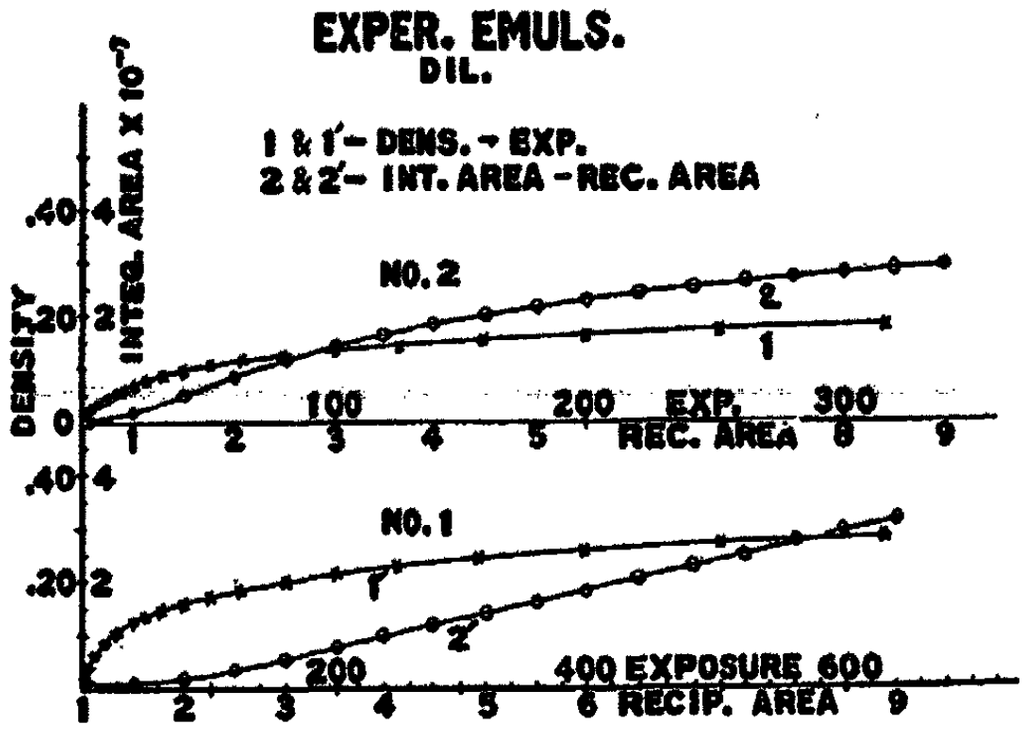

EXPER. EMULS.
DIL.
1 & 1'– DENS. – EXP.
2 & 2'– INT. AREA – REC. AREA
INTEG. AREA X 10⁻⁷
DENSITY
NO. 2
NO. 1
EXP.
REC. AREA
RECIP. AREA
EXPOSURE
100
200
300
400
600

Fig. 3

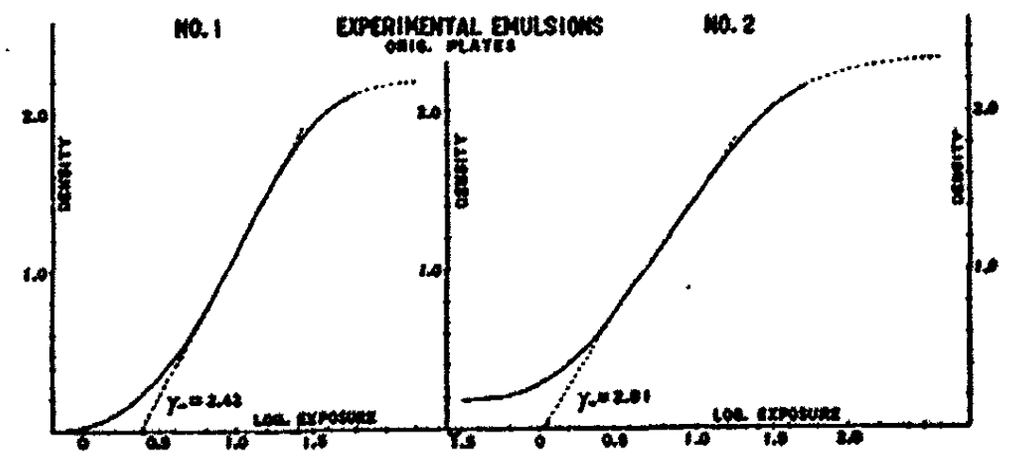

NO. 1
EXPERIMENTAL EMULSIONS
ORIG. PLATES
NO. 2
DENSITY
LOG. EXPOSURE

Fig. 4

version of silver halide of given grain size to density, at same gamma as in Fig. 4. This correction will be applied when present work on the photometric constant is completed.

It will be seen that the "synthetic" curves give a "cut," as found by Renwick, but a very prolonged underexposure region, and do not show very satisfactory correspondence with the actual sensitometric curves. The very prolonged "underexposure" effect corresponds, however, to the fact that no allowance has been made for reduction of available light energy in the thickness of the film, scattering of light and other effects. With these corrections it appears possible that the comparison may be improved.

Ideally, it would seem that the one-grain layer would be the most satisfactory for comparison. The difficulty lies in the measurement of very small "densities"—of the order 0.002 to 0.20—with sufficient precision. Work on this is in prog-

TABLE I

Experimental Emulsions Nos. 1 and 2

| $\frac{1}{x} = \phi i$ | No. 1 | | No. 2 | |
|---|---|---|---|---|
| | Integ. area in $\mu^2$ $\times 10^{-7}$ (conc.) | Integ. area in $\mu^2$ $\times 10^{-6}$ (dil.) | Integ. area in $\mu^2$ $\times 10^{-7}$ (conc.) | Integ. area in $\mu^2$ $\times 10^{-6}$ (dil.) |
| 0.5 | — | — | 0.3 | 0.75 |
| 1.0 | 1.5 | 0.53 | 6.9 | 17.3 |
| 1.5 | 3.0 | 1.06 | 20.4 | 51.0 |
| 2.0 | 5.5 | 1.9 | 34.5 | 86.3 |
| 2.5 | 10.5 | 3.7 | 46.8 | 117 |
| 3.0 | 15.5 | 5.5 | 56.1 | 140 |
| 3.5 | 20.5 | 7.2 | 64.5 | 161 |
| 4.0 | 26.5 | 9.3 | 72.6 | 182 |
| 4.5 | 32.5 | 11.5 | 79.8 | 200 |
| 5.0 | 38.5 | 13.6 | 85.5 | 214 |
| 5.5 | 44.5 | 15.6 | 90.3 | 226 |
| 6.0 | 51 | 17.9 | 94.8 | 237 |
| 6.5 | 58 | 20.2 | 99.6 | 249 |
| 7.0 | 64 | 22.3 | 104.7 | 262 |
| 7.5 | 70 | 24.6 | 108.0 | 270 |
| 8.0 | 77 | 27.1 | 110.7 | 277 |
| 8.5 | 88 | 29.3 | 114.3 | 281 |
| 9.0 | 89 | 31.4 | 116.7 | 292 |

TABLE I (*Continued*)
Experimental Emulsions Nos. 1 and 2

| | | No. 1 | | No. 2 | |
|---|---|---|---|---|---|
| Log E | E | D(conc.) (from graph) | D(dil.) (from graph) | D(conc.) (from graph) | D (dil.) (from graph) |
| $\bar{1}.5$ | 0.316 | —— | —— | 0.180 | —— |
| $\bar{1}.6$ | 0.398 | —— | —— | 0.180 | —— |
| $\bar{1}.7$ | 0.501 | —— | —— | 0.185 | —— |
| $\bar{1}.8$ | 0.631 | —— | —— | 0.201 | —— |
| $\bar{1}.9$ | 0.794 | 0.002 | —— | 0.232 | —— |
| $\bar{1}.95$ | 0.891 | 0.01 | —— | —— | —— |
| 0 | 1.00 | 0.02 | —— | 0.28 | —— |
| 0.1 | 1.26 | 0.06 | 0.03 | 0.34 | 0.02 |
| 0.2 | 1.59 | 0.105 | 0.033 | 0.41 | 0.021 |
| 0.3 | 2.00 | 0.18 | 0.036 | 0.49 | 0.022 |
| 0.4 | 2.51 | 0.25 | 0.04 | 0.60 | 0.024 |
| 0.5 | 3.16 | 0.34 | 0.043 | 0.72 | 0.026 |
| 0.6 | 3.98 | 0.46 | 0.046 | 0.86 | 0.029 |
| 0.7 | 5.01 | 0.60 | 0.05 | 1.01 | 0.032 |
| 0.8 | 6.31 | 0.78 | 0.056 | 1.16 | 0.036 |
| 0.9 | 7.94 | 0.95 | 0.063 | 1.31 | 0.040 |
| 1.0 | 10.00 | 1.12 | 0.07 | 1.46 | 0.045 |
| 1.1 | 12.59 | 1.30 | 0.078 | 1.60 | 0.053 |
| 1.2 | 15.9 | 1.48 | 0.086 | 1.72 | 0.062 |
| 1.3 | 20.0 | 1.65 | 0.095 | 1.83 | 0.071 |
| 1.4 | 25.1 | 1.80 | 0.104 | 1.93 | 0.079 |
| 1.5 | 31.6 | 1.92 | 0.114 | 2.02 | 0.088 |
| 1.6 | 39.8 | 2.01 | 0.125 | 2.09 | 0.097 |
| 1.7 | 50.1 | —— | 0.136 | —— | 0.105 |
| 1.8 | 63.1 | —— | 0.148 | —— | 0.114 |
| 1.9 | 79.4 | —— | 0.160 | —— | 0.123 |
| 2.0 | 100 | —— | 0.173 | —— | 0.131 |
| 2.1 | 126 | —— | 0.186 | —— | 0.140 |
| 2.2 | 159 | —— | 0.200 | —— | 0.149 |
| 2.3 | 200 | —— | 0.213 | —— | 0.157 |
| 2.4 | 251 | —— | 0.226 | —— | 0.166 |
| 2.5 | 316 | —— | 0.240 | —— | 0.175 |
| 2.6 | 398 | —— | 0.253 | —— | —— |
| 2.7 | 501 | —— | 0.266 | —— | —— |
| 2.8 | 631 | —— | 0.280 | —— | —— |

ress, and a more satisfactory comparison will then be possible. These relations between the size-frequency curves and the density-exposure function are admittedly tentative. A sta-

tistical relation between size of grain and sensitiveness may exist, as already noted, either in consequence of a corresponding distribution of photocatalyst, e. g., colloid silver, or as a result of a discrete structure of radiation. The possibility of the sensitiveness of the grains varying with their sizes in consequence of content of colloid silver may be illustrated as follows. It is well known that the spectral absorption of colloid silver sols varies with the (average) size of particle. Suppose a series of absorption curves plotted for increasing average size of colloid particles. At any given wave-length, for each grade of colloid silver, a different value of the specific absorption coefficient will exist. It is feasible that in crystals of different sizes in one emulsion adsorbed colloid silver might be present in different grades, e. g., it might be more condensed the greater the size of the crystal.[1] Consequently, we should have a value of the absorption coefficient varying with the size of grain. Alternatively, only the mass and not the distribution of colloidal silver might vary. These possibilities are given by way of illustration; meanwhile, experimental tests will be made by following microscopically the action of desensitizing (oxidizing) agents on one-grain layers. It appears possible that this may yield a crucial test as between the "photocatalytic" and the "quantum" hypotheses. A statistical distribution of "photocatalyst" could give results to a certain point, similar to a quantum theory, but desensitizing (by destruction of photocatalyst) should differentiate between them.

## Summary

1. The existence and nature of statistical variation of sensitivity among silver halide grains is discussed.

2. A mathematical expression for photolysis in a homogeneous system is developed in relation to the density-exposure function.

[1] Compare certain considerations advanced in a recent paper on "The Action of Soluble Iodides and Cyanides on the Photographic Emulsion" by S. E. Sheppard: Phot. Jour., **62**, 89 (1922) and in "The Silver Halide Grain of Photographic Emulsions" by A. P. H. Trivelli and S. E. Sheppard: ibid., pp. 55–56.

3. The relation of statistical variation of inertia to the density-exposure function is discussed. It is concluded that under certain conditions the first derivative of the density, exposure function will correspond with the inertia-variation function or curve.

4. Conditions permitting this correspondence are noted; if the size-frequency correspond with the sensitivity-frequency, then the curve of "reciprocal size-frequency" gives the inertia-variation curve, integration of this the density-exposure function.

*Rochester, N. Y.*
*May 1, 1922*

# HYDROCYANIC ACID: AN AMMONO CARBONOUS ACID, AN AMMONO FORMALDEHYDE AND A FORMIC ANAMMONIDE

BY EDWARD C. FRANKLIN

## Introduction

The theoretically possible formulae $C(OH)_2$ and $C(NH_2)_2$, in which the valence of carbon is assumed to be two, may be written to represent respectively an aquo and an ammono carbonous acid.[1] The removal of the elements of water from the hypothetical compound of the formula $C(OH)_2$ leaves carbon monoxide, which latter thus appears as the anhydride of an unknown carbonous acid.[2] The analogous loss of ammonia from the hypothetical ammono carbonous acid $C(NH_2)_2$ and from formamidine, $HC(NH)NH_2$, which is formally an ammono formic acid, leaves hydrocyanic acid represented in the former case by the formula H-N=C, in the latter, by H-C≡N. The first formula represents hydrocyanic acid as an ammono carbonous acid, the second as an ammono formaldehyde and at the same time as formic anammonide. It is also to be noted that the formula H-C≡N, assuming a compound of this constitution to have acid properties, represents a "carbono," or a "methano" acid.[3]

[1] In so far as the writer is aware there is nothing in the behavior of either formic acid or formamidine which lends any support to an assumption that they are tautomeric substances. Although the well-known examples of tautomerism represented by the formulas $HPO(OH)_2$ and $P(OH)_3$ for phosphorus acid, $HNO_2$ and $NO(OH)$ for nitrous acid and $HSO_2(OH)$ and $SO(OH)_2$ for sulfurous acid might lead one to expect formic acid to show tautomeric properties, it is a matter of fact that no esters of carbonous acid analogous to the esters of nitrous, phosphorous and sulfurous acids are known. Attempts to prepare a di-potassium salt of formic acid, using liquid ammonia as a solvent, have resulted in failures.

[2] It is generally recognized that carbon monoxide is not to be looked upon as an anhydride of formic acid.

[3] Just as the replacement of one hydrogen atom in the molecule of water by a negative group results in the formation of an aquo acid, and as a similar substitution of one or two atoms in the molecule of ammonia gives rise to the formation of ammono acids, so there results a similar activation of carbon-bound

In the following pages it will be shown first, that the properties of the metallic cyanides are in harmony with the view that they are metallic ammono carbonites, second, that free hydrocyanic acid shows conspicuously the properties of an ammono aldehyde, and third, that the free acid is at the same time to be looked upon as formic anammonide.

### Hydrocyanic Acid: An Ammono Carbonous Acid

Ammono acids are compounds related to ammonia as the ordinary oxygen, or aquo, acids are related to water.[1] That is to say, they are derivatives of ammonia in which one or two of the three hydrogen atoms of ammonia are replaced by negative or acidifying groups. Nef's formula then represents hydrocyanic acid as an ammono carbonous acid, for obviously H·N=C may be looked upon as an ammonia molecule in which two hydrogen atoms are replaced by a negative[2] divalent carbon atom.

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hydrogen when one, two or three hydrogen atoms in the molecule of methane are replaced by acidifying groups. Numerous instances of this activation of carbon-bound hydrogen are known as, for example, in the hydrocarbons acetylene and its homolog, triphenyl methane, cyclopentadiene, inden and fluoren, and in such compounds as acetonitrile, malononitrile, tricyanomethane, mono-, di- and trinitromethane, cyanoacetic ester, malonic ester, etc. The hydrocarbons enumerated above may be looked upon as carbono or methano acids, the remainder as mixed acids in the same sense that acetamide, for example, is a mixed aquo ammono acid. (Cf. Eighth Int. Cong. App. Chem., **6**, 128 (1912).)

Certain considerations have led Dr. M. Kharasch (private communication) to the conviction that in mercuric cyanide the metal is in combination with carbon rather than with nitrogen. If this be true then mercuric cyanide is a salt of a methano acid.

[1] Franklin: Am. Chem. Jour., **47**, 287 (1912); Eighth Int. Cong. App. Chem., **6**, 119 (1912).

[2] The acidifying influence of unsaturated carbon is well known. For example acrylic and maleic acids are much stronger acids, respectively, than propionic and succinic acids; tetrahydropyrrol $\ulcorner CH_2—CH_2—CH_2—CH_2—NH\urcorner$ shows the properties of a secondary amine, while pyrrol $\ulcorner CH—CH—CH—CH—NH\urcorner$ is an acid of sufficient strength to show its acid properties in liquid ammonia solution (Cf. Franklin: Jour. Phys. Chem., **24**, 81 (1920)). In such compounds as acetylene and propiolic acid the high degree of unsaturation determines the ionization of even carbon-bound hydrogen as is shown by the existence of

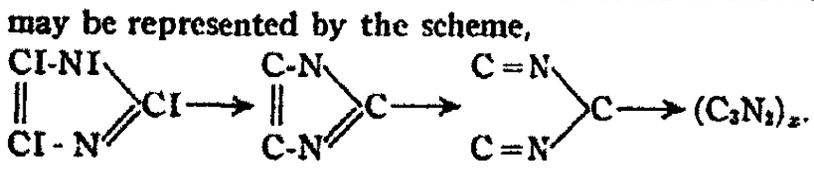
*The Action of Ammonia or of a Mixture of Nitrogen and Hydrogen on Carbon.*—Many of the elements are converted into oxides when heated in contact with oxygen or water. So also a limited number similarly form nitrides when heated with nitrogen or ammonia. For example oxygen converts metallic magnesium to magnesium oxide while nitrogen acts on magnesium to yield magnesium nitride. These are analogous reactions and in a general sense are of course processes of oxidation. It will be convenient, however, in the discussions which follow to use the terms nitridation and nitridize in describing reactions in which nitrogen plays a part analogous to that played by oxygen in ordinary simple processes of oxidation.

Contrary to what might perhaps be expected neither carbonous nitride[1] nor carbonic nitride is formed when carbon is heated in an atmosphere of nitrogen. Exposed to a high temperature in contact with a mixture of nitrogen and hydrogen, or with ammonia, carbon is converted into hydrocyanic acid; while, heated in the presence of an alkali metal and either nitrogen, ammonia or a mixture of nitrogen and hy-

salts of the respective formulas CH≡CNa, NaC≡CNa and NaC≡CCOONa.

It is of course true that the cyanogen group, -C≡N, also possesses acidifying functions so that it possibly makes little or no difference, in so far as the acid properties alone of hydrocyanic acid are concerned, which of the two formulas, H-C≡N or H-N=C, is assigned to it. Indeed it is probably the loosening effect on the carbon hydrogen union in the one case by negative nitrogen, and on the nitrogen hydrogen union in the other by the negative influence of unsaturated carbon which makes it impossible to assign a definite formula to the acid. The hydrogen is fixed in neither the one position nor the other.

[1] By heating tetraiodoimidoazol Pauly and Waltzinger (Ber. deutsch. chem. Ges., **46**, 3129 (1913)) have prepared an amorphous, soot-like compound of the formula $(C_3N_2)_x$ which is undoubtedly to be looked upon as a polymorphic form of carbonous nitride. The reactions involved in the formation of this compound may be represented by the scheme,



$\longrightarrow (C_3N_2)_x$. Cyanogen, it may be noted, is not a nitride of carbon in the sense that compounds of the formulas $C_3N_2$ and $C_3N_4$ (Cf. Jour. Am. Chem. Soc., **44**, 507 (1922)) are respectively carbonous and carbonic nitrides or that carbon monoxide and carbon dioxide are oxides of carbon.

drogen, a metallic cyanide is formed. Obviously the formation of hydrocyanic acid in the one case and of alkali cyanide in the other may reasonably be interpreted as the nitridation, respectively, of carbon and hydrogen to ammono carbonous acid and of carbon and the alkali metal to an ammono carbonite.

It will be recalled that the formation of calcium cyanamide by the action of nitrogen on a mixture of metallic calcium and carbon, or on calcium carbide as practiced in the commercial fixation of nitrogen, has been shown[1] to be a process of nitridation strictly analogous to oxidation. Calcium carbide heated in an atmosphere of nitrogen is nitridized to calcium ammono carbonate just as when heated in contact with oxygen it is oxidized to calcium aquo carbonate, as represented by the equations, $CaC_2+N_2 = CaCN_2+C$ and $CaC_2+2O_2 = CaCO_3+CO$.

It is interesting to note that in the presence of the alkali metals the nitridation of carbon extends only to the formation of ammono carbonites while in the presence of calcium an ammono carbonate is found.

*The Action of Sodium Amide on Carbon.*— It has been found[2] that fused sodium amide at a temperature of 350°–400° dissolves carbon to form disodium cyanamide in accordance with the equation $2NaNH_2 + C = Na_2CN_2 + 2H_2$, and that at a higher temperature disodium cyanamide in the presence of carbon undergoes reduction to sodium cyanide as represented by the equation $Na_2CN_2 + C = 2NaNC$. These reactions are important in the present connection for the reason that the one represents the nitridation of carbon to an ammono carbonate and the other the reduction of an ammono carbonate to an ammono carbonite.

The analogous oxidation of carbon to an aquo carbonate is known. Bussy[3] has shown that sodium carbonate is formed

[1] Franklin: Jour. Am. Chem. Soc., **44**, 486 (1922).

[2] German Pats.: 90999, Zeit. angew. Chem., 10, 288 (1897); 148045, Zentr., 1904 I, 411; 149678, Zentr. 1904 I, 908.

[3] Jour. Pharm., 8, 266. Cf. Netto, German Pat. 45105; Ber. deutsch. chem. Ges., 21, Ref. 864 (1888).

in accordance with the equation, $C + 3NaOH = Na_2CO_3 + Na + 3H$, when sodium hydroxide is brought into contact with highly heated carbon.

*Nitridation of Sodium Cyanide to Disodium Cyanamide.*—Sodium cyanide may be nitridized to sodium cyanamide, just as it may be oxidized[1] to sodium cyanate, or sulfidized to sodium thiocyanate but not by simply heating in the presence of nitrogen.

No observations of the conversion of cyanide of sodium or potassium into the corresponding salts of cyanamide by heating in the presence of nitrogen are on record. Moreover, efforts made in this laboratory to nitridize sodium cyanide by heating the cyanide at varying high temperatures in an atmosphere of nitrogen—alone and in the presence of iron or platinum acting as possible catalysts—have not met with any success. These experiments were undertaken on the presumption that possibly sodium cyanide might be nitridized in accordance with the equation, $3NaNC + N_2 = Na_2CN_2 + NaC_2N_3$ to form a mixture of disodium cyanamide and sodium dicyanimide. The nitridation of sodium cyanide is easily accomplished however in the presence of metallic sodium in the manner represented by the equation $NaNC + Na + N = Na_2CN_2$.[1]

Sodium cyanide is also readily converted into sodium cyanamide by fusion with sodium amide in accordance with the equation $NaNC + NaNH_2 = Na_2CN_2 + H_2$.[3] Both this and the preceding equation represent the nitridation of sodium ammono carbonite to an ammono carbonate.

*The Conversion of Barium Cyanide into Barium Cyanamide.*—Drechsel[4] found that barium cyanamide is formed when barium cyanide is heated out of contact with atmospheric air. The reaction involved is represented by the equation $Ba(CN)_2 = BaCN_2 + C$ and is interesting as an example of the Can-

[1] Cf. p. 175.

[2] Drechsel: Jour. prakt. Chem., [2] 21, 81 (1880).

[3] German Pat. 124977, Chem. Zentr., 1901 II, 1100.

[4] Jour. prakt. Chem., [2] 21, 83 (1880); Cf. Askenasy and Grade: Zeit. Elektrochemie, 28, 130 (1922).

nizzaro reaction. Of the two ammono carbonous acid radicals in barium cyanide the one undergoes nitridation to an ammono carbonic acid radical the other simultaneously suffering reduction to elementary carbon. Since calcium cyanamide in the presence of carbon is not reduced at the high temperatures to which it is exposed in its manufacture, it may be assumed that calcium cyanide at a high temperature undergoes a similar change, although apparently such a reaction has not been experimentally demonstrated.

*Nitridation of Sodium Cyanide to Disodium Cyanamide by Sodium Azide.*—When sodium azide is added to fused sodium cyanide the latter is converted into disodium cyanamide in accordance with the equation $NaNC + NaN_3 = Na_2CN_2 + N_2$ which represents the conversion of ammono carbonite of sodium into an ammono carbonate by the nitridizing action of sodium ammono nitrate.[1] Since sodium azide is easily decomposed by heat, it is of course possible to look upon this salt simply as a source of nitrogen and metallic sodium, in which case this process of nitridation becomes identical with that discussed above. But even so the nitridizing action of sodium ammono nitrate must be looked upon as analogous to the oxidizing action of ordinary sodium nitrate for it may be assumed that the oxidizing action of this salt is due to the oxygen set free at high temperatures.

To 2 gm of sodium cyanide maintained in a state of fusion in a platinum crucible, 2.7 gm of sodium azide were added in successive small portions. The salt dissolved with brisk effervescence and with the evolution of considerable heat as was shown by the incandescence accompanying the reaction. The effervescence was assumed to be due to the escape of

[1] In explanation of observations to the effect that hydrazoic acid possesses oxidizing (nitridizing) properties strikingly similar to those of nitric acid Turrentine (Jour. Am. Chem. Soc., **34**, 385 (1912); Cf. Thiele: Ber. deutsch. chem. Ges., **44**, 2522 (1911); Franklin: Eighth Int. Cong. App. Chem., **6**, 119 (1912)) proposed the formula, H-N=N≡N for this acid and pointed out that it is thereby represented as the nitrogen analog of ordinary nitric acid. Further experimental evidence in support of the view that hydrazoic acid is a nitric acid of the ammonia system will be given in a later paper.

nitrogen. The gas was however not collected and identified. The melt was dissolved in water and the solution thus formed tested for hydrocyanic acid with negative results. On adding to the solution first aqua ammonia, then ammoniacal silver nitrate an abundant yellow precipitate was formed. This substance was shown to be di-silver cyanamide by observation of its mildly explosive decomposition on heating and its characteristic yellow color and by a determination of its silver content. 0.2418 gm of the substance gave 0.2674 gm AgCl. Calc. for $Ag_2CN_2$: Ag, 84.4. Found 83.5.

*Nitridation of Sodium Cyanide to Sodium Dicyanimide by Means of Cyanogen.*—In a recent paper[1] it has been shown that sodium dicyanimide, the sodium salt of an ammono carbonic acid of the formula $HC_2N_3$, or rather $H_3C_6N_9$, may be obtained in fair yield by heating a mixture of sodium cyanide and mercuric cyanide.

It is of particular interest in the present connection to note that the scheme $NaNC + C_2N_2 = NaN(CN)_2 + C$, in accordance with which the reaction takes place, represents the nitridation of sodium cyanide or sodium ammono carbonite to an ammono carbonate of sodium. Cyanogen functions in this reaction as a nitridizing agent and as such must of course undergo reduction, probably to elementary carbon, possibly to carbonous nitride.

*The Action of Carbon Monoxide and of Carbon Dioxide on Sodium Amide.*—Both carbon monoxide and carbon dioxide act energetically on sodium amide[2] to form in the one case,

[1] Franklin: Jour. Am. Chem. Soc., **44**, 486 (1922).

[2] Beilstein and Geuther (Liebig's Ann., **108**, 93 (1857)) first observed the action of carbon dioxide on sodium amide and represented the reaction as taking place in accordance with the equation $CO_2 + 2NaNH_2 = Na_2CN_2 + 2H_2O$ ($C_2O_4 + 2NaNH_2 = C_2N_2H_2 + 2NaO + 2HO$). That sodium carbonate was also formed in their experiments is shown by their statement that much carbon dioxide was evolved on neutralizing the solution of the reaction product with nitric acid. These results have been confirmed in this laboratory. According to Beilstein and Geuther the action of carbon disulfide on sodium amide yields sodium thiocyanate. This result is interesting in showing that a mixed carbonate (a·thio ammono carbonate) is thus formed whereas the action of carbon dioxide on sodium amide yields not a mixed carbonate but a mixture of the aquo carbonate and an ammono carbonate.

as represented by the equation, $2NaNH_2 + CO = NaNC + NaOH + NH_3$, sodium cyanide, and in the other, as represented by the equation, $6NaNH_2 + 3CO_2 = Na_2CN_2 + 2Na_2CO_3 + 4NH_3$ to form a mixture of sodium cyanamide and sodium carbonate.

Just as ordinary carbonic acid, an aquo acid, acts upon sodium hydroxide, an aquo base, to form sodium carbonate, an aquo salt; and as cyanamide, an ammono carbonic acid, acts upon sodium amide,[1] an ammono base, to form sodium cyanamide, an ammono carbonate; so the equation given above represents the action of aquo carbonic acid, or rather its anhydride, on an ammono base to give a mixture of aquo carbonate and ammono carbonate of sodium.[2]

As carbon dioxide is the anhydride of carbonic acid so carbon monoxide may be looked upon as the anhydride of an unknown carbonous acid, though of course such a view receives little or no support from the behavior of carbon monoxide toward aquo bases. Its action on sodium amide, however, is in entire harmony with this assumption for, as Beilstein and

[1] Reaction takes place in liquid ammonia solution or in the fused state but not in water solution. All known ammono bases and a large majority of ammono salts are energetically hydrolyzed in the presence of water. (Cf. Jour. Am. Chem. Soc., 35, 1457, Footnote (1913).)

[2] Although quantitative determinations of the relative amounts of sodium cyanamide, sodium carbonate and ammonia formed by the action of carbon dioxide on sodium amide have not been made it seems fairly well established that the equation given above represents the net result. It may be that the action begins with the formation of sodium cyanamide as represented by the equation $2NaNH_2 + CO_2 = Na_2CN_2 + H_2O$. If so, then the water liberated hydrolyses unchanged sodium amide to sodium hydroxide which in turn reacts with carbon dioxide to form sodium carbonate. Or it is possible that sodium carbonate is initially formed in accordance with the equation $2NaNH_2 + 3CO_2 = 2Na_2CO_3 + H_2CN_2 + NH_3$. In this case the cyanamide simultaneously formed will be acted upon by unchanged sodium amide to form sodium cyanamide. Finally, the action may begin with the formation of a mixed aquo ammono carbonate of sodium, namely, sodium cyanate (or even sodium carbamate for this aquo ammono carbonate is known to be formed by the action of carbon dioxide on sodium amide in the presence of liquid ammonia) as represented by the equation $NaNH_2 + CO_2 = NaNCO + H_2O$. Any sodium cyanate formed, however, will be immediately converted into a mixture of sodium carbonate and sodium cyanamide since it has been observed in this laboratory that a mixture of these two salts is formed when sodium cyanate is added to fused sodium amide.

Geuther have shown,[1] it is absorbed readily by fused sodium amide to form sodium cyanide in accordance with the equation $CO + 2NaNH_2 = NaNC + NaOH + NH_3$. This equation may therefore be said to represent the action of carbonous anhydride on an ammono base to form an ammono carbonite. Carbonous anhydride is ammonolyzed by the action of sodium amide to form sodium ammono carbonite and water.

It is interesting to compare the action respectively of carbon dioxide and carbon monoxide on sodium amide. In the former case a mixture of carbonates is formed, in the latter the ammono carbonite only and this clearly for the reason that the aquo carbonite is incapable of existence. Sodium hydroxide remains in the fused mixture unacted upon, excepting in so far as sodium formate may possibly be formed.

Another reaction strictly similar to the foregoing, due to Maquenne,[2] is represented by the equation $Ba_3N_2 + 2CO = 2BaO + Ba(CN)_2$. Barium nitride which is the nitrogen analog of barium oxide (that is to say it is a basic nitride related to the ammono bases, barium amide and barium imide, as barium oxide is related to barium hydroxide), reacts with carbonous anhydride to form barium oxide and barium ammono carbonite. Again noting the fact that aquo carbonites are unknown, one is prepared to find Maquenne's product a mixture of barium oxide and cyanide.

*Oxidation of Potassium Cyanide to Potassium Cyanate.*—As is well known potassium cyanide is easily oxidized to potassium cyanate. Since cyanic acid is a mixed aquo ammono carbonic acid,[3] it is obvious that the reaction involved in the conversion of a metallic cyanide into a cyanate consists simply in the oxidation of an ammono carbonite to an aquo ammono carbonate.

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[1] Liebig's Ann., **108**, 93 (1857).

[2] Ann. Chim. Phys., [6] **29**, 223 (1893).

[3] Urea, carbamic acid, cyanic (isocyanic) acid, cyanuric acid, ammeline, cyanurea, guanylurea, etc., are carbonic acids derived simultaneously from water and ammonia. They are therefore aquo ammono carbonic acids. (Cf. Franklin: Am. Chem. Jour., **47**, 287 (1912); Eight Int. Cong., 6 pp. Chem., **6**, 119 (1912).

Similarly the conversion of potassium cyanide into potassium thiocyanate is to be looked upon as the sulfidation of ammono carbonite of potassium into a thio ammono carbonate.

Inversely it is a simple matter to reduce these mixed carbonates to the ammono carbonite, that is to say, potassium cyanate and thiocyanate are readily reduced to potassium cyanide.

*Reduction of Ammono Carbonates to Ammono Carbonites.*—The view that sodium cyanide is sodium ammono carbonite while the sodium derivatives of cyanamide and dicyanimide are ammono carbonates leads to the expectation that the latter should be reducible to the former. As a matter of fact, such reductions are easily accomplished. The sodium ammono carbonate of the formula $NaN(CN)_2$ is reduced to sodium cyanide, with the separation of cyanogen and nitrogen, simply by heating to redness, or with the evolution of nitrogen by heating in the presence of metallic sodium. Potassium melonate $K_3C_9N_{13}$, has been shown in another place[1] to be an ammono carbonate of potassium. Liebig's observation[2] to the effect that this salt when heated is converted into potassium cyanide has been confirmed in this laboratory.

The alkali metal cyanamides are readily reduced to cyanides by heating with carbon. The analogous reduction of an aquo carbonate to an aquo carbonite is of course unknown. The reduction of carbon dioxide to carbon monoxide by hot carbon and the formation of potassium formate by the action of metallic potassium on moist carbon dioxide are as closely analogous to the reduction of ammono carbonates to ammono carbonites as the circumstance that aquo carbonites are incapable of existence will permit. Drechsel[3] found that nascent hydrogen converts cyanamide into methyl amine and ammonia, a reaction which is obviously analogous to that involved in the reduction of carbonic acid to methyl alcohol. The parallel

[1] Franklin: Jour. Am. Chem. Soc., **44**, 486 (1922).
[2] Liebig's Ann., **95**, 275 (1855).
[3] Drechsel: Jour. prakt. Chem., [2] **11**, 319 (1875).

reactions are represented by the equations $NCNH_2 + 3H_2 = CH_3NH_2 + NH_3$ and $CO(OH)_2 + 3H_2 = CH_3OH + 2H_2O$.

*The Ammonolysis of Ethyl Carbylamine.*—As is well known the alkyl derivatives of hydrocyanic acid exist in two isomeric forms, namely, as the nitriles and isonitriles with the respective formulas RCN and RNC. The nitriles may be looked upon as ammono ketones which at the same time show the behavior of acid anammonides.[1] The isonitriles are formally esters of ammono carbonous acid and as such should be susceptible to ammonolysis to form an ammono acid and an ammono alcohol just as aquo esters upon hydrolysis yield aquo acids and alcohols.

As a matter of fact such an ammonolytic decomposition, or saponification, of ethyl isocyanide[2] has been accomplished by warming the ester in contact with either sodium amide or potassium amide in the absence of solvent and also by dissolving the ester in liquid ammonia, adding an equivalent quantity of potassium amide (which it will be recalled is readily soluble in liquid ammonia) and heating the mixture for a few hours at a temperature of 80°. The product of the reaction consisted of a limited amount of tarry material together with an abundant yield of hydrocyanic acid and ethyl amine. The reaction insofar as the latter two products are concerned is in accordance with the equation, $C_2H_5NC + KNH_2 = C_2H_5NH_2 + KNC$, which represents the ammonolysis of ethyl ammono carbonite into the ammono alcohol, ethylamine, and potassium ammono carbonite. The analogy between this reaction and the familiar saponification of an ordinary ester is so obvious as to require no further emphasis.

Looked upon as the ethyl ester of ammono carbonous acid ethyl isocyanide undergoing hydrolysis instead of ammonolysis might be expected to yield either ethyl alcohol and hydrocyanic acid, or ethyl amine and aquo carbonous acid, or, since carbonous acid is incapable of existence, its isomer formic acid.

[1] The significance of this statement will be discussed in a later paper.

[2] The writer is under obligation to Professor C. W. Porter of the University of California for the ethyl carbylamine used in these experiments.

As is well known, the hydrolytic decomposition of ethyl isocyanide follows the latter course.

*The Oxidation of Methyl Carbylamine to Methyl Isocyanate.*—Another reaction in support of the view that methyl isocyanide is an ammono carbonite of methyl is due to Gautier.[1] Warmed gently in contact with mercuric oxide methyl isocyanide is oxidized to methyl isocyanate. The equation, $CH_3NC + HgO = CH_3NCO + Hg$, in accordance with which the reaction takes place represents the oxidation of an ester of ammono carbonous acid to the corresponding ammono ester of a mixed aquo ammono carbonic acid. Similarly Gautier showed that methyl isocyanide is sulfidized by the action of sulfur at 130° to methyl isothiocyanate, the ammono methyl ester of a thio ammono carbonic acid.

### Hydrocyanic Acid: An Ammono Formaldehyde

The carbonyl and cyanogen groups are well known to possess many properties in common. It seems reasonable therefore to look upon hydrocyanic acid, assuming for it the formula H-C≡N, as a nitrogen analog[2] of formic aldehyde and as such to expect it to show the properties of an ammono formaldehyde. As a matter of fact hydrocyanic acid shows conspicuously most of the properties characteristic of the aldehydes. It undergoes polymerization and condensation, as formaldehyde does. It forms acid sulfite, water and alcohol addition products, reacts with hydroxylamine and hydrazine, and is reducible to an ammono alcohol as is shown in some detail in the following pages.

*Polymerization.*—The same strong tendency to polymerization which is a characteristic property of formaldehyde is exhibited also by hydrocyanic acid. In the presence of alkalies or salts hydrocyanic acid undergoes polymerization to brown amorphous substances of unknown constitution.

*Aldol Condensation.*—Hydrocyanic acid undergoes condensation in a manner strictly analogous to the familiar aldol

[1] Gautier: Ann. Chim. Phys., [4] 17, 228 (1869).

[2] Cf. infra p. 185.

condensation characteristic of the aldehydes. Just as formaldehyde condenses to glycollic aldehyde so two molecules of hydrocyanic acid similarly condense in the manner represented by the equation $HCN + HCN = CH\begin{cases}NH^1\\CN\end{cases}$

Hydrocyanic acid with a triple bond between carbon and nitrogen as contrasted with a double bond between carbon and oxygen in formaldehyde should be capable of forming not only a dimolecular but also a trimolecular condensation product and accordingly it has been found[2] that aminomalononitrile is formed when hydrocyanic acid is allowed to stand in the presence of potassium carbonate or cyanide. The reaction, represented by the equation $3HCN = HC\begin{cases}CN\\CN\\NH_2\end{cases}$, is strictly analogous to that which takes place when formaldehyde condenses to glycolic aldehyde. It therefore follows that aminomalononitrile is an aldol of the ammonia system.

*The Cyanhydrine Reaction.*—This reaction, especially familiar as the basis for the Kiliani synthesis of the sugars, which takes place when hydrocyanic acid is allowed to act on an aldehyde is to be looked upon as an aldol condensation between an aquo aldehyde and an ammono formaldehyde as will be clear from an inspection of the equations,

$$CH_2O + CH_2O = CH_2\begin{cases}OH\\CHO\end{cases}, \quad HCN + 2HCN = HC\begin{cases}CN\\CN\\NH_2\end{cases}$$

and $CH_2O + HCN = CH_2\begin{cases}OH\\CN\end{cases}$, which represent the aldol

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[1] Nef: Liebig's Ann., **287**, 337 (1895); Willstätter and Wirth; Ber. deutsch. chem. Ges., **42**, 1915 (1909); Michael and Hibbert (Liebig's Ann., **364**, 70, Footnote 31 (1909)) state that this condensation product has the structure represented by the formula, HN=CH-N=C.

[2] Lange: Ber. deutsch. chem. Ges., **6**, 99 (1873); Wippermann, **7**, 768 (1874).

condensation as taking place first, between two molecules of aquo formaldehyde, second, between three molecules of an ammono formaldehyde and, third, between an aquo formaldehyde and an ammono formaldehyde.[1]

*Acid Sulfite Addition Product.*—Another characteristic property of the aldehydes is that of uniting with sodium or potassium acid sulfite to form the well known acid sulfite addition products. Von Pechmann and Manck[2] have shown that hydrocyanic acid reacts with potassium acid sulfite to form a compound of the formula $HC\begin{<}^{SO_2OK}_{SO_2OK}\end{>}NH_2$ which is obviously the analog of the compound of the formula $H_2C\begin{<}^{OH}_{SO_2OK}\end{>}$ formed by the action of potassium acid sulfite on formaldehyde.[3]

*Oxime Formation.*—Formaldehyde reacts with hydroxylamine in accordance with the equation $H_2CO + H_2NOH = H_2C{=}NOH + H_2O$, to form formaldoxime. In an entirely similar manner hydrocyanic acid and hydroxylamine interact as represented by the equation $HCN + H_2NOH = HC\begin{<}^{NH_2}_{NOH}\end{>}$ to form formamidoxime.[4] In the one case water is completely separated, in the other the analogous elimination of ammonia extends only to the formation of an amino group. For com-

[1] Aldol condensations between hydrocyanic acid and formaldehyde to form either iminoformaldehyde or aminomalonic aldehyde in accordance with the equations,

$HCN + CH_2O = HC\begin{<}^{NH}_{CHO}\end{>}$ and $HCN + 2CH_2O = HC\begin{<}^{CHO}_{CHO}\end{>}NH_2$ have apparently never been observed.

[2] Ber. deutsch. chem. Ges., 28, 2374 (1895).

[3] An addition product to the formula $HC(NH)SO_2OK$, which one might expect to obtain by the interaction of equimolecular quantities of hydrocyanic acid and potassium acid sulfite, has apparently never been made.

[4] Lossen and Schifferdecker: Liebig's Ann., 166, 295 (1873).

plete separation of ammonia the reaction between hydrocyanic acid and hydroxylamine would have to take the course represented by the equation $2HCN + 3H_2NOH = \begin{matrix} HC=NOH \\ \quad\quad\rangle NOH \\ HC=NOH \end{matrix} + 2NH_3$ to give an oxime which is unknown.

*The Action of Phenylhydrazine on Hydrocyanic Acid.*—As is well known phenylhydrazine reacts with formaldehyde to form a phenylhydrazone of the formula $CH_2=NNHC_6H_5$. If now phenylhydrazine is to show a similar behavior towards hydrocyanic acid then formamidphenylhydrazone $NH_2CH=NNHC_6H_5$ or a phenylhydrazone of the formula $(CH)_2(NNHC_6H_5)_3$ should be formed when phenylhydrazine is allowed to act on hydrocyanic acid.

It is interesting to recall that Fischer[1] reported the formation of a compound of the former formula as the product of such action. Later, however, it was found[2] that the compound obtained by Fischer was oxamidphenylhydrazone $NH_2\text{-}C=NNHC_6H_5$[3] instead of formamidphenylhydrazone

$$\begin{matrix} NH_2\text{-}C=NNHC_6H_5 \\ | \\ HC\langle \begin{matrix} NH_2 \\ NNHC_6H_5. \end{matrix} \end{matrix}$$

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[1] E. Fischer: Ber. deutsch. chem. Ges., 22, 1933 (1889).

[2] Fischer and Müller: Ibid., 27, 185 (1894).

[3] The preparation of this compound by Senf: Jour. prakt. Chem., [2] 35, 531 (1887); the formation of oxamidhydrazone $\begin{matrix} NH_2C=NNH_2 \\ | \\ NH_2C=NNH_2 \end{matrix}$ (Curtius and Dedichen, [2] 50, 245 (1894); 52, 272 (1895)) and of oxamidoxime $\begin{matrix} NH_2C=NOH \\ | \\ NH_2C=NOH \end{matrix}$ (Fischer: Ber. deutsch. chem. Ges., 22, 1931 (1889)) by the action respectively of phenylhydrazine, hydrazine and hydroxylamine on cyanogen are examples of reactions in which cyanogen, looked upon as an ammono diketone plays a part entirely similar to that played by hydrocyanic acid and by formaldehyde when they react with hydroxylamine. Compare the action of hydroxylamine on hydrocyanic acid discussed above.

Fischer's method of preparing oxamidphenylhydrazone therefore involves the oxidation (nitridation) of hydrocyanic acid to cyanogen—whether before or after the formation of the hydrazone Fischer and his coworker did not determine—and is a result not less interesting in its bearing on the view that hydrocyanic acid is an ammono aldehyde than the one first announced. For the reaction reminds one of the familiar oxidizing action of phenylhydrazine in excess in converting the sugars into osazones and of the action of hydrazine on formaldehyde and glyoxylic acid as observed by Curtius, Darapsky and Müller.[1] Just as the action of hydrazine on formaldehyde and glyoxylic acid was found by these investigators to consist in the oxidation of the two aquo aldehydes to carbonic acid and oxalic acid respectively as represented by the equations $CH_2O + H_2O + 2NH_2NH_2 = CO_2 + 4NH_3$ and $CHO.COOH + H_2O + 2NH_2NH_2 = (COOH)_2 + 2NH_3$, so the ammono formaldehyde HCN is oxidized (nitridized) by phenylhydrazine to cyanogen, a product, occupying a position between hydrocyanic acid and an ammono carbonic acid, whose water analog[2] is unknown.

*The Action of Hydrazine on Hydrocyanic Acid.*—Very recently[3] it has been found that hydrocyanic acid and hydrazine react with each other in accordance with the equation $2H\,CN + 3H_2NNH_2 = (HC)_2(NNH_2)_3 + 2NH_3$. The reaction thus represented is clearly analogous to that involved in the action of hydrazine on formaldehyde which Stolle[4] found to be in accordance with the equation $H_2C=O + H_2NNH_2 = H_2C=NNH_2 + H_2O$.

[1] Curtius, Darapsky and Müller: Ber. deutsch. chem. Ges., 39, 3413 (1906).

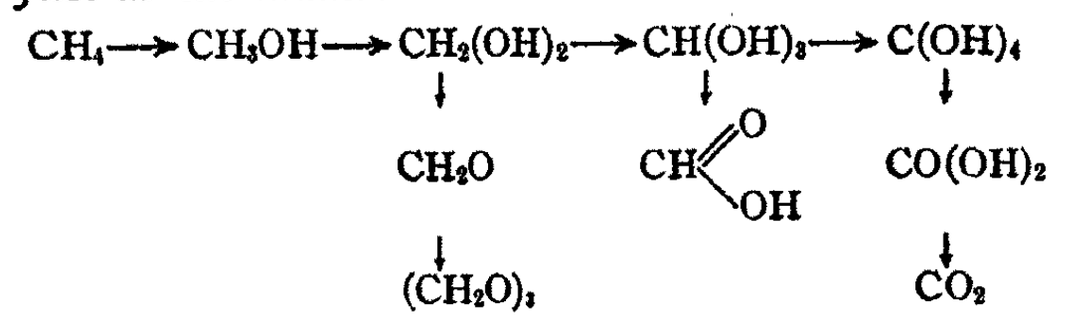
[2] Perhaps the nearest one can come to an oxygen analog of cyanogen would be a compound of the formula $OC=CO$ which is of course unknown. Why it is that ethylene $CH_2=CH_2$, and ketene $CH_2=CO$ are capable of existence while in carbon monoxide, hydrocyanic (or the isonitriles) and fulminic acid the carbon atoms fail to function as tetravalent to form compounds represented by the respective formulas $OC=CO$ $HNC=CNH$, $RNC=CNR$ and $HONC=CNOH$ is an interesting but, up to the present, unanswered question.

[3] Müller and Herrdegen: Jour. prakt. Chem., [2] 102, 127 (1921).

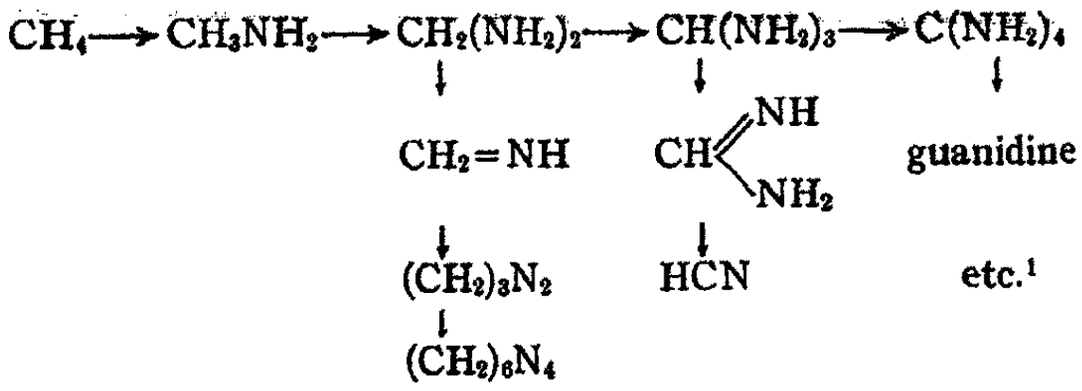
[4] Ber. deutsch. chem. Ges., 40, 1505 (1907).

## Hydrocyanic Acid: A Formic Anammonide

Just as the familiar scheme




is frequently made use of for showing the relations between the successive oxidation products of methane so a similar scheme comprising a series of analogous nitridation products may be written as follows:




Examination of these schemes shows the compounds in the nitridation series corresponding to methylene glycol and formaldehyde are those represented by the formulas $CH_2(NH_2)_2$, $CH_2=NH$ and $(CH_2)_3N_2$[2] while hydrocyanic acid appears as the final deammonation product, not of a disubstituted methane but of the hypothetical compound $HC(NH_2)_3$ and formamidine. Since formamidine is, at least formally,[3] an

[1] Cf. Franklin: Jour. Am. Chem. Soc., **44**, 486 (1912), where the compounds guanidine to cyamelon inclusive are shown to be ammono carbonic acids.

[2] The ammono alcohols, ethers, aldehydes and ketones will be discussed in a later communication.

[3] Unfortunately attempts have not yet been made to determine whether metallic salts of formamidine may be prepared. In support of the view that it is an ammono formic acid notwithstanding its "basic" properties the following facts are briefly summarized. First, guanidine, an amidine-like derivative of carbonic acid and ordinarily described as a "strong base," has been shown to be an ammono carbonic acid (Franklin: Jour. Am. Chem. Soc., **44**, 486 (1922)), second Bamberger and Lorenzen (Liebig's Ann., **273**, 300 (1893)) have prepared a silver salt diphenylacetamidine and in this laboratory the same amidine has been found to react with potassium amide in liquid ammonia solution to form a potassium salt; third, Stieglitz and his coworkers

ammono formic acid, its deammonation product should be looked upon as an acid anammonide. That is to say, in the presence of water hydrocyanic acid should be hydrated to a mixed aquo ammono formic acid or hydrolyzed completely to aquo formic acid; ammonation might be expected to convert it into ammono formic acid; and on treatment with alcohol it should yield an ester. As is well known hydrocyanic acid may be converted successively into formamide and formic acid. It is not known to unite with ammonia to form formamidine but inversely the latter compound in the form of its hydrochloride is deammonated to hydrocyanic acid by simply heating as represented by the equation $HC(NH)NH_2 . HCl = HCN + NH_4Cl$. In the presence of hydrochloric acid and alcohol hydrocyanic acid is esterified in accordance with the equation $HCN + C_2H_5OH = HC(NH)OC_2H_5$ to formimido ethyl ester.

It is true that these reactions, excepting of course the hydrolysis of formamide to formic acid, resemble the action respectively of water, ammonia and alcohol on aldehydes to form "aldehyde hydrates," aldehyde ammonias and half acetals. Since however the respective addition products of hydrocyanic acid are all acids it follows that hydrocyanic acid in addition to its aldehydic properties also possesses the characteristic properties of an acid anammonide. It is a matter of some importance to note that toward the alkali hydroxides in excess as well as toward ammonia[1] hydrocyanic

(Am. Chem. Jour., 39, 29, 166 (1908)) made a convincing case for the view that Pinner's "imidoethers" RC(NH)OR′ are in reality esters and that furthermore the hydrogen of the imido group is acid; fourth, methylformamide, isomeric with formimido methyl ester, is an acid, for, while salts of this particular compound have not been made, Titherley (Jour. Chem. Soc., 71, 466 (1897)) has prepared the sodium salt of formamide and it has been found in this laboratory that acetamide (Franklin and Stafford: Am. Chem. Jour., 28, 95 (1902)) and acetanilide (Franklin: Jour. Am. Chem. Soc., 37, 2291 1915)) react in liquid ammonia solution with metallic amides to form salts; and fifth, Dains (Jour. Am. Chem. Soc., 31, 1153 (1904)) has called attention to the existence of certain striking resemblances between the alkyl formamidines and the orthoformic esters.

[1] If, as is maintained by Michael and Hibbert (Liebig's Ann., 364, 64 (1909)), hydrocyanic acid is a merotrope with the nitride formula then the free acid is an ammono formaldehyde or formanammonide while in the form of its salts and in the isonitriles it exists as ammono carbon ous acid.

acid does not act as an acid anammonide but as anammono carbonous acid as has been shown in the first part of this paper.

*Hydrocyanic Acid and Methyl Amine.*—Looked upon as an ammono aldehyde[1] hydrocyanic acid is related to methyl amine as ordinary formaldehyde is related to methyl alcohol. Accordingly the familiar reduction of hydrocyanic acid to methylamine[2] and the inverse oxidation of methyl amine to hydrocyanic acid[3] may be looked upon, in the one case as the reduction of an ammono formaldehyde[4] to an ammono methyl alcohol, in the other as the oxidation of an ammono alcohol to an ammono aldehyde. Since, however, hydrocyanic acid is a tautomeric compound showing simultaneously the properties of an ammono formaldehyde, a formic anammonide, an ammono carbonous acid, and, possible even of a carbono, or methano, acid, it is a matter of indifference whether one assumes that it is a formaldehyde, a formic anammonide or a carbonous acid which is formed by the oxidation of methyl amine or which on reduction yields methylamine.

## Summary

In this paper an attempt has been made to show that hydrocyanic acid possesses simultaneously the properties of an ammono carbonous acid, of a formaldehyde of the ammonia system, and of a compound related to ammonia as the unknown formic anhydride is related to water.

*Ammono Carbonous Acid, HNC.*—The following reactions some of which are new, have been interpreted in support of the view that hydrocyanic acid is a carbonous acid of the ammonia system. First, the formation of hydrocyanic acid when carbon is heated in the presence of a mixture of nitrogen

[1] As indicated above (p.183) a compound of the formula $(CH_2)_3N_2$ of which hexamethylenetetramine is a dimer is a nearer analog of formaldehyde.

[2] Mendius: Liebig's Ann., **121**, 139 (1862); Debus, **128**, 201 (1863).

[3] Bamberger and Seligmann: Ber. deutsch. chem. Ges., **35**, 4299 (1902).

[4] The reduction of formic acid to methyl alcohol would be the strictly analogous reaction if one were permitted to assume an hypothetical carbonous acid as undergoing reduction.

and hydrogen, or with ammonia; second, the action of nitrogen in converting sodium cyanide, in the presence of metallic sodium, into sodium cyanamide; third, the formation of sodium cyanamide by the action of sodium azide on sodium cyanide; fourth, the formation of sodium dicyanimide by the action of cyanogen on sodium cyanide; fifth, the action of sodium amide on carbon, carbon monoxide and on carbon dioxide; sixth, the reduction of sodium cyanamide and of sodium dicyanimide to sodium cyanide; seventh, the oxidation of sodium cyanide to sodium cyanate; eighth, the ammonolysis of ethyl carbylamine to ethyl amine and hydrocyanic acid; ninth, the oxidation of methyl carbylamine to methyl isocyanate and the action of sulfur in converting methyl carbylamine into methyl isothiocyanate, and finally, the reduction of hydrocyanic acid to methylamine.

*An Ammono Formaldehyde, HCN.*—The reactions herewith summarized have been discussed in detail for the purpose of showing that hydrocyanic acid is also to be looked upon as a formaldehyde of the ammonia system. First, hydrocyanic acid polymerizes readily to products of unknown constitution, second, it undergoes condensation to form aldol-like condensation products, third, it forms addition compounds with the acid sulfites, fourth, it reacts with hydroxylamine phenylhydrazine and with hydrazine in much the same manner as formaldehyde reacts with the same reagents, and finally the relation of hydrocyanic acid to methyl amine as that of an aldehyde to an alcohol, is shown by the well known reducibility of the former to methyl amine on the one hand and the fact that methylamine may be oxidized to hydrocyanic acid on the other.

*Formic Anammonide, HCN.*—The relation of hydrocyanic acid to formamide, formamidine and the formimido esters respectively is shown to be analogous to that of the acid anhydrides to the acids.

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# NEW BOOKS

**Smell, Taste, and Allied Senses in the Vertebrates.** *By G. H. Parker. 21 × 14 cm; pp. 192. Philadelphia and London: J. B. Lippincott Co., 1922. Price: $2.50.*—The chapters are entitled: nature of sense organs, anatomy of the olfactory organ; physiology of olfaction; vomero-nasal organ; the common chemical sense; anatomy of the gustatory organ; physiology of gustation; interrelation of the chemical senses. There are a number of interesting paragraphs, as the following quotations will show, pp. 49, 64, 73, 85, 104, 148, 150, 173.

"The common belief that the olfactory stimulus consists of minute material particles suspended in the air current of the olfactory organ is supported by the observation that odors may be carried on the wind in a definite direction many miles. Odors do not emanate from a given center and disperse in all directions as sound and light do. Moreover many substances, such as arsenic, that are odorless under ordinary circumstances, give out an odor after they have been heated sufficiently to volatilize. The fact, discovered in 1917 by Woodrow and Karpman, that the adaptation time for olfaction—the time needed for an olfactory sensation to wane completely—is directly proportional to the vapor tension of the odorous material shows that olfactory stimulation is due to the activity of gaseous particles. These and other like observations have led to the conclusion, now generally accepted, that the olfactory organs are normally stimulated by material particles, and not by disturbances of a non-material character."

"As early as 1895 von Uexküll observed that dogfishes from which the olfactory membranes had been removed did not respond to the presence of food whereas normal dogfishes three to five minutes after food had been introduced into their tank, sought it with great eagerness. In these experiments no attempts were made to exclude sight or to ascertain the effects of the operation. In experiments carried out by me in 1910 an attempt was made to gain more conclusive evidence. Five normal catfishes (Amiurus) were allowed to swim in an aquarium in which were hung two wads of cheese cloth one containing concealed earthworms, and the other made of cloth only. In the course of an hour the wad containing the worms was seized eleven times by the fishes notwithstanding the fact that from time to time this wad was interchanged in position with the other. During the same period the wad without worms was passed over by the fishes many times and never excited any noticeable reaction.

"Ten catfishes were next prepared for further experimentation; in five of these the olfactory tracts were cut and from the remaining five the barbels, the seat of the chief external gustatory organs, were removed. After the fishes had recovered from these operations, they were put in an aquarium into which was introduced a wad of cheese cloth containing minced earthworms. During the first hour the wad was seized 34 times by fishes without barbels but with normal olfactory organs and, though often passed over by fishes with cut olfactory tracts, it was never seized by any of these and was 'nosed' only once by one of them. None of these fishes paid any attention to a wad of cloth containing no worms. Repetitions of these tests gave uniformly similar results and led to the conclusion that the olfactory organs of the catfish are serviceable in

sensing food at a distance much beyond that at which the organs of taste are capable of acting; in other words, catfishes truly scent their food.

"Similar experiments on the killifish (Fundulus) gave like results Parker (1911). Here, however, the olfactory organs were excluded, not by cutting the olfactory tracts, but by stitching up the anterior nares. As a result of this operation the fish no longer responded to hidden food, but quickly reacquired this power after the anterior nares had been reopened. These results were confirmed in work on dogfish (Mustelus) by Sheldon (1911), and on the swellfish (Spheroides) by Copeland (1912). Sheldon closed the nares of the dogfish with cotton plugs and, in 1914, I showed that when only one nostril is thus plugged, the fishes turn persistently toward the side of the open nostril. Such responses indicate that in the seeking of food under normal conditions, dogfishes, and probably other fishes as well, turn toward the side on which the concentration of odorous particles is greater. The certainty of this operation would increase in proportion as the nostrils of a given fish are separated one from the other laterally. A good example of an animal in which this condition reaches its maximum is seen in the hammerhead shark in which the nostrils, as well as the eyes, are carried on the remarkable lateral projections that extend sidewise from its head into the sea.

"The turning response of dogfishes under the conditions mentioned in the preceding paragraph has a striking resemblance to the circus movements in the tropic reactions of many of the lower animals and, were it not that fishes are so highly organized, it might be accepted at once as a response of that kind.

"As a result of the evidence thus far accumulated, it seems quite clear, contrary to the opinions expressed by Nagel and others, that many fishes scent their food much as air-inhabiting animals do and that they must be regarded as possessing powers of olfaction fairly comparable with those of the higher forms. This opinion is in entire harmony with the well known fact that fishes, especially sharks, can be drawn from a long distance by ill-smelling bait or by oily fish carcasses ground up and thrown into the water as in the practice of chumming. The extremely small amount of substance needed in these operations agrees well with what is known of olfaction among air-inhabiting vertebrates and reaches almost infinitesimal proportions as is indicated by the work of Olmsted (1918) on Amiurus."

"Haller and particularly Linnaeus proposed systems of odors that have formed the bases for many of the modern classifications such as the one given by Zwaardemaker (1895). In this odors are arranged in nine general classes each of which may contain two or more subdivisions. These nine classes are briefly as follows:

1. Ethereal odors; three subdivisions: odors of fruits, beeswax, ethers.
2. Aromatic odors; five subdivisions: odors of camphor, cloves, lavender, lemon, bitter almond.
3. Balsamic odors; three subdivisions: odors of flowers, violet, vanilla, cumarin.
4. Ambrosial odors; two subdivisions; odors of amber, musk.
5. Alliaceous odors; three subdivisions; odors of hydrogen sulphide, hydrogen arsenide, chlorine.
6. Empyreumatic odors; two subdivisions: odors of roast coffee, benzole.
7. Caprilic odors; two subdivisions: odors of cheese, rancid fat.
8. Repulsive odors; two subdivisions: odors of deadly nightshade, bedbug.
9. Nauseating odors; two subdivisions: odors of carrion, faeces.

"A survey of this classification shows at once that more or less of it is associative and subjective and hence artificial, for what may be repulsive to one person may be just the reverse to another. It is, therefore, not surprising that some of the recent students of this subject, as for instance Henning (1916), have advised the complete abandonment of such arrangements and have sought to establish by a thorough re-testing of odors an impersonal and reasonable classification. As the result of an extended and judicious re-examination of odors Henning has come to the conclusion that they fall into six fundamental classes as follows:

1. Spicy odors, such as those of fennel, sassafras oil, anise, and cloves.
2. Flowery odors, such as those of heliotrope, cumarin, and geranium oil.
3. Fruity odors, such as those of oil of orange, citronella, oil of bergamot, and acetic ether.
4. Resinous or balsamic odors, such as those of turpentine, of Canada balsam, and of eucalyptus oil.
5. Burnt odors, such as those of tar and pyridine.
6. Foul odors, such as those of carbon bisulphide and of hydrogen sulphide.

"Although each of these six classes, according to Henning, is represented by a number of odors, it is not absolutely separated from the others, but between any pair of them there are numerous odors that assume intermediate positions. The six classes, however, are the striking predominant elements in this complex and are in no sense submerged in the general array of odors. Henning has tried to make clear his idea of the relations of these six classes by imagining them located one at each corner of a three-sided prism which he calls the olfactory prism."

"Valentin observed that when ether and balsam of Peru were smelled at the same time, one by one nostril and the other by the other nostril, the odors are perceived not together but alternately and Valentin believed that there was a sensory conflict here as in vision, when one eye is directed to a field of one color and the other eye to one of another color. Aronsohn (1886) noted a similar conflict between the smell of camphor and that of oil of lemon. He also discovered that under similar circumstances one smell could overcome another. Thus the smell of camphor was neutralized by the smell of petroleum, cologne water, oil of juniper and so forth. This question was investigated much more fully by Zwaardemaker (1895) who employed for this purpose his double olfactometer. By this means it was comparatively easy to balance odors and then lead one into one nasal cavity and the other into the other cavity. In this way complete neutralization could be attained with great accuracy."

"The form of nerve terminal that is concerned with the reception of chemical irritants in the skin of vertebrates is well indicated in the catfish Amiurus. If a bait in the form of a piece of meat or the like is held close to the flank of one of these fishes, the animal is very likely to turn suddenly and snap it up. This is not a surprising response, for the sides of these animals are well provided with taste-buds. They are also supplied with lateral-line organs. Both these sets or receptors may be eliminated by cutting on the one hand, the branch of the facial nerve that is supplied to the taste-buds of the side of the body and, on the other, the lateral-line nerve that is distributed to the lateral-line organs of the same

region. After the fish has recovered from such an operation, it will no longer respond to a bait held near its flank, but the skin of this region is still perfectly open to stimulation by sour, saline, and alkaline solutions."

"The head and especially the eight barbels about the mouth of Amiurus are richly supplied with taste-buds. These organs, like those on the human tongue are apparently extremely sensitive to metals probably because of the slight electric currents produced by these bodies, for the fishes respond with great readiness to a weak constant current from a dry cell. If such a current is led into an aquarium through a water-filled glass tube and out again by a similar tube, the water acting as a conductor, catfishes can be readily stimulated by bringing such tubes close to them. If the current is sufficiently reduced (a little less than a microampere) the fishes will approach the open ends of the tubes and nibble at the current as though it were a bait, thus giving evidence that the organs stimulated are the gustatory receptors."

"The four well-recognized tastes are normally excited by very different stimuli. The sour taste is dependent upon the cation, hydrogen. The saline taste is called forth by a number of anions: chlorine, bromine, iodine, and the sulphate and nitrate ions. The bitter taste has as stimuli the alkaloids, such cations as magnesium, ammonium, and calcium, and possibly the anion of picric acid. The sweet taste depends upon such organic compounds as the sugars and alcohols, and on saccharine, on lead acetate, and on hydroxyl and glucinum ions. The four tastes, therefore, are excited by entirely independent groups of stimuli and it is a matter of importance to ascertain in what other respects they are independent."

"The sour taste is best developed on the lateral edges of the tongue and diminishes from these regions toward the tip, the base, and the central anaesthetic area. The saline taste is most pronounced at the tip and on the lateral margins of the tongue and diminishes at the base; toward the central area it ends rather abruptly. The bitter taste is most characteristic of the base of the tongue especially in the region of the vallate papillae whence it diminishes rapidly toward the central area and over the lateral edges to the tip. The sweet taste is at its maximum at the tip of the tongue and diminishes thence along the lateral margins to the base. Thus sour is represented by two marginal regions, saline by a horse-shoe shaped area at the tip, bitter by a single center at the base, and sweet by one at the tip. It is difficult to explain these differences in the distribution of the tastes except on the assumption of an independent sensory mechanism for each taste."

"Smell and taste, though thus most closely involved in the feeding reflexes, are nevertheless perfectly distinct. As long ago as 1821 Cloquet (Larguier des Bancels, 1921) showed that, on closing the nose by pinching the nostrils, smell can be eliminated and only taste remains. Under such circumstances it is surprising to those who have not previously tried the experiment to discover how small a proportion of our food sensations are due to taste and how large a one to smell. A cold in the head commonly eliminates smell and leaves taste. It reduces a person to a state in which food is often described as without flavor, rof only sour, saline, sweet, and bitter tastes can be sensed and onion produces the same sweetish taste that apple does." *Wilder D. Bancroft*

**Distillation Principles and Processes.** *By Sidney Young. 22 × 15 cm; pp. xiii + 509. New York and London: Macmillan and Co., 1922. Price: $10.50.*—The first half of the book deals with the general theory; the second half with the manufacturing processes. Under the second heading are included: distillation of acetone and normal butyl alcohol on the manufacturing scale, written by Joseph Reilly and F. R. Henley; distillation of alcohol on the manufacturing scale, written by F. R. Henley and Joseph Reilly; fractional distillation as applied in the petroleum industry, written by James Kewley; fractional distillation in the coal tar industry, written by T. H. Butler; the distillation of glycerine, written by E. Briggs; the distillation of essential oils, written by T. H. Durrans.

Professor Young is of course the leading authority in the world on distillation and this book is consequently authoritative. The theoretical part takes twenty chapters: introduction; the boiling point of a pure liquid; vapor pressures of mixed liquids; boiling points of mixed liquids; composition of liquids and vapor phases (2); directions for carrying out a fractional distillation; theoretical relations between the weight and composition of distillate; relation between the boiling points of residue and distillate; modifications of the still-head; continuous distillation; fractional distillation as a method of quantitative analysis; methods by which the composition of mixtures of constant boiling point may be determined; indirect methods of separating the components of a mixture of constant boiling point; general remarks; sublimation.

An interesting case is that of chloroform, p. 214. "It had been found that chloroform prepared from acetone was distinctly inferior as an anaesthetic to that made from alcohol and the most probable explanation appeared to be the presence of minute quantities of irritating products of decomposition, such as chlorine, carbonyl chloride, or hydrochloric acid in the chloroform derived from acetone. Careful experiments by Wade and Finnemore showed, however, that the acetone' chloroform contained no foreign substance beyond the alcohol and water which are always present, whereas the 'alcohol' chloroform contained a minute quantity of a volatile impurity. It was suspected that this might be ethyl chloride, and. . .finally, direct proof the presence of ethyl chloride was obtained in the first fractions, not only from the mixtures to which minute quantities of that substance has been added, but also from the chloroform prepared from alcohol. Not the slightest indication of its presence, on the other hand, could be detected in the first fraction from 'acetone' chloroform. It was thus proved that the superior anaesthetic properties of 'alcohol' chloroform are due to the presence of ethyl chloride—probably about 0.5 percent or 2 cc per Winchester quart—and it was found by Mr. Rowell at Guy's Hospital that 'acetone' chloroform to which a small quantity of ethyl chloride has been added is therapeutically identical with chloroform made from alcohol."

Most of us did not know that fractionation of an aqueous solution of formic, acetic, and butyric acids containing relatively little acetic acid, p. 216, causes the acids to come over in the reversed order of their boiling points. This is because the butyric acid and water boiling-point curve has a minimum point and the formic acid and water curve a maximum point.

Under sublimation, p. 226, we read that "the triple-point pressures of arsenic and of arsenious oxide are higher than the atmospheric pressure, and

true sublimation takes place when these substances are heated and their vapours are condensed. . . The sublimed oxide is obtained either as a hard vitreous cake or as a loose friable mass according to the temperature at which the operation is conducted. In Wales the vitreous 'white arsenic' or arsenic glass is obtained by causing the sublimation to take place under slightly increased pressure."

On p. 352 is the statement that "vacuum distillation in the petroleum industry has not, up to the present, received the attention it deserves. Plants for the distillation of lubricating oils are often operated under vacuum but this is seldom sufficiently high to give the best results, in many cases, indeed, being so low as to have little marked effect on the distillation."

Colloid chemists will be interested in two statements, pp. 363, 367. "The [blast furnace] tar comes off similarly in a fog suspended in the gas, but is a physically different form, which makes it even more difficult to separate from the gas." "One of the greatest difficulties a tar distiller is faced with is the elimination of water, which, as already stated, is present in varying proportions. The tar is generally allowed to settle in large wells or tanks, from the bottom of which it is pumped into the stills. Its water content is thus reduced to anything below 5 percent. Some tars cannot be even partially freed from water in this way, as an emulsion forms, and no separation takes place even after long standing. These high water tars generally contain a large percentage of free carbon, and the difficulty experienced with any individual tar in separating water by mere settling may almost be taken as a measure of its free carbon content. The cost of distilling out only a few parts per hundred of water is very considerable; and in some cases it is as high as that of distilling off the remaining 30–40 percent of volatile products."

The use of Raschig or Lessing rings in fractional distillation, pp. 137, 399, 400, is an interesting return towards one of the early types of laboratory apparatus.

Special problems arise with the essential oils, p. 450. "So far we have only dealt with the steam distillation of the essential oil which has already been freed from the non-volatile organic matter with which it occurs in the natural state. The presence of this non-volatile matter introduces technical problems of some importance, and it is necessary so to prepare the raw material that the influence of the non-volatile matter is diminished as far as possible.

"In any given distillation the rate will depend not only on the vapour pressure of the essential oil and the quantity of heat supplied, but also on the rate at which the volatile oil is liberated from the accompanying non-volatile matter. This last factor produces a lag which under unfavorable conditions may be of serious moment, and the object of this preliminary treatment of the raw material is to reduce this lag to a minimum. It is possible roughly to estimate the value of the lag and thus to determine the best condition of the raw material for distilling. If the lag be nil, then the rate of distillation of the oil will be the same as that in the absence of the non-volatile matter, other conditions being equal; any slower rate will be a measure of the lag.

"In order to reduce the lag to a minimum the raw material must be reduced to such a state that the steam, introduced for the purpose of volatilizing the essential oil, can readily penetrate the mass and yet can come into contact with every particle of essential oil in as short a time as possible. At first sight

the obvious treatment would be to reduce the raw material to an exceedingly fine powder; this, however, is seldom feasible and introduces subsequent difficulties through lack of porosity.

"Frequently the raw material is best distilled without any previous treatment, as for instance in the case of leaves, twigs, petals, flowers, buds, grasses, and similar material, but occasionally the problem is one of considerable difficulty and a compromise between the fineness of division and the porosity of the mass is the best that can be attained. If the material were of course texture, such as blocks of wood, the time necessary in order to distil out the oil would be excessive and a heavy consumption of fuel would result; but if the other extreme had to be dealt with, such as a fine powder, the mass would become more or less impervious to the steam, which, in consequence, would find its way through the mass by means of fissures, leaving the greater part untouched. This latter difficulty can generally be overcome by diluting the charge with water in a quantity sufficient to render the resulting paste mobile.

"Various methods for the treatment of large pieces of wood and branches present themselves. It is generally sufficient to chop branches up into short lengths, relying on expansion and capillary action to cause the oil to extrude during the distillation. The American practice in the case of the various pine oils is to chop the branches into pieces of one-half to one inch long and of less than half an inch in diameter; pieces of this size yield their oil readily and the lag is comparatively small. Wood in the form of large blocks is one of the most difficult to deal with, and a large amount of power may have to be utilized to reduce it to a state suitable for distillation. The procedure generally is to saw it into suitable lengths and then to rasp it to a coarse powder; alternative methods are to split it or tear it apart along the grain, or to shave it into chips, or to splinter or crush it by means of heavy crushing jaws similar to those used for crushing rocks. Rosewood and sandalwood are generally reduced to small chips by means of a 'craboteuse' chipping or planing machine.

"Seeds and berries can frequently be distilled without preliminary treatment in spite of the enclosing epidermis, the heat of the steam and the increase of internal pressure due to the expansion of the contents and to osmosis being sufficient to rupture the epidermis and to set free the contents, but if the epidermis be too tough it is necessary to rupture it mechanically before distillation. Schimmel found that uncrushed Ajowan seeds yielded 20 percent less oil than crushed seeds, although the former were distilled twice as long as the latter. It is desirable that seeds similar to Ajowan, such as aniseed, caraway, and thyme, should be crushed."

"The constituents of essential oils with a few exceptions, such as camphor, safrol, menthol, thymol, are relatively unstable bodies and tend to decompose or polymerize under the action of heat; thus geraniol isomerizes to cyclogeraniol, anethol forms various polymers, citral decomposes to cymene and methyl heptenone, citronellal isomerizes to isopulegol, cinnamic aldehyde resinifies, and so on. Obviously therefore, it is desirable as far as possible to limit both the temperature and the duration of a distillation. The temperature can be reduced by conducting the distillation under diminished pressure. Theoretically the diminution of temperature may be so great that the boiling point of the substance could approach the absolute zero. Practically, however, we are limited

by the efficiency of our vacuum pumps, the air-tightness of our stills and the efficiency of our condensers. It is a task of very great difficulty on the technical scale to obtain a diminished pressure or "vacuum" of one-fifth of a millimetre, and more often the vacuum available is of the order of 10 or 20 mm. Under a pressure of 20 mm the majority of the constituents of essential oils boil at temperatures considerably in excess of 100°C, hence unless very efficient and refined apparatus be available it is better to resort to steam-distillation, since in this case the temperature cannot exceed 100° C," p. 475. *Wilder D. Bancroft*

**An Introduction to the Chemistry of Radioactive Substances.** *By A. S. Russell. 19 × 13 cm; pp. xi + 173. Toronto; The Macmillan Company of Canada, 1922. Price: $2.00.*—The subject is presented under the following headings: the sources of the radio-elements; the beginnings of radio-activity and the disintegration theory; the disintegration theory; atomic number; the periodic system, and the structure of the atom; the three disintegration series; the ten types of radio-elements and the group-displacement law; isotopes; description of the types of radio-elements; the analytical chemistry of uranium; the analytical chemistry of thorium; the separation of the radio-elements in dividually; radio-elements as indicators and the properties of bodies at small concentrations.

On p. 38 the author points out that "the charge on the nucleus determines the configuration of the external electrons, and since the configuration of the external electrons is assumed to be the seat of all ordinary physical and chemical properties of the atom, the charge on the nucleus is the fundamental property of the atom. On it the physical and chemical properties depend. If it be altered in any way so that the charge is decreased or increased, the configuration of the external electrons will be radically altered, and the physical and chemical properties likewise will be radically altered; alteration of the charge on the nucleus, therefore, leads to an entirely different atom.

"Three facts may be emphasized in connection with this:

(1) The chemical elements are apparently not so independent of one another as chemists thought prior to the discovery of radio-activity. It has been found, as has been said above, that all have essentially the same structure. The difference between one element and another is largely a difference in the amount of charge carried by the nuclei of the two sets of atoms.

(2) The nature and magnitude of the nucleus of the atom has been shown by recent work in physics to be such that an alteration of the nucleus by artificial means is an extraordinarily difficult undertaking. Change of such conditions as temperature or pressure has no effect on the nucleus. This difficulty in attacking the nucleus explains why it is that, although the difference between the atoms of different elements is a simple one, it is very difficult to bring about transmutation of one element into another artificially.

(3) Radio-elements are those whose atoms' nuclei are spontaneously and continuously being transformed into the nuclei of atoms of other elements."

On p. 77 the author gives a good summary of the properties of isotopes. "Isotopes, then, have by definition the same positon in the periodic classification, i. e., the same atomic number. They possess also, as has been found experimentally, identical chemical properties. But they differ in radio-active proper-

ties, and they may differ in atomic weight. Before this represented the full state of knowledge the question arose: Do isotopes possess any identical physical properties? After the publication of Marckwald's work, and before that of the workers mentioned above, the writer came to the conclusion that isotopes probably possessed identical physical properties except those of radio-activity and atomic weight. To commence an attack on this problem Rossi and the writer investigated the arc spectrum of preparations of thorium and its isotope ionium. They showed that it was impossible to detect a difference in the arc spectra of pure $ThO_2$, and of a mixture of $ThO_2$ and $IoO_2$, containing approximately 20% of the latter in circumstances such that an impurity of 1.5% of a body of high atomic weight was easily detected. From these experiments they concluded that the arc spectra of thorium or ionium were identical, and they generalize this result to include all isotopes. Since then these results have been confirmed and numerous investigations have been made of the physical properties of different groups of isotopes.

"As a result of these experiments, isotopes have been found to differ in the following properties: radio-activity; atomic weight; properties which depend upon atomic mass, such as density and solubility expressed in grams per cc or per litre. These may be called individual properties.

"Isotopes have been found to be identical in the following properties: atomic number and X-ray spectrum; chemical properties; arc spectrum; atomic volume, molecular solubility, density expressed in mols per litre; volatility; melting and freezing points; electro-chemical potential; diffusion velocity of ions in solution; refractive index; magnetic susceptibility, and others. These may be called type properties.

"Each of these thirteen properties has not been specifically investigated in every isotope, but sufficient experiments have been done to render it very probable that what is experimentally proven for such isotopes as have been examined holds throughout."

On p. 84 we read that the existence of isotopes may be deduced easily from Rutherford's nuclear theory of the atom. "The chief point of the theory necessary for this purpose is that the charge on the nuclus conditions the chemical properties of the atom, the mass of the nucleus having an influence which must be very small. Hence atoms whose nuclei have the same charge have the same chemical properties. Now it is possible for nuclei to have different compositions and yet possess identical charges, since the charge (which is positive) is a net one, being the algebraic sum of the positive and the negative charges which the nucleus contains; the number of charges may vary so long as their algebraic sum is constant. A nucleus with a given charge may consequently have various compositions. Hence it is that isotopes have different radio-active properties, for radio-activity, being a property of the nucleus, must be a function of its composition."

To the reviewer the last chapter—on radio-elements as indicators—was the most interesting because he learned most from it. "A large and interesting field of work has been opened up by using radio-active isotopes of common elements to indicate what is occurring to the latter in chemical operations. Different properties of compounds of an element like lead or thallium, which has radio-active isotopes, may be investigated at extremely small concentrations by

using the radio-active properties of the isotopes for purposes of identification and measurement. The concentration at which a radio-active body can be estimated quantitatively by the methods of radio-activity is, of course, many times less than by the methods of spectroscopy, which are the most refined ways of detecting and estimating inactive substances. By assuming that the radio-active body has exactly the same chemical and physical properties as its inactive isotope, the properties of the inactive body may be investigated in concentrations down to the extreme limit at which the most sensitive radio-active isotope can be detected. For example, $10^{-12}$ miligrams of ThB can be detected by the methods of radio-activity; therefore the properties of lead at this concentration may be investigated.

"The following are some of the properties of these bodies that have been investigated with radio-active indicators: solubilities of difficultly soluble salts; the volatility of different compounds at small concentrations; the rate of diffusion of an atom (or a molecule) of a metal in a block of itself, or of a metal ion in a crystalline compound of the metal; the existence of new compounds.

"These are determined directly. An experiment is carried out as follows: A large quantity of indicator is accurately determined by electroscopic measurements. It is put into solution and added to a solution of a compound containing the metal of the compound whose solubility is under investigation, and thoroughly stirred. The difficultly soluble compound is then quantitatively precipitated with its radio-active isotope from the solution, washed, dried, and weighed. The salt is next shaken up with water at a given temperature until the solution is saturated with it. The same fraction of the indicator as of the salt goes into solution. The known volume of water is then filtered from the salt, evaporated to dryness, and the amount of the indicator determined accurately by electroscopic measurements. The solubility of the indicator is then calculated in the ordinary way, and this is the solubility of the difficultly soluble compound.

"This method works excellently for difficultly soluble salts like $PbCrO_4$ and PbS, whose solubilities cannot be measured properly by direct method, and which are usually measured indirectly—for example, by measurements of electrical conductivity.

"Hevesy, Paneth, and Frl. Róna determined the solubility of lead chromate by the method above, using RaD as indicator, and found its solubility to be $2 \times 10^{-7}$ mol per litre.

"The existence of $BiH_3$ and of a hydride of lead has been shown by the use of indicators. $BiH_3$ corresponds to $AsH_3$ and $SbH_3$, but has only recently been prepared. Paneth demonstrated its existence as follows: He collected the active deposit of thorium (ThB + ThC) on thin magnesium and dissolved the whole in dilute HCl. The gases evolved were passed through cotton-wool into an evacuated electroscope. The gas in the electroscope was found to decay with the period of ThC showing that, in addition to hydrogen, a gaseous product of ThC had been evolved. This is very probably $ThC.H_3$, and since ThC is an isotope, the method indicates how $BiH_3$ may be prepared. Paneth found that only one or two parts per thousand of the ThC on the magnesium combined with hydrogen in this way, which indicates the difficulty of forming $ThC.H_3$ (and therefore of $BiH_3$) by this method. Having thus shown the existence of

$BiH_3$ by a radio-active indicator, Paneth succeeded further in preparing this compound by ordinary means. In a similar way he has succeeded in preparing a hydride of lead."

On p. 167 the author discusses the use of actinium B in electrometric measurements. "The normal potential of nickel is −0.53 volt. If nickel be rendered passive, however, as it is when dipped into a hydrochloric acid solution its potential becomes approximately + 0.5 volt, because on it is then deposited nearly pure C. The degree of passivity of nickel due to certain reagents may be measured conveniently and quickly by the radio-active method. On nickel rendered slightly passive was found to be deposited approximately 75% of the equilibrium amount of AcC. This corresponds, as the curve shows, to a potential difference of about −0.4 volt. When rendered more passive it was proved that 90% of AcC was deposited on it. This corresponds to a potential difference of +0.1 volt. The radio-active method should have a wide application in studying the passivity of metals." The reviewer does not see the especial advantage of this and he finds difficulty in accepting the author's view that nickel is active in nickel sulphate solution and passive in nickel chloride solution. That is not the experience of the electrochemists. *Wilder D. Bancroft*

**Einstein's Relativitätstheorie und ihre Stellung im System der Gesamterfahrung.** *By Karl Bollert. 23 × 16 cm; pp. 70. Dresden and Leipzig; Theodor Steinkopff, 1921.*—This little book is an attempt to trace the philosophical consequences of Einstein's Relativity from the standpoint of the Kantian theory of knowledge.

The first half of this book contains a brief exposition of Einstein's theory. The treatment is adequate for the purpose in hand. It is worth noting, however, that the statement of the fundamental postulates of the Special Theory is misleading, if not definitely wrong. The First Postulate is not commonly understood to make the assertion, "all motion is relative," and to rest therefore upon epistemological grounds, but to state that "only motion relative to matter has physical significance," and thus to express an experimental fact. The expression of this fact is made by the author to form part of the Second Postulate.

In the second part of the book the author presents the development of human knowledge of the world as a process of objectification of experience. In everyday life one conceives of objects as things outside one's self and as existing in space and time and this concept was taken over and refined by the older physics. Relativity, however, makes space and time vary with the state of motion of the observer, while the spaces and times of all observers are included as individual aspects or perspectives in a fundamental four-dimensional continuum just as the two-dimensional perspective views that we see individually are included in ordinary space. The continuum alone is truly real, just as formerly space and time were so regarded, for always "that which runs unchanged like a golden thread through the whole available range of experience must be accepted by our thought simply as existing."

Now Kant taught that time and Euclidean space were separate forms of thought innate in the mind and that we could not possibly force our experience into any other conceptual mold. What becomes of this view if space is non-Euclidean and is fused with time? So, too, with the Kantian categories of un-

changing substance and causal relationship: what becomes of these when masses vary with speed and there is no objective time that is valid for the whole universe?

The author finds the solution of this problem in the fact that even in the General Theory of Relativity the old physics is still valid within indefinitely small elements. Thus is Kant vindicated; the "a priori character of certain forms of thought is not brought into question" by Relativity; "these forms of thought enter into the foundation of Einstein's view of the world just as they did with Newton, or as they must in any conception of Nature whatever."

The author must be awarded a technical victory, but the writer cannot feel that he has really got to the bottom of the matter. Undoubtedly the ultimate elements of thought must be things that are the same at all times and for all minds, else a science universally intelligible and valid over a range of time would be impossible. But these ultimate constant terms might conceivably be far more abstract than such concepts as that of mass. And the writer thinks he is able to conceive of an orderly world in which space would be, say, five-dimensional, or even dis-continuous, or in which all ordinary physical constants would be subject to a steady secular variation. The present security of the Kantians may be but temporary.

The author's discussion of this problem, while perhaps not deep, is clear and interesting. *E. H. Kennard*

**The Theory of Allotropy.** *By A. Smits. Translated by J. Smeath Thomas. 22 × 14 cm; pp. xiii + 307. New York and London: Longmans, Green and Co., 1922. Price: $7.00.*—The theory of allotropy consists of the explicit assumption that the solid, liquid, and presumably the gaseous, phases of any so-called one-component systems always contain two or more constituents whenever two or more allotropic modifications of the substance are known. Since allotropic modifications occur with practically all solids, this means that all the phases in a so-called one-component system are mixtures. If equilibrium is reached practically instantaneously these systems will be unary to all intents and purposes. If equilibrium is reached slowly, these systems will be binary if observations are made quickly and unary if plenty of time is given. The theory is therefore essentially an extension to the solid state of the principles developed by Roozeboom and by the reviewer for systems in which two modifications occur in the melt.

Instead of presenting the matter fairly simply, the author has complicated it in a way which seems to the reviewer quite unnecessary, by plotting thermodynamic functions. He also leaves it very obscure whether, in such cases as phosphorus, he is considering merely the occurrence of two modifications in the melt or two modifications in the solid; also whether we are dealing with one or two solid phases and how we know it. In some cases the author does not play quite fair. On p. 98 he discusses Ostwald's Law of Successive Transformations without pointing out that it is not a law and that not even Ostwald ever applied it except for temperatures below the transition point. On p. 222 he shows that when mercuric vapor is cooled suddenly to a temperature above that of the transition point, the yellow modification comes out and never the instable red modification. He adds that "this is in complete agreement with our rule, but it is entirely opposed to the Law of Successive Transformations, for accord-

ing to it the metastable modification should appear first above the transition point also." On the same page the author discusses at length the fact that the yellow modification of mercuric iodide is formed when a concentrated solution is poured into cold water; but ignores the more interesting fact, reported fifty years ago by Carey Lea, that the red modification comes out if the solution is poured into a cold porcelain basin. While he could presumably have explained this, he did not do so.

On p. 175 the author cites the different views in regard to whether there really are such minute concentrations of silver ions as we postulate from electromotive force measurements in cyanide solutions. The author's summing up was not helpful to the reviewer. "In the author's opinion the matter must be looked at in this way. All the above-mentioned calculations of concentrations are, in reality, extrapolations into a concentration region, in which ordinary thermodynamical methods of calculations are no longer really applicable. No great value can therefore be attached to the absolute magnitudes of the calculated concentrations; it is possible, after all, that these concentrations are in reality a certain amount greater than the calculated values, and we must consequently be most cautious when these amounts are considered as arithmetical quantities. It must be emphasized, however, that these considerations do not alter the significance of the solubility products and solubility quotients so far as this theory is concerned." We can predict confidently that we shall have rain or snow, and fair weather; somewhat warmer, unless the temperature falls.

Metallic iron is considered by the author to consist, p. 377, of electrically neutral iron, ferrous ions, and ferric ions, the last two of which are only partially miscible in the solid state. It is obvious that if we change the relative concentrations of these hypothetical constituents, we shall get new properties. Passivity and polarization are expressed in terms of this hypothesis with hydrogen, hydroxyl, and chlorine ions functioning as positive and negative catalysts as desired. It seems to the reviewer that it would have been better if the author had covered less ground and had gone over the smaller portion more carefully. The book cannot be recommended. *Wilder D. Bancroft*

**Laboratory Manual of Colloid Chemistry.** *By Harry N. Holmes. 23 × 15 cm; pp. xii × 127. New York: John Wiley and Sons, 1922. Price: $2.00—* The experiments are grouped under sixteen heads: suspensions—coarse and fine; dialysis and diffusion; condensation methods of preparation; dispersion methods of preparation—peptization; coagulation; protective colloids; solvated colloids; surface tension; emulsions; viscosity; adsorption from solution; adsorption of gases; reactions in gels; experiments with the ultramicroscope, soils and clays; special topics. This is a very good book and covers a great deal of ground. Of course no student could possibly do all the experiments as part of any regular course; but the author has suggested five groups which he considers could be run through by working twelve clock-hours per week for half a year. The groups are for students of colloid chemistry, medicine, agriculture, geology, and industrial chemistry.

The variation of the color of cuprous oxide with the degree of dispersion, p. 3, was new to the reviewer; so also was the experiment on centrifuging certain emulsions, p. 60. The author's chromatic emulsions are given, p. 64. The germ

theory of lubrication appears on p. 113. The view of Wilson is referred to p. 55, that the film on an emulsion is ordinarily plastic rather than viscous.

The reviewer believes that the arrangement of the book is unsound and that one ought to study adsorption before one takes up colloidal solutions. That is a matter of opinion, however, and time will show who is right. On p. 2 there seems to be a bad misprint. Part of the text for Exp. 3 is put after Exp. 6. The Exp. 5 on the same page is a very striking one. For personal reasons the reviewer would have welcomed a discussion of the theory of Exp. 77 on pectin jelly, p. 39. The theoretical part of the book is not its strong point, however. The author gives a discussion on rhythmic banding, p. 99, which involves the solubility product although it has been proved conclusively that this is not a phenomenon of supersaturation. Some reference to the work of Bradford should have been made. It is evident that a good experiment means more to the author than any theory, which explains his extraordinary catholicity. There is no attempt made to separate the sheep from the goats. Fischer, Loeb, and the reviewer all look alike to the author and probably he is the only man about whom that could be said.

The book is so far ahead of any other laboratory manual on colloid chemistry that no comparison is possible. The author is to be congratulated and his book will certainly be adopted in all laboratories. In the preface the author says that not only theoretical chemists but industrial men are expressing the belief that a great many of their problems are colloidal. In the blurb the enthusiastic press agent has changed it to "theatrical chemists," which may have been intentional but we hope not. *Wilder D. Bancroft.*

**Atomic Form.** *By Edward E. Price. 19 × 12 cm; pp. viii. + 143. New York and London: Longmans, Green and Company, 1922. Price: $1.75.*— The author considers that "the suggestion that the atom is a system of negatively charged corpuscles revolving around a positively charged centre cannot readily be reconciled with the power which each element possesses of building up its own crystalline form with its great stability, sharp edges, and smooth faces." He therefore decides to consider the carbon atom as a tetrahedron in which the faces are isosceles triangles with the base equal to the normal to the base. This is called a carbonoid. By fitting two of them together he gets an ethyloid which "is more convenient in shape than the carbonoid and far exceeds in symmetry and compactness all the other groups." Three ethyloids can of course be arranged to give a benzenoid, "which has twelve faces all exactly alike, and all occupying similar positions in the figure. This is a very compact and symmetrical figure and should have great stability and special features and characteristics separating it from all other combinations of either carbonoids or ethyloids."

The possibilities of these things are discussed in twelve brief chapters, entitled: introductory; the carbonoid and ethyloid; benzene and some of its derivatives; the allotropic forms of solid carbon; law of even numbers; tautomerism; isoprene and rubber; triphenyl-methane; optical activity of carbon compounds; condensed rings; cyclic compounds; concluding observations.

*Wilder D. Bancroft*

# STRUCTURAL COLORS IN FEATHERS. I

BY CLYDE W. MASON[1]

A-1586

## Introduction

BY WILDER D. BANCROFT, ÉMILE M. CHAMOT AND ERNEST MERRITT

Physicists distinguish between pigment and structural colors. Pigment colors depend on the chemical nature of the material and are due to the absorption of certain wave-lengths by the molecules. Structural colors depend upon, or are modified by, the physical arrangement of the material. The colors produced by a prism are structural colors and so are the diffraction colors of gratings and the interference colors of thin films. With turbid media in which the particles are small relatively to the wave-lengths of light, the shorter or blue wave-lengths are scattered much more than the longer or red wave-lengths. In consequence such a medium is reddish by transmitted light and bluish when seen from the side. These blues are called Tyndall blues, typical cases being the blue of the sky, of cigarette smoke, of skimmed milk, and of blue eyes. In all these cases of structural colors, the colors can be produced starting with materials which are in themselves colorless. The rain drops which give rise to the rainbow are colorless; a diffraction grating may be a sheet of colorless glass with parallel lines ruled on it; a thin film of a colorless oil will give us interference colors, and we can get the Tyndall blues by suspending a colorless powder in water. The arrangement of the material is what gives rise to the colors. In feathers the reds, yellows, and blacks are pigment colors; the whites, blues, and the metallic or iridescent colors are structural colors; and practically all the non-metallic greens are a structural blue combined with a pigment yellow.

[1] The investigation 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.

No theory of structural colors in feathers is well established as yet. While everybody admits that there is no blue pigment in the non-metallic, blue feathers, such as those of the bluebird, the indigo bunting, the blue jay, and the kingfisher, there is no agreement as to the exact cause of the blue. The most widespread explanation is that it is a prismatic color, apparently because a prism may give the spectrum colors, and blue is one of the spectrum colors. Nobody has attempted to explain how the hypothetical prisms could be arranged so as to give a blue color and nobody has explained why these hypothetical prisms should never be arranged so as to give a structural red or a structural yellow. Haecker has shown to the satisfaction of the chemist and the physicist that the structural blue is what is known as Tyndall blue and is due to the scattering of light by very small air-bubbles in the horny mass of the feather; but this explanation has not been accepted by the zoölogists.

When we come to the metallic or iridescent colors, such as those of the peacock and the humming-bird, the confusion is even worse, because the question is still open whether they are structural colors or pigment colors. Michelson[1] is quite convinced that the metallic colors are due to selective reflection from a pigment surface such as occurs with many of the solid aniline dyes. He points out that a thin film of fuchsine (magenta) reflects just the yellow and green which it refuses to transmit, and it accordingly shimmers with a metallic golden-green color. He says that on applying the simpler general tests of metallic reflection to the case of iridescent plumage of birds, scales of butterflies, and wing-cases of beetles, one is at once struck with the close resemblance these bear to the aniline colors in every particular. After making comparative measurements on a beetle having a lustre resembling burnished copper and on a thin film of magenta, Michelson says that "the correspondence between the two sets of curves is so remarkable that it leaves no room to doubt that in this case the metallic coppery color of the wing-case is due to an extremely

[1] Phil. Mag., [6] 21, 554 (1911).

thin film of some substance closely analogous to the corresponding aniline dye." In another paragraph he says that "the total number of specimens which have been examined is perhaps not so large as it should be to draw general conclusions, and it is clearly desirable that it be extended; but, so far, the evidence for surface film, as the effective source of the metallic colors in birds and insects is entirely conclusive." Among the birds studied by Michelson were the peacock and the humming-bird.

This would seem to be convincing, coming from a man like Michelson; but Lord Rayleigh[1] does not consider the question as settled and rather believes that the colors are the colors of thin films. He points out that with ordinary unpolarized light the colors due to selective reflection appear to change much less with the angle of incidence than do the metallic colors of birds and beetles. "Neither in the case of fuchsine nor of diamond green G—the second dye specially discussed by Walter—or with any other dye hitherto examined have I seen an adequate change of color without the use of the nicol to eliminate vibrations in the plane perpendicular to that of incidence. In the absence of a nicol there is little sign of the blue seen with it from fuchsine at 70° incidence. Much greater changes with more saturated color are exhibited by the wing-cases of beetles when so examined." In a foot-note there is the statement that "through the kindness of Sir James Dewar I have had the opportunity of experimenting with a good many dyes from the Badische Anilin-Fabrik. Following Walter, I have used warm alcoholic solutions spread upon previously warmed glass plates. Latterly I have examined some more dyes for which I am indebted to Prof. Green. In no case have I seen any considerable change of well-developed color unless the light was polarized."

It was found impossible to extract any colored pigment in any way. Treatment with hot, dilute nitric acid, or with hypochlorites removed the dark pigment but left the dye on the structure, which is the seat of the special coloration.

[1] Phil. Mag., [6] 37, 98 (1919).

Dr. Eltringham reports that after such treatment the wing-case of the beetle transmits complementary colors to those which it reflects and reflects the same colors from both sides.

In another paragraph Rayleigh says that "the colors reflected at moderate angles seem highly saturated. At perpendicular incidence the prism shows next to nothing beyond the uninterrupted red and red-orange, and on inclination the green region appears well isolated. The impression left upon my mind is that the phenomena cannot plausibly be explained as due to surface color, which in my experience is always less saturated than the transmission color, and that, on the other hand, the interference theory presents no particular difficulty, unless it be that of finding sufficient room within the thickness of the cuticle. But the alternations cannot be those of plane strata extending without interruption over the whole area of the color."

In the obituary notice of Lord Rayleigh, Schuster[1] points out that in one of the last papers published before his death, Rayleigh discusses the various theories which have been proposed to account for the vivid colors shown in animal structures such as beetles' wings, maintaining—though with some reserve—his own predilection for the one which depends on the beam reflected from a laminated medium, or one possessing a periodic structure.

Still another explanation has been put forward in the case of certain butterflies and beetles. In many cases there are a number of more or less parallel lines, sometimes as many as twenty-five thousand to the inch. This suggests a diffraction grating and it has been claimed that some of the brilliant colors are diffraction colors, though no attempt is made to show that any diffraction grating could be imagined which would give the colors actually obtained. While Walter has pointed out that neither prisms nor gratings give any colors when exposed to a uniform light, this has apparently been forgotten and is not used by anybody as a test for the existence or non-existence of the so-called prismatic or diffraction colors.

[1] Proc. Roy. Soc., 98A, XL (1921).

A study of the question of structural colors in feathers indicated this is apparently a problem calling for a co-operative research on the part of men representing different fields. This point of view was put before the Heckscher Research Council, and on July 1, 1921 a grant (No. 37) was made, for the study of structural colors in feathers, to a committee consisting of Messrs. Bancroft, Chamot, and Merritt, representing physical chemistry, chemical microscopy, and physics respectively. As an unofficial member representing ornithology, the committee has had the enthusiastic co-operation of Mr. Fuertes, who was really responsible, initially, for the starting of the whole investigation. In addition, the work of the committee has been facilitated by the courtesy of Prof. A. A. Allen of Cornell University and of Dr. Frank M. Chapman of the Natural History Museum in New York, who have furnished many interesting features.

For the experimental side the committee has been fortunate in securing the assistance of Mr. Clyde W. Mason, assistant in chemical microscopy at Cornell University. It is to his skill and perseverance that the successful outcome of the investigation is due. Since Mr. Mason has done all the experimental work and has written it up himself, the rest of the report appears as his work.

The general results of the work are to confirm Haecker's views on the structural blues and Rayleigh's views on the metallic colors. It is hoped that the additional evidence now submitted will be considered sufficient to clear up the general problem of structural colors in feathers. The committee feels that this investigation is a striking illustration of the value of co-operative research in certain fields. No single member of the committee could have obtained these results in the time—if at all.

## White Feathers

In his papers on the colors of colloids Bancroft[1] has assembled the statements of various investigators as to the causes of the colors which are found in feathers. The lack of

[1] Jour. Phys. Chem., **23**, 356, 365, 445 (1919).

agreement in the explanations quoted is sufficient justification for the presentation of the following paper, which is an attempt to evaluate and to correlate the work previously done, in the light of additional investigations by the author.

All color manifestations fall into two classes: the structural colors, which are due to the modification of the constituents of light by some special structure which it encounters and the pigment colors, which are due to the absorption of certain of the colors which compose white light, by passage through a particular substance, which we say possesses color.

Structural colors, as the name implies, are caused by a particular arrangement or form of matter, which is capable of separating the components of ordinary white light, some of which reach the eye of the observer and are perceived as color. No pigment or colored substance, as we ordinarily use the term, is needed to produce such an effect. The prism is the most familiar example of a color-producing structure. The colors of thin films, of turbid media, and of diffraction gratings are other types of structural colors.

All of these have been mentioned in the literature as the cause of certain of the colors found in feathers, and a detailed study of these different types of color production is necessary if any of them are to be recognized as existing in feathers.

The influence of the state of subdivision of matter on light falling upon it is very striking, and bears an important relationship to the color perceived.[1] A transparent colorless object is visible by virtue of the light which it reflects or refracts to the eye of the observer.[2] If reflection and refraction are eliminated by surrounding the substance with a medium having the same index of refraction, the substance is invisible.[3] A glass rod in oil of cedar is invisible for this reason. If the substance is colored, such as a colored crystal, and is surrounded by a medium of the same refractive index, it appears simply as a colored portion of the medium which surrounds it, and is

[1] Bancroft: "Applied Colloid Chemistry," 196 et seq. (1921).
[2] Wood: "Physical Optics," 98 (1911).
[3] Tyndall: "Light and Electricity," 39 (1895).

visible only by virtue of its color. The color is the result of the absorption of some of the constituents of the incident light, the remainder of which reaches the eye and appears colored. The intensity of color depends on the thickness of the colored substance traversed by the light. Thin layers of colored material appear almost colorless.

If we have a transparent substance finely powdered, a large proportion of the incident light will be reflected and refracted. Moreover, some of this reflected and refracted light will reach the eye of the observer, even though it is to one side of the path of the direct beam, giving what is commonly called "diffuse reflection."[1] Thus powdered glass, chopped ice, sugar, foam, clouds, paper, etc., appear white because of the large amount of light scattered by their multitude of surfaces, though in mass they appear transparent.[2] If a transparent colored substance is finely divided it appears almost white, for the white light which falls upon it is scattered as in the case of chopped ice, while any light which enters the substance can traverse only a very thin layer before it is reflected or refracted out. As a result almost no absorption takes place and the light is only slightly colored. Thus powdered copper sulphate, chrome alum, ruby glass, etc., appear almost white, though they are highly colored in mass. If such a fine powder is surrounded by a liquid of the same refractive index as its own, the original color of the material in mass is restored. If the powder is composed of a transparent, colorless substance, it is no longer white when immersed in liquid of the appropriate refractive index. Instead it becomes almost perfectly invisible, since absorption, reflection, and refraction of light are at a minimum under these conditions. As examples of this we have wet snow, oiled paper, wet cloth, etc., all appearing less white and more transparent than the dry materials; the refractive index of the liquid is, in each of the above cases, nearer in value to that of the solid than is the refractive index of air. If the two refractive indices are

[1] Von Bezold: "Die Farbenlehre," 58.

[2] Tyndall: "Light and Electricity," 59 (1895).

closely matched the effect is, of course, much more noticeable. For example, the transparent "windows" used in some envelopes are made of paper which has been impregnated with material which has the same index of refraction as the paper fibers, thus eliminating the reflection and refraction which cause opacity.

If the powder is composed of a substance transparent, but colored in mass, on immersion in a liquid of the proper refractive index, reflection and refraction, the causes of the white appearance, are eliminated, but absorption, the cause of the color, is unaffected. In this case the powder is visible only by virtue of its absorbing power for certain constituents of white light, and appears nearly the hue of the material in mass. Common examples include mud, wet colored cloth, wet water-color paintings, etc., appearing much lighter when dry and becoming more deeply colored when wet. Highly colored crystalline substances serve best to demonstrate this effect. For example, chrome alum is deep purple, almost black, in mass. It may readily be powdered fine enough to produce a pale lavender powder. This powder, immersed in a liquid of refractive index about 1.48 [xylene ($n = 1.49+$) will serve] becomes as deep a purple as the original unpowdered crystals. Copper sulphate in fine powder is almost white. Immersed in liquids of refractive index about 1.53 (balsam, nitrobenzene, etc.), the blue of the coarse materials reappears. Many other highly colored substances give effects almost as striking, appearing almost white in fine powder and colored when immersed in liquid of refractive index near to their own.

It must, therefore, be recognized that the observed color of finely divided transparent material is in general lighter than the color which the material has in mass,[1] the difference being due to an admixture of white to the light which reaches the eye, as well as to the lessening of the amount of absorption, because of the shorter distances traveled within the fine particles. The net result is a less saturated tint of the same hue as that of the massive material.

[1] Bancroft: Jour. Phys. Chem., 23, 154 (1919).

White, then, is caused by the reflection and refraction of light at the surfaces of small optical inhomogeneities (particles, bubbles, fissures, etc.) which may or may not be composed of colored material. Such reflection and refraction cannot take place if the system is optically homogeneous, that is, if the particles, etc., are surrounded by a medium of the same refractive index as their own.

The existence of white due to any other cause than structure such as outlined above, is highly improbable, and from a logical basis, impossible. Some means of "scattering" the incident light without any marked absorption of any of its constituents is necessary, in every case, for an object to appear white. Certainly all the ordinary objects which are called white owe this whiteness to structure of the sort stated above. Milk, magnesia, paper, whitewash, porcelain, white paint, etc. are composed of material actually transparent, finely divided and acting on the incident light as has been explained in the preceding paragraphs.

No more familiar example can be cited than ordinary white paint, which is a suspension in linseed oil, etc. of fine transparent particles of basic lead carbonate, zinc sulphide barium sulphate and other solids, all of which are known to be colorless and transparent in mass. The degree of fineness of these particles, as the manufacturer knows, contributes largely to the "whiteness" or hiding power of the paint. The refractive index of the particles is also important, and the manufacturer endeavors to make use of a material of refractive index widely different from that of linseed oil, so that reflection and refraction of light by the particles of solid shall be as great as possible. Indeed, certain white powders (silica, barytes, etc.) cannot be employed effectively as paint pigments because their indices of refraction are too near that of linseed oil, and reflection and refraction are thus almost eliminated.[1]

Even the so-called "white pigments" found in nature may be shown to be of the same character, actually owing their

[1] Gardner: "Paint Researches," 43 (1917).

whiteness to structure. The white color of flowers is due to their cellular, optically inhomogeneous, structure. The tiny cells, filled with juices, serve to reflect and refract the light very completely. In some flowers these cells may be seen with the naked eye as in the narcissus the petals of which have a frothy white appearance. Crushing the flower removes the juice and destroys the minute structure, resulting in a transparent appearance. The white of birch bark must be ascribed to the same cause, for it may be rendered colorless and transparent by penetration with cresol, etc. In this case the bark is porous and the pores are filled with air, which is seen to escape as bubbles when the cresol replaces it in the pores. The white bark of the sycamore behaves similarly, though here the outer surface of the cellular layer is distinctly rough, and thus increases the diffuse reflection of the incident light, giving a chalky appearance, which is destroyed by penetration with cresol.

The white pigment found in the bellies of fish has been shown by Pouchet to be due to tiny plate-like or needle-like crystals of transparent material, this structure being recognized as the cause of the white. Cunningham and McMunn[1] confirm Pouchet's findings, and point out that the particles of transparent material in the white part of the fish's skin are crystals of guanin. Guanin may also occur in large crystals in fish in some cases, and is known to be colorless and transparent.

Certain butterflies (*Pieridae*) have been credited with white pigment, but Hopkins[2] has shown that this white pigment is really uric acid in finely divided form. Uric acid is colorless and transparent in mass.

White feathers have generally been recognized as having their color due to structure, rather than to pigment. Newbigin in "Colour in Nature," Beddard in "Animal Coloration," Poulton in "Colours of Animals" (Internat. Sci. Series), Von Bezold in "Theory of Color in Relation to Arts and Industry,"

[1] Phil. Trans., London, **186B**, 765 (1893).
[2] Phil. Trans., **186B**, 661 (1896).

Gadow[1] and others have subscribed to this view, but a definite statement as to the mechanism of the production of white by the feather structure seems to be lacking. For this reason a more detailed study of white, as found in feathers, is undertaken in this paper.

The white appearance of feathers, like all other whites, is due to structure, as pointed out above. Two types of white may be recognized; white which disappears if acted upon by liquid of the proper refractive index; and white which is unaffected by liquid of any refractive index whatsoever. Both are caused by the reflection and refraction of light at the surfaces of a multitude of minute optical inhomogeneities in the structure of the feather, the nature of these inhomogeneities being the point of difference between the two types.

The barbules of white feathers play the chief part in the production of a general effect of white as the naked eye observes the feather. The barbules of typical white feathers, such as those of the white Leghorn, turkey, pigeon, duck, peacock, etc., are seen under the microscope, to be colorless, transparent, more or less spatulate processes on the barbs of the feather. They possess no significant internal structure, and when mounted in balsam, cresol, etc., are transparent and almost invisible to the eye. Their surfaces are often somewhat roughened. These innumerable, transparent, colorless barbules present an enormous number of surfaces to the light which falls on the feather, and because of the reflection and refraction which takes place at these surfaces, a large proportion of the incident white light is sent to the eye from whatever position the feather is viewed. Thus the feather appears white, exactly as snow, cotton, paper, etc., appear white.

When, however, the feather is thoroughly wetted with balsam or cresol ($n = 1.54$) the reflection and refraction at these numerous minute surfaces is eliminated, for the liquid has approximately the same index of refractions as that of the barbules themselves. The index of refraction of the barbules or other material may be determined under the microscope

[1] *Proc. Zoöl. Soc., London,* **1882,** 409.

by use of the "Becke line" test or by using oblique illumination, methods for comparing refractive indices familiar to the petrographer or chemical microscopist.[1] With the reflection and refraction eliminated, the feather appears transparent and one may read through it with ease. The barbs are not rendered transparent by this surface wetting, and appear as white lines in the transparent plane of the feather, but since they do not occupy a large proportion of the space the effect as a whole is one of transparency. This is analogous to paper becoming transparent when oiled, and is very easily observable.

Of similar origin is the white observed in the barbs or shafts of white feathers. In this case the reflection and refraction which gives the effect of white takes place at the surfaces of pores in the walls of the cells of the barbules, or at the surfaces of the bubble-like, cellular, pithy material in the core of the quill, these surfaces being in contact with air. The structure of these pores, bubbles, etc., is readily observable under the microscope and they are seen to be actually transparent and colorless if a thin section of the part of the feather in question is examined with moderate magnification. As might be expected, if the air in these pores and interstices is replaced by a liquid of the proper index of refraction, the effect of white is destroyed, and this part of the feather appears transparent. The process of replacing the air by liquid is hindered by the fact that most feathers have the porous structures encased by a transparent, almost impermeable layer of keratin, which covers the barbs and shafts. Prolonged soaking in the liquid will bring about permeation of the porosities of the feather, but the effect may be obtained more rapidly by laying open the porous part by sectioning. Longitudinal, oblique, or transverse sections permit the liquid to permeate the feather rapidly, and the porosities may be filled in a few moments, while the air in them may be seen to escape, under the microscope. Cresol ($n = 1.54$) was found to produce the most perfect transparency. This can only

[1] Johannsen: "Manual Petrographic Methods," 256, 271 (1918).

be due to the elimination of reflection and refraction by rendering the whole porous part of the feather optically almost homogeneous, by replacing the air in the porosities by liquid of the same index of refraction as the material of the feather. Other liquids of about the same index of refraction give like effects, but if the index of refraction of the liquid differs widely from 1.54 the white appearance is not completely destroyed, and only partial transparency is obtained. The average index of refraction of feather material is about 1.54, as determined by immersion methods (Becke test, oblique light, etc.).

The "clearing" of tissue as a step in its preparation for study, is a process familiar to the biologist, which is essentially similar to the treatment of the feather just mentioned. If the cells are filled with air, their details can only be studied if they are rendered more or less perfectly transparent, while if the cells are filled with liquid, it must usually be replaced by another liquid of the refractive index nearer that of the cell walls, in order that the finer details of structure shall not be obscured by too great reflection and refraction at their surfaces. The liquid mounting commonly used, balsam, has a refractive index (1.54) close enough to that of most organic tissue, to accomplish this very satisfactorily.

The second type of white found in feathers differs from those just mentioned, in that liquids, of any refractive index whatsoever, have no effect on it. This may be found in certain white quills (white turkey, goose, hen, etc.) and usually occurs in the outer sheath of keratin, which appears a translucent white to the naked eye. Microscopic examination shows, however, that this keratinous sheath layer is really transparent, but is fibrous and composed of numerous elongated cells, closely packed together to form the horny layer. The refraction and reflection which causes the whitish appearance is due, in this case, to the fact that, although no air-filled cavities exist, some parts of the cells are of different refractive index from other parts, this difference being sufficient to bring about enough refraction and reflection to give a white appearance to this structure. Since there are no empty cavities,

this material cannot be rendered optically homogeneous by penetration of liquid. However, since the differences in index of refraction between the various parts of the individual cells which compose this layer are relatively small, reflection and refraction are not very marked and the white produced is distinctly transparent, and plays a very small part in giving the feather its white appearance.

Such causes of white in feathers will of course exert a marked influence on the appearance of a pigmented feather if this structure is present. There seems to be little difference in structure between white and pigmented feathers, the porous pith of the quills, the numerous reflecting surfaces of the barbules, and the fibrous cells in the sheath layer being present in both white and pigmented feathers.

However, very heavy pigmentation is necessary to give a strong color to the feather, for all these structures tend to lighten the color. Pigmented feathers appear darker and more strongly colored when wetted or penetrated by a liquid of the proper index of refraction, because of the elimination of the reflection and refraction which ordinarily lessen their absorption and increase their "scattering" of light. This is directly analogous to the darkening to orange of a pale yellow powder of potassium bichromate when wetted with a liquid of refractive index near 1.7 (the index of refraction of potassium dichromate).

We may say that the apparent color of the pigment is lightened if the feather possesses the structure which would produce white in an un-pigmented feather and since all feathers possess this structure to a greater or less extent, their color is lighter than the true color of the pigmented keratin, unmodified by structure. If the feather is so heavily pigmented as to be dark brown or black, almost opaque, the effect of the structure on the lightness of the color is negligible.

The white or albino varieties of birds which are normally colored are white simply because of the absence of their pigment. The structure is present in both the colored and white varieties, the absence of pigment allows it to produce white instead of simply lightening the color of the pigment somewhat.

Whitman[1] states that albinism is a deficiency of pigment [which may develop in later life] rather than any special development of white.

To summarize—white is due in all cases to reflection and refraction of the incident light by surfaces of optical inhomogeneities in the structure of the material. Transparency is observed when the material is optically homogeneous.

White feathers conform to the above, and may be rendered transparent by replacing the air in contact with their minute surfaces by a liquid of the proper index of refraction, which renders them optically homogeneous. Some of the less opaque whites may be due to non-porous, optically inhomogeneous structure, and this cannot be rendered more transparent by treatment with liquid.

## Structural Blues

The colors due to turbid media are represented in feathers by the non-iridescent blues. Krukenberg[2] states that he has been unable to extract any blue dye from blue feathers, and this is the experience of others who have attempted to do so. Haecker and Meyer's[3] explanation of the blue color of feathers is that they are so-called Tyndall blues of turbid media. Their proof of this is consistent and adequate, and is further substantiated by a more detailed comparison of the properties of blue feathers with those of media which show the Tyndall blue, as given below.

It has long been recognized that the blue of the sky, of smoke, of blue eyes, of skim milk, of fine precipitates in liquids, etc., is a structural or optical color, dependent on the size and relative refractive index of very fine particles rather than on any actual coloration that they possess.[4] Tyndall[5] first ex-

[1] Carnegie Inst. Pub. No. 257, 2, (1919).
[2] Vergleichend-physiol. Stud., 1, V, 98 (1881); 2, V, 154 (1882).
[3] Zoöl. Jahrbuch. Abt. Syst. Geol. Biol. Thiere, 15, 267 (1902).
[4] Bancroft: "Applied Colloid Chemistry," 200 (1921).
[5] Phil. Mag., [4] 37, 385 (1869).

plained this color and it is often spoken of as the Tyndall blue.[1]

If the small particles of a system of the sort described on the preceding pages are of dimensions of the order of the wave-length of blue light, only the shorter of the waves which make up a beam of white light are scattered. The longer wave-lengths are not affected and pass through the space occupied by the small particles, unchanged. Thus the red and yellow of the spectrum are transmitted by such a system and the blue and violet, the shorter wave-lengths, are scattered. Such a system appears turbid reddish orange by transmitted light, and turbid blue by scattered or reflected light. The blue of a turbid medium shows best against a dark background, which serves to prevent any transmitted light from reaching the eye. Indeed, it may appear whitish or almost colorless against a light background. Thus smoke often appears reddish against the light, blue against shadow, and pale gray against a neutral background.

The intensity of the blue of the scattered light depends, not only on the size of the particles, but also on their concentration; the scattering of blue light is more complete the more particles of the proper size are present. Relatively sparsely distributed particles, even though of proper magnitude, give a transparent blue, while if they are present in dense numbers, the blue appears of the same hue, but of much greater depth and intensity. In like manner, a thin layer of the turbid medium gives a transparent blue of little depth, while a thick layer of the same medium gives a much stronger color. Corresponding effects on the intensity of color of the transmitted light are produced by concentration and by thickness of the layer.

If the particles which scatter the light are of magnitude sufficient to scatter the longer wave-lengths, the scattered light is no longer a clear, deep blue, but more of a whitish blue, and if all wave-lengths are scattered, by relatively large particles, the scattered light is white.

[1] Wood: "Physical Optics," 624 (1911).

Tyndall showed the effect which the size of smoke particles had on the color of the smoke, larger particles giving a whiter smoke.

Rendering the medium optically homogeneous destroys the blue color, for the scattering of light by fine particles cannot take place if the particles are of the same refractive index as the medium which surrounds them. As a matter of fact even approximate agreement between the refractive indices of the particles and the surrounding medium is sufficient to cause a very marked decrease in the intensity of the scattered light.

The behavior of a collodion jelly serves to illustrate this fairly well. A limpid solution of colloidon, if allowed to evaporate slowly forms a soft turbid bluish jelly, which possesses the distinctive properties of media which give the Tyndall blue.

That jellies are two-phase systems, and possess a certain structure, is well established.[1] The exact nature of this structure is not of importance here; it is recognized, however, as of a porous or spongy character. Apparently a collodion jelly is no exception, for it is possible by gentle pressure, to squeeze out liquid from the jelly in considerable amount. This liquid, a mixture of alcohol and ether, apparently exists *as such* in the pores of the jelly, like water in a sponge, and is rather easily removed or replaced by a simple mechanical means. This liquid will diffuse out from the jelly when it is immersed in another liquid with which alcohol-ether is miscible. Such liquids include kerosene, water, cresol, cedar oil, phenyl chloride and other organic liquids. The diffusion of the alcohol-ether out from the jelly is plainly visible when it is placed in such a liquid—cresol, for instance—since the alcohol-ether is of different refractive index from the cresol, and may be seen to form a layer surrounding the piece of jelly. If the cresol is stirred, the alcohol-ether mixes with it, giving an appearance like water mixed with syrup.

If the cresol is stirred, or replaced by cresol unmixed with alcohol-ether, in the course of a few hours no further diffusion from the jelly is seen, while its appearance is strikingly changed.

[1] Bancroft: "Applied Colloid Chemistry," 240 (1921).

Instead of the original whitish blue, the jelly is perfectly colorless and transparent, and, moreover, its outlines are almost perfectly invisible in the cresol. On removing it from the cresol, the jelly appears like a clear colorless piece of glass though it has not lost its gelatinous character. This is a similar process to the "clearing" of collodion (celloidin) imbedded sections by means of creosote or cedar oil, a procedure familiar to all biologists.

The most obvious explanation for all this is that the alcohol-ether, which originally filled the pores, has been replaced by the cresol, just as a water-soaked sponge might have the water replaced by oil. The change in the appearance of the jelly is a result of this replacement, for the original turbid blue is undoubtedly due to the scattering of light by the infinitesimal pores of the jelly, which are filled with alcohol-ether. If the alcohol-ether is replaced by cresol, the scattering of light is eliminated, though the jelly has its original porous and gelatinous character. The pores, filled with cresol, do not scatter the light; therefore no blue color is observable. The system is optically homogeneous, and transparent.

The effect depends on the refractive index of the liquid which replaces the alcohol-ether in the pores of the jelly, as shown by the following table.

TABLE I

| Liquid | Refractive Index ($N$) | Turbidity (color) | Outline |
|---|---|---|---|
| Monobromo naphthalene | 1.66 | marked | distinct |
| Carbon bisulphide | 1.625 | marked | distinct |
| Iodobenzene | 1.61 | moderate | distinct |
| Bromoform | 1.58 | very slight | faint |
| Cresol | 1.54 | none | invisible |
| Chlorobenzene | 1.525 | none | invisible |
| Cedar Oil | 1.51 | none | almost invisible |
| Xylene | 1.494 | very slight | very faint |
| Turpentine | 1.474 | slight | distinct |
| Kerosene | 1.443 | moderate | distinct |
| Alcohol | 1.37 | moderate | distinct |
| Water | 1.33 | very marked | distinct |

Apparently the nature of the penetrating liquid plays no part, provided that the alcohol-ether mixes with it, and that it does not dissolve collodion. The rate of penetration, however, varies greatly with the liquid, but may be hastened by stirring, etc. The effects may be produced by passing the same jelly through several liquids.

It will be noted from the table that liquids of about $n = 1.54$, cause the most complete disappearance of color, turbidity, and outline, while liquids of $n$ markedly greater or less than this value give color and turbidity.

The penetrated, transparent, jelly may be rendered turbid and of the original color, by immersion in and penetration by a liquid of refractive index markedly different from 1.54, and indeed, if the liquids used are mutually miscible, the same specimens of jelly may be carried through several different refractive indices, and after penetration has taken place, the appearance of the jelly is definite for a given refractive index of the liquid, irrespective of its previous color, etc.

The natural interpretation is that the pores of the jelly, filled with alcohol-ether, scatter blue light because the refractive index of the alcohol-ether in the pores differs markedly from that of the surrounding spongy medium, whatever this medium (cellulose nitrate?) may be. When the pores are filled with a liquid of $n = 1.54$ no scattering takes place because they are now of the same refractive index as that of the surrounding spongy medium. The disappearance of the outline of the jelly points to this also. The intensity of the scattered light depends on the difference between the refractive index of the spongy medium of the jelly, and that of the liquid which fills its pores.

The scattered light from a turbid medium is polarized, provided the particles are small enough to give a blue color to this scattered light. Lord Rayleigh's explanation of this is given by Wood.[1]

This polarization may be easily observed by viewing a beam of light in a turbid medium through a nicol prism, at

[1] "Physical Optics," 625 (1911).

right angles to the path of the beam. The vibrations of the scattered light are in the plane normal to the direction of the beam in the turbid medium, and a nicol prism placed to intercept vibrations in this plane renders the beam invisible through it. If the nicol is rotated the beam is visible through it only when the nicol is in position to transmit vibrations normal to the direction of the beam. The light scattered by the turbid medium is almost perfectly cut out when the nicol is set to transmit only vibrations in the plane parallel to the direction of the beam. This rather striking effect is easily demonstrated with blue smoke, collodion jelly, milk and water, partially devitrified Jena glass—in fact, any medium which gives the Tyndall blue. If the blue is whitish, the polarization of the scattered light is not so complete, and not all of it can be cut out by the nicol prism. Whitish blue appears to be caused by larger particles than those which give darker blue.

A more sensitive means of detecting this polarization is by viewing the scattered light through a nicol prism, as above, with a "1st order red" gypsum plate between the nicol and the turbid medium. The "1st order red" gypsum plate is used by petrographers to detect slight polarization in the study of crystals with the petrographic microscope.[1] It substitutes a color change for the light and dark change which occurs ordinarily as a nicol is rotated in a beam of polarized light. The beam of light in the turbid medium, viewed as above, with the "1st order red" gypsum plate in front of the nicol prism, appears alternately greenish blue and reddish purple, as the nicol is rotated, instead of being alternately visible and invisible, as it is when only the nicol is used. This color change is more easily observed than the change in intensity, particularly if the polarization is only partially complete, and serves as a very sensitive means of detecting even slight polarization of the scattered light. Another means of detecting the polarizing properties of a turbid medium may be demonstrated by passing a beam of plane polarized light through a turbid medium.

[1] Johannsen: "Manual Petrographic Methods," 386, 393 (1918).

The polarizing apparatus, usually a nicol prism, should be capable of rotation, so that the plane of the polarized light may be changed. It is observed that, with such an arrangement, if the beam in the turbid medium is horizontal and is viewed from above, the scattered light is only visible when the plane of vibration of the incident beam is horizontal. If the polarizing nicol is turned through 90°, so that the vibrations of the incident beam are in the vertical plane, no scattered light is visible from above. In other words, the scattered light is visible only when the line of vision is normal to the plane of vibration of the incident beam of polarized light. This results in the novel effect of a beam of light through the turbid medium, visible from above, but invisible from the side, or *vice versa*. The "1st order red" gypsum plate may be applied to this arrangement to render the detection of slight polarization more easy. It is placed between the polarizing nicol prism and the turbid medium. Then, on revolving the nicol, the beam in the turbid medium, viewed from above, appears alternately reddish purple and greenish blue. With the nicol in the proper position it is thus possible to have the beam appear reddish purple from above, and greenish blue from the side. The optics of the above experiments is relatively simple, and need not be discussed here. As tests for the polarization of the light scattered by a turbid medium, they are easily carried out, and are of considerable sensitiveness.

Lord Rayleigh[1] has established another relationship, not so easily observable, regarding the intensity of the scattered light. He has calculated and observed the scattered light to vary inversely as the fourth power of the wave-length.

$$\text{Intensity} = K/\lambda^4$$

Tyndall blue, important as it is in the field of color, is worthy of some detailed examination by the student of structural color, particularly since "seeing is believing" and a specimen serves to show, far more strikingly than any description, the distinctive properties of this type of color. Blues

[1] Phil. Mag., [4] **41**, 107, 274 (1871).

of varying degrees of perfection have been obtained by several different methods, and study of them has shown their common nature. Dilute milk and water, dilute soap solution, sulphur precipitated from dilute sodium thiosulphate solution by sulphuric acid, or from an aqueous solution of hydrogen sulphide by exposure to the air, resin, mastic, balsam, etc., precipitated from dilute alcoholic solution by pouring it into an excess of water—all give Tyndall blues of more or less perfection. The best results are obtained from the last method, though a trial or two may be necessary to produce a good blue. These methods are all open to the objection that the minute particles formed are not of particular uniformity and tend also to agglomerate on standing, both resulting in whitish blues. Collodion jelly evaporates if exposed to the air, and gives only whitish blues at best. Tyndall's[1] experiments were performed on smokes, from cigars, incense, chemical interaction of gases, etc. These give good blues, but are not easily controlled, and the particles tend to agglomerate, forming whitish blues or white.

An excellent specimen for the study of Tyndall blue may be prepared by heating a piece of Jena glass tube or rod in a muffle or combustion furnace, or other device for insuring fairly uniform heating, at a temperature just below the softening point of the glass. Two hours heating is generally sufficient, but the time required is shorter at higher temperatures. It is best to allow the glass to cool and to examine it at intervals against a dark background. If the blue has not yet developed the heating may be resumed. A strong, clear, blue results, unless heating has been too prolonged, when an opal-white is obtained.

The blue color of such a specimen appears to be due to partial devitrification of the glass, with the formation of tiny crystal nuclei, which scatter the light with the production of blue. These particles may be seen under the microscope with 4 mm or higher power objectives if a horizontal beam of light is projected through a piece of the glass, on which the microscope is focussed. Other illumination should be absent.

[1] Phil. Mag., [4] 37, 385 (1869).

With careful focussing and some adjustment of the illuminating beam, the blue color seen in the field may be resolved into a dense mass of tiny points of blue light. This crude ultramicroscope arrangement with a little adjustment, serves fairly well to detect the minute particles present in other Tyndall blue media. The white obtained by long heating of the Jena glass is caused by growth of the minute crystal nuclei, their increased size permitting them to scatter all wave-lengths of light instead of the shorter wave-lengths only. As a matter of fact, the light transmitted by such a piece of white glass is orange-red, however, probably because of the presence of particles of different sizes, some of which are large enough to scatter all wave-lengths of light, while others scatter only the blue and transmit only the red end of the spectrum. Strictly speaking, therefore, the white really contains considerable blue, which is not readily perceived in the presence of the white, while this white Jena glass, instead of being more or less opaque on account of the scattering of white light, transmits reddish orange because the scattering is not complete for all wave-lengths. The light which is transmitted owes its color to the smaller particles present, the larger particles serving only to produce opacity and not color. The color of the transmitted light is, of course, rendered more visible because white light, an admixture of which would obscure it, is eliminated by the scattering effect of the larger of the particles. This specimen of partially devitrified Jena glass possesses the characteristic properties of a Tyndall blue medium, is stable at all ordinary temperatures, may be easily prepared, and gives blues ranging from deep indigo to pale sky blue or white, depending on the extent to which devitrification has been carried. The blues of such specimens rival the richest of those found in feathers. The color may be brought out most strikingly by painting part of the inside of the glass (if it is in the form of a tube) with black paint, though any dark background serves to show the blue color of the scattered light. The color of the transmitted light, yellow, is of course seen by looking through the glass at white light. When these two colors are mingled,

as by internal reflections in the glass tubing, greenish blues result.

The examination of some specimen of a Tyndall blue medium is of considerable value as an aid to the understanding of this work, which can be most convincing only when the color in question has been seen by the reader. Certainly any study of the blue color of feathers is inadequate unless this blue, the nature of which has been established, is available for purposes of comparison.

The properties of a medium which gives a Tyndall blue may be summarized as follows:

1. Particles, or other optical inhomogeneities, of a refractive index different from that of the medium which surrounds them. No color if refractive indices are not different.

2. Dimensions of these particles of the order of the wavelength of blue light [something less than 0.6$\mu$].

3. Scattered light blue, transmitted light reddish. Blue seen only when transmitted light is cut off.

4. Depth or shade of blue dependent on size of particles. Large particles give whitish blue or white.

5. Scattered light polarized, vibrations in plane normal to the direction of the incident beam. Completeness of polarization dependent on size of particles.

6. Intensity of scattered light inversely proportional to fourth power of wave-length.

Any substance which possesses the Tyndall blue should show these properties, which were taken as the criteria for the analysis of the nature of the non-iridescent blues of feathers.

## Blue Feathers

No instance of non-iridescent blue in feathers, other than in the barbs alone, has been reported. A typical blue feather, that of the common blue jay, shows the following structure in the barbs.

1. A transparent, colorless, horny, outer layer, or sheath, 10–15 microns in thickness, which apparently serves as a protective coating for the barbs.

2. Beneath this a layer of cells, polygonal as seen from the surface, about 15 microns in diameter and the same in depth. The boundaries of these cells are ordinarily invisible, and by reflected light they give the appearance of a thick layer of blue enamel. (Described by Fatio who called it "émail.")

3. Beneath the layer of cells, and occupying the central portion of the barb, lie closely-packed, hollow, medullary cells, which contain a dark, granular pigment (melanin) mainly on the walls of the cells.

Gadow[1] summarizes his description of the barbs of a typical blue feather as follows:

1. A transparent, apparently homogeneous sheath of ceratinine.

2. One layer of prismatic (polygonal) cells.

3. A brownish pigment.

He recognizes the prismatic or polygonal cells as the seat of the blue color, but his reasoning as to the cause of the color production is incorrect, as will be pointed out.

Sections, longitudinal, transverse, and oblique, show these relationships more clearly than does the barb as a whole. The blue color is plainly localized in the layer of cells immediately underlying the outer sheath of the barbs. Removal, by longitudinal sectioning, of the outer sheath layer, or of the pigmented medullary cells does not affect the appearance of the blue cells, as they are examined with reflected light. It is apparent that the blue of the feather originates in this layer of polygonal cells, and detailed study of them is necessary for an explanation of its nature.

The cells are seen to be distinct and separate, like tiles in a floor. Their color is turbid blue by reflected light and turbid reddish brown by transmitted light. A most striking phenomenon is that the cells, when laid bare by removal of the outer sheath, or of the medullary portion of the barb are rendered colorless and transparent by immersion in xylene. The change takes place cell by cell, and as it does so the details

[1] Proc. Zoöl. Soc., London, **1882**, 409.

of structure become visible. The cell walls are seen to be 3–4 microns thick, apparently rough or granular on their inner surfaces, with a central cavity, roughly spherical in shape, 4–5 microns in diameter. The color is apparently only in the cell walls.

As the xylene evaporates the original color and turbidity of the cells are restored. A similar effect is shown with other liquids, and it appears to be related to the refractive index of the liquid which permeates the cell, rather than to its chemical composition. Liquids of refractive index less than about 1.49 (xylene) give less striking changes. The color of the cell walls is not completely destroyed. and they are not rendered perfectly transparent unless the refractive index of the liquid used is about 1.54 ± .04, though the line cannot be sharply drawn. Liquids of refractive index greater than 1.58 fail to destroy the color or to render the cell walls transparent. The change produced increases with the *difference* of the refractive index of the liquid from 1.54. The refractive index of the cell walls as determined is actually very close to 1.54. The nature of the liquid which is used plays no part in the change, except as it may govern the rapidity of penetration, which apparently depends largely on the thickness of the keratin sheath layer.

Ortho-cresol is the most satisfactory of the liquids used, both from the standpoint of its refractive index, which agrees almost perfectly with that of the cell walls, and from the rapidity with which it penetrates the feather. Even the entire feather of the jay, with the blue barbs protected by a thick sheath of keratin, is permeated in about four days. The blue color of the cells is destroyed, they are rendered almost perfectly transparent and invisible, and the black pigment in the medullary cells is plainly visible. The feather, permeated by ortho-cresol, appears black. As the ortho-cresol evaporates, or is washed out by alcohol, the original coloration of the feather is perfectly restored. This is in entire accordance with Haecker and Meyer's[1] observations. "There can be no question but

[1] Zoöl. Jahrb. Abt. Syst. Geol. Biol. Thiere, 15, 267 (1902).

that the air in the box-cells and especially in the pores in the walls is the cause for the phenomenon that the cells in question are reddish yellow by transmitted light and sky-blue by reflected light.

"The objection might be urged that all this was true for air-dried feathers of old bird skins; but that the important factors might be different for feathers taken freshly from the living birds. While this objection seems an unreasonable one in itself, it was tested by making the same experiment on a blue feather plucked freshly from a living *Ara* (*Sittace macao* L.). The displacement and disappearance took place in the same way and was accompanied by the same color changes as with the *Cotinga* feathers.

"In connection with this fundamental experiment it will be well to discuss the experiments with other liquids. Liquids with about the same refractive indices as Canada balsam, such as xylene, benzene, and cedar oil (immersion oil) give the same phenomena as Canada balsam. Since these liquids are much less viscous, the changes take place more rapidly and sometimes almost instantaneously. The final result was great transparency and complete lack of color in the impregnated parts of the feather. A different phenomenon occurs both with liquids having a smaller index of refraction and with those having a larger one. On treating with alcohol, which wets the walls very readily, the border cells in the places where the rind has been damaged by scraping, become instantaneously a transparent golden yellow by transmitted light and a bright blue by reflected light. The air bubbles remain for perhaps ten minutes in the hollow spaces inside the box cells. When they disappear the places in question become pale yellow by transmitted light and pale blue by reflected light if one uses a low-power objective. The color is more marked with water than with alcohol. When water flows into the border cells at the damaged places, the cells appear chiefly reddish yellow by transmitted light and marine-blue or sea-green by reflected light. When a Seibert 2 mm objective is used, the cell walls appear a full yellow by transmitted light

and distinctly granular, while the lumina of the cells are orange. The pores thus remain permanently visible when filled with water.

"If one changes to substances which have higher refractive indices than Canada balsam, xylene, etc., and takes, for instance, mixtures of benzene and carbon disulphide, one finds at first no more color effect than with Canada balsam. If the amount of carbon bisulphide is increased to a ratio of $CS_2 : C_6H_6 = 3:1$, traces of color appear; when the ratio is 7:1 or with pure carbon bisulphide, a marked color effect is produced. With low magnification (Seibert objective 16 mm Oc 8) the scraped portions are distinctly yellow by transmitted light and distinctly blue by reflected light.

"Since experiments, made one after another with the same feather, always gave the same results, it is clear that the color disappears when the box-cells and their pores are filled with a liquid having the same index of refraction as the cell wall. The color appears as soon as the refractive index of the imbibed substance is markedly different from that of the cell wall, regardless of whether it is smaller (alcohol or water) or larger (carbon bisulphide)."

The data are given in Table II, the first color being for reflected and the second for transmitted light.

"This table shows that the feathers are colorless when the box-cells are filled with a liquid having an index of refraction for sodium light of about 1.52 and that color appears when the imbibed liquid has an index of refraction markedly greater or smaller than 1.52. We, therefore, conclude that the index of refraction of the cell substance for sodium light is 1.52."

Study of the actual process of permeation of the cell walls is rather difficult, on account of the rapidity with which it proceeds when the cells are exposed, as in a section, to the action of the liquid. Tiny air bubbles are often noted at the outer edges of the cells, as the liquid penetrates, and a small bubble is often entrapped in the central cavity. As the liquid evaporates air suddenly seems to be sucked into the cells through the walls, the central cavity fills with air, and the cell walls are restored to the original blue.

TABLE II

| | Refractive index for Na light | |
|---|---|---|
| Pure $CS_2$ | 1.627 | Distinct color, pale blue and pale yellow |
| $CS:C_6H_6$ 7:1 by volume | >1.558 | Distinct color, pale blue and pale yellow |
| $CS_2:C_6H_6$ 1:1 by volume | >1.558 | Traces of color |
| $CS_2:C_6H_6$ 1:1 by volume | 1.558 | No color |
| Canada balsam, Av. | 1.54 | No color |
| Cedar oil | 1.515 | No color |
| Xylene | 1.502 | No color |
| Benzene | 1.501 | No color |
| Alcohol | 1.362 | Distinct color, light blue and golden yellow, changing to pale blue |
| Water | 1.333 | Strong color, sea-green and reddish yellow. Great transparency but pores visible. |
| Air | 1.000 | Strong color, cloudy blue and cloudy reddish yellow. Not transparent. |

All this points to some fine porosity of the cell walls, and careful examination shows innumerable tiny pores, filling the cell walls, and giving them a turbid, spongy appearance. A 4 mm or higher power objective is necessary to reveal this porous character. Their diameter is estimated at less than 0.3 microns.[1]

"According to observations made with the highest power, Seibert and Zeiss objectives, the diameter of the pores in a *Malurus* feather is about 0.3$\mu$, while that in a *Cotinga* is certainly smaller. The observed diameter of the canals is thus smaller than the wave-lengths of red light (0.8$\mu$) and lies close to the limit of what we can detect optically. It is possible that the canals have still finer branches which are too small to be detected under the microscope. The walls of the cell substance are thus pierced by air-filled tubes having a diameter

[1] Haecker and Meyer: Loc. cit.

less than that of the wave-length of light. In other words, we have a transparent medium in which are transparent substances having dimensions small in comparison with that of wave-length of light, and having an optical density different from that of the medium. The refractive index of the medium is about 1.52 and of the transparent embedded substance [air] about 1.0003."

A section of the cells in ortho-cresol appears with the dark field illuminator to be practically invisible. A few scattered points of blue light appear, probably pores in which the air has not been displaced by cresol. If the cresol is absorbed at one side of the cover glass by blotting paper, while alcohol is applied at the opposite side, the cresol in the pores of the cell walls is replaced by alcohol, and as a result the pores show up plainly, the whole of the cell walls appearing filled with innumerable tiny points of blue light, hardly distinguishable as separate points. Water may be substituted for alcohol in the same manner, when the intensity of the points of light is further increased, while, if the liquid is allowed to evaporate, the blue scattered by the air-filled pores is so bright as to give the effect of an almost solid color.

The dry preparation, seen by transmitted light, is yellowish orange, this color disappearing as alcohol, or better, cresol, replaces the air in the pores.

This yellow or orange color, seen by transmitted light in the blue cells of blue feathers, has been confused with pigment color. Gadow says[1] "the color of the cones [polygonal cells] is pale yellowish, or, if this is only the reflection of the underlying pigment, they are colorless." This is decidedly not the case, for the color exists unchanged, even when the dark pigment backing has been removed by longitudinal or oblique sectioning, and, moreover, disappears completely when these polygonal cells are penetrated by a liquid of suitable refractive index. These cells, thus penetrated, show no tinge of color, but are transparent and colorless, conclusively proving the absence of any appreciable amount of pigment, and, more

[1] Proc. Zoöl. Soc., London, 1882, 409.

particularly, the marked effect which permeation by liquid has on their apparent color. When examined on a dark field, the cells are seen by virtue of the light which they scatter and reflect. This scattered light is blue. The dark pigment layer which lies beneath the blue cells serves as a dark background to prevent transmitted light from interfering with the production of the blue. If this dark pigment layer is removed by longitudinal sectioning, the blue color is seen only when the transmitted light is cut off by some sort of dark backing.

A dark background may be supplied by painting the back and barbules of the white tips of the blue feather with India ink or by mounting the feather on a black slide, or even by examining on a dark field by reflected light. If surface reflections are eliminated by immersion in a liquid of 1.54 refractive index, the bluish color is plainly visible. Such crude methods of supplying a dark backing are of course far from being as perfect as that in the blue feather, since the empty medullary cells are not rendered dark by an external treatment. A more perfect black backing may be supplied by painting the back of the feather with India ink. The white portions of the jay feathers, thus treated, appear distinctly bluish. By transmitted light these barbs are reddish yellow. Permeated by the appropriate liquid, they are colorless. Unless the background of India ink is supplied, the turbid structure of the white portion of the feather will not appear blue, for the empty, unpigmented, medullary cells scatter white light like bubbles of air, and serve as a light background, thus obscuring the blue. If the medullary portion of the barb is removed by sectioning there is no apparent structural difference between the porous cells in the blue and white parts of the feather.

It is highly probable, however, that the pores in the cell walls of the barbs of the white portions of the feather are larger than those in the blue portions. This would account for the less perfect blue obtained, even when the black backing is supplied, as well as for the less perfect phenomena observed with polarized light, etc. Accurate measurements of these

pores are of course impossible by any direct means, since their dimensions are close to the limit of resolution of the ordinary microscope, and the diffraction patterns visible with a dark-field illuminator, or similar device, are not true measures of the actual size of the particles.

Removal of the pigment by prolonged bleaching with hydrogen peroxide (3%) destroys the blue, though if the pigment is only partially bleached the blue is unchanged. Examined on a dark field, the barbs of a feather which has been almost perfectly bleached appear a pale whitish blue, on account of the loss of the dark backing, particularly since the medullary cells which were originally black now seem to scatter light and act as a light background, thus lessening the blue by mixing with it transmitted light. Swelling is also a factor, as will be shown. Blue feathers, painted on the under surface with India ink, are little affected by bleaching, because of the stability of India ink toward bleaching agents. Thus the dark backing is not destroyed and the blue persists until the bleaching has been carried so far as to swell or destroy the structure of the feather.

Surface reflections from the outer layer of keratin of blue barbules may be eliminated by immersion in a liquid of about 1.54. The refractive index of the liquid may be adjusted to be very nearly equal to the refractive index of this keratin layer, since it is possible by simple tests (Becke oblique light, etc.) to determine whether the refractive index of the liquid is greater or less than that of the keratin layer, and a few trials serve to match the refractive indices of the two media to within .005. [A mixture of oil of cloves (1.538) and oil of anise (1.557) serves very well.] Such a preparation consists essentially of the polygonal cellular layer, surrounded by an optically homogeneous medium, for the keratin and the immersion liquid are optically almost identical. Light, illuminating the preparation therefore, suffers no change until it strikes the polygonal cellular layer.

A portion of a blue barb, mounted as above, and illuminated by a horizontal beam of light, appears blue when ex-

amined by the microscope, as it lies on the stage. This blue is fully as bright as the color seen in ordinary light, and must be due to some sort of scattering of the light, since surface reflection is avoided by the immersion.

Examination through a nicol prism mounted as an analyzer on the microscope, shows that the scattered blue light is polarized, though not perfectly, and that the plane of the vibration of this scattered light is normal to the direction of the incident beam. Rotating the analyzing nicol gives partial extinction when the plane of vibration of the nicol is parallel to the direction of the illuminating beam.

A more sensitive means of detection of the polarization employs the "1st order red" plate, placed below the nicol. Instead of the darkening or extinction as the nicol is rotated, a color change takes place and the scattered light changes from greenish blue to pinkish blue as the nicol is rotated. This is much more easily observed, and constitutes a more delicate method of detecting polarization of the scattered light. Polarization of the scattered light is far from complete though it is unmistakable.

As an alternative method, the barbs mounted as above may be illuminated by a horizontal beam of polarized light, and the change in intensity of the scattered light noted as the plane of vibration of the illuminating beam is changed. In this case the intensity is distinctly less when the vibrations of the polarized beam are in the vertical plane. Here, again, the "1st order red" plate may be inserted between the nicol prism and the preparation when, instead of a variation in the intensity of the scattered light, the barbs appear alternately pinkish blue and greenish blue as the plane of vibration of the illuminating beam of polarized light is changed.

The incompleteness of the polarization of the scattered light, as observed, must be due to the presence of some relatively large pores which scatter the light without polarizing it. Their presence would of course dilute all the effects which might otherwise be obtained if only very small pores were present since they would serve only to mingle white, unpolarized

light with the blue scattered and polarized by the finer pores. This is undoubtedly one reason why the white parts of the blue jay feathers do not give nearly as marked effects with polarized light as do the blue parts, even though the structure is essentially the same.

"It[1] has been shown by Lord Rayleigh that if white light penetrates such a combination of two transparent substances differing in optical density, a diffuse reflection of light takes place at the embedded bodies, the blue light being scattered the most. Since the intensity of the reflected light of any color varies inversely as the fourth power of its wave-lengths ($I = Const/\lambda^4$), the scattering of the short-waved, blue rays will be relatively large while the red and yellow rays will predominate in the transmitted light.[2] In our case the development of the blue is favored by the fact that the red and yellow rays which pass through the cells are absorbed by the black layer of pigment and therefore cannot be seen by the observer. The best way to determine whether this hypothesis applies is to compare the blue light reflected from the feathers quantitatively with the light reflected from a white surface. If the blue feather behaves like Rayleigh's medium there will be a relative increase in the blue rays [which can be calculated] while in the reflection from a white substance, the ratio of the intensities of the single colors will remain the same as that in the incident light.

"The measurements were made by projecting the light from the blue feathers of a stuffed *Malurus* skin on one-half of the slit of a new model König spectrophotometer while the light from a piece of white paper was projected on the other half of the slit. Both bird and paper were illuminated by an electric arc light, the rays from which had been made parallel by a suitable arrangement of lenses. In a second series of observations the bird-skin was replaced by a piece of white paper

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[1] Haecker and Meyer: Zoöl. Jahrb. Abt. Syst. Geol. Biol. Thiere, 15, 267 (1902).

[2] Lord Rayleigh considers the blue color of the sky as due to light scattered by particles suspended in the air.

and the reflection of the blue feather compared with that of the white paper. For the sake of completeness a spectroscopic examination was made of the light reflected from a shiny, blue paper and from a pigmented paper, the blue color of which was as much like that of the feather as possible. The data are given in Table III. Column 1 gives the wave-

TABLE III

| Wave-length | Malurus | $1/\lambda^4$ | $\frac{1}{I}\lambda^4 = 1/C$ | Shiny, blue paper | Blue pigmented paper |
|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 |
| | % | | | % | % |
| 0.656 | 20.6 | 5.40 | 26.2 | 28.2 | 21.1 |
| 0.630 | 21.7 | 6.35 | 29.3 | 19.1 | 16.5 |
| 0.604 | 23.5 | 7.52 | 32.0 | 16.3 | 16.6 |
| 0.581 | 26.2 | 8.77 | 33.0 | 16.4 | 17.1 |
| 0.566 | 27.4 | 9.74 | 35.5 | 17.1 | 18.5 |
| 0.548 | 28.8 | 1.09 | 38.5 | 21.6 | 23.8 |
| 0.531 | 34.2 | 12.58 | 36.8 | 26.6 | 27.7 |
| 0.516 | 39.3 | 14.11 | 35.9 | 31.8 | 32.2 |
| 0.505 | 43.3 | 15.37 | 35.5 | 39.8 | 38.4 |
| 0.492 | — | 17.06 | — | 45.1 | 41.4 |
| 0.481 | 47.6 | 18.69 | 39.3 | 56.7 | 52.6 |
| | | | Av. = 35.6 | | |

length to which the photometric measurement relates. In columns 3, 5 and 6 are given the intensities I of the light reflected from the blue *Malurus* feathers, the blue gloss paper and the paper containing the blue pigment, expressed in percentages of the intensity of light reflected from white paper, the same conditions. The numbers in the third column are proportional to $1/\lambda^4$ and column 4 gives the quotients.

$$\frac{1/\lambda^4}{I} = 1/C$$

which must be constant if the box-cells behave like Rayleigh's medium. As a matter of fact, marked variations from the average $I/C = 35.6$ occur only in the extreme red and the extreme blue, when the experimental error is large owing to the lack of sensitivity of the eye to these colors. When column 2 is

plotted against column 1 the resulting curve of the *Malurus* feather coincides very well with the theoretical in the region from 0.6 to 0.5$\mu$ . . .

"This hypothesis also accounts for the previously mentioned fact that when liquids are sucked up which have a greater or a smaller reflective index than that of the cell substance, the same blue is obtained as when the pores are filled with air. According to Lord Rayleigh the intensity of the reflected light varies with the square of the difference between the refractive indices of the medium and the embedded substance. It is thus independent of the sign of the difference and therefore independent of whether the pores are filled with carbon bisulphide or with water. If the difference in the refractive indices is very slight, as when the canals are filled with water, the blue will be less predominant than when the pores are filled with air. As a matter of fact the water-soaked feather is somewhat more green than the unchanged feather.

"The hypothesis calls for a predominance of yellow and red in the transmitted light and this can be seen with the box-cells after removing the pigment layer and with the border cells where the course of the rays does not carry them through the pigment layer. All the color phenomena observed with blue feathers can thus be accounted for satisfactorily and it has been possible to show that the box cells have the required characteristics of canals with a diameter less than a wave-length of light and an index of refraction differing from that of air."

From the above observations made on typical blue feathers it has been shown that the feathers satisfy the criteria chosen as a means of detecting Tyndall blue or the blue of a turbid medium. The scattered light is blue, the transmitted light, yellowish; the blue requires a dark background to show up plainly; the blue may be rendered colorless and transparent by rendering the color-cells optically homogeneous; pores of dimensions of the order of the wave-length of blue light actually exist; the scattered light is polarized in the proper plane, and its intensity is inversely proportional to the

fourth power of the wave-length; variations in shade of blue occur, and are apparently due to the presence of relatively larger pores. In short, the parallelism between non-iridescent blues of feathers and the blue of a turbid medium is so complete that no reasonable doubt can exist as to their identity, particularly since no structures capable of acting as prisms, thin films, or diffraction gratings are present, to be considered as possible causes of the color.

In the light of the evidence presented, Gadow's theory of the blue of feathers must be discarded completely. It is to be regretted that his explanation is still accepted and quoted, though it has been doubted and even disproved by several later investigators. A statement of his views seems necessary here, in order that their unsatisfactory features may be pointed out.

Gadow[1] ascribes the blue to ridges in the outer surfaces of the color-cells, which produce the color by diffraction, in the manner of a diffraction grating. His drawings show no ordered arrangement of these ridges, which would be necessary for a grating effect, nor does he explain how a grating could produce only the one color, blue. This error is a common one; gratings possess ridges and cause color; ridges are found in a colored substance, and the color is straightway ascribed to them. Gadow admits that the understanding of the production of the color would be "an almost superhuman task. We know only the result, namely—blue color;" yet the laws of color production by gratings, have long been established and grating colors possess definite properties which serve to identify them. The presence of ridges in the feather is incidental. Many blue feathers show no signs of them.

Gadow has not definitely located the blue in the walls of the color-cells, nor has he recognized any connection between the color by reflected light (blue) and that by transmitted light (yellowish). He has not observed any change in color under the influence of a penetrating liquid, though if he studied sections mounted in balsam he could hardly have failed to

[1] Proc. Zoöl. Soc., London, 1882, 400.

notice some penetration. Apparently the blue of a turbid medium is not considered as a possible cause of color. Haecker[1] has pointed out the inadequacy of Gadow's explanation, but only in later paper,[2] does he reach the conclusion that the blue of non-iridescent feathers is the same as that of a turbid medium (Tyndall blue) and not a diffraction color. "The blue color is due to:

(1) The difference between the refractive indices of the cell substance and air without involving the hypothesis that this difference is distinctly greater for blue than for red.

(2) The small size of the pores whose diameter is small in comparison with a wave-length of light."[3]

The findings in the present paper confirm Haecker's theory completely and emphasize the untenable nature of Gadow's views.

### Identification Tests for Tyndall Blue in Feathers

To establish the presence of a structure producing blue in feathers, all the criteria outlined above may be made use of; but this involves time and effort, together with a certain degree of practice. The more simple of the tests applied in the above instance serve very nicely to detect the Tyndall blue, and if further confirmation is necessary the whole series of examinations can be carried out.

The most simple test to apply is, of course, examination of the color by transmitted and by reflected light.

The reflected light should be distinctly bluish, and may be seen best by immersing the feather in a liquid of refractive index about 1.55, to eliminate confusing surface reflections. Balsam serves very well as a mounting liquid for this purpose.

Feathers so mounted may be examined directly by transmitted light, but since there is almost invariably a layer of dark

[1] Archiv. Mikr. Anat., **35**, 68 (1890).

[2] Haecker and Meyer: Zool. Jahrb. Abs. Syst. Geol. Biol. Thiere., **15**, 267 (1902).

[3] Cf. Rayleigh: Phil. Mag., [4] **41**, 274 (1871); [5] **47**, 375 (1899); Bock: Wied. Ann., **68**, 674 (1899).

brown pigment beneath the blue cells of the barbs, the appearance by transmitted light is not particularly conclusive unless only cells which are not backed by dark pigment are examined. Those near the edge of the barbule are usually suitable, though a much more reliable method is the examination of oblique or longitudinal sections, in which the cells are separated from the dark pigmented backing. In such preparations their color by transmitted light is yellow to reddish orange, depending on the intensity of the scattering of light.

Conclusive proof that the blue is not a pigment color may be obtained by soaking the blue feather for some days or weeks in cresol (ortho-cresol acts most rapidly). The resulting transparency, with complete disappearance of all color except that due to the dark brown pigment layer, is evidence of the "structural" nature of the blue. The complete restoration of the color by thorough washing in alcohol and drying, is proof that no blue pigment has been removed by the cresol.

Oblique or longitudinal sections again serve to simplify the test, for the penetration of the liquid into the porous walls of the blue cells is almost instantaneous, and its removal nearly as rapid. Various liquids may be tried and the appearance of the feather as penetrated by them correlated with their refractive indices.

The polarization, to a greater or less degree, of the scattered light may be detected as outlined above, the effect of pressure in darkening the blue, may be observed, etc., but appearance of the color cells by reflected and by transmitted light, and the destruction of the color by penetration with liquids are easily observed by any one, and are sufficient to establish the nature of any blue in question with a minimum of time and effort.

It must be pointed out that the common test of holding a blue feather to the light does not prove the absence of blue pigment or the presence of "structural" blue. The dark brown color of feathers observed under these conditions is due to the dark brown pigment (melanin) present in the barbules and barbs of the feather. Any feather which has this

pigment in it will appear the same dark color against the light, whatever its color by reflected light may be. Moreover, a dark brown feather which had a layer of blue pigment over the brown would behave in the same manner, appearing blue by reflected light and dark brown by transmitted light.

It is only when the effect of the dark pigment is eliminated that any reliable determination of the nature of the blue can be made. This involves microscopic study, preferably of sections of the barbs.

### Additional Properties of Blue Feathers

Nearly all blue feathers, to a greater or less degree, show a change in the color by reflected light, depending on the relative positions of observer, feather, and illumination. This is particularly noticeable in the case of the blue feathers and of *Procneas virides*, *Calliste lacuna*, *Pionus chalcopterus*, *Sialia arctica*, and other birds of similar bright blue color. When these feathers are held between the source of light and the eye of the observer in such a way that one sees the light reflected from the surface, they appear in general a deep, almost indigo, blue. If the observer stands with his back to the source of light so that he is between it and the feather, the color of the feather by reflected light is a lighter, more greenish, blue.

The angle at which the light falls on the feather, or that from which the feather is observed apparently does not affect the color; the relative positions of illumination and observer are the factors which control the appearance.

Light is thrown on this behavior by study of an "artificial blue feather" consisting of a piece of partially devitrified Jena glass tubing, the blue color of which closely approximates the blues of feathers, and possesses the distinctive properties of the Tyndall blue. Such a piece of glass is deep blue as seen against a dark background, while the transmitted light is yellowish orange. It is found that a distinctly light greenish blue color, very similar to that observed in the feathers, is observed when the glass is in such a position that both the blue of the scattered

light and the yellow of the transmitted light can reach the eye. Thus a greenish blue color is not impossible from a Tyndall blue medium, provided the scattered and transmitted colors are observed simultaneously, by allowing light to pass through the turbid medium (yellow) to the eye which is at the same point observing the scattered light (blue). Reflections from the inner surfaces of the glass tube supply the transmitted light, which, seen through the blue of the scattered light gives a greenish blue as a result of the mingling of the two colors.

In the feathers it is observed that the central cavities in the color cells, which have walls of the Tyndall blue, are empty. They might be compared to bubbles of air distributed more or less regularly in the turbid medium which forms the walls of the color-cells, and which composes the color-producing layer.

As is well known, bubbles appear relatively dark by transmitted light, since a large proportion of the incident beam does not pass through them but is reflected back at their surfaces. The most probable explanation of the blue-green color change observed in blue feathers is that when the observer is on the side opposite from the illumination, the empty bubble-like cavities of the color-cells serve to some extent as a dark background for the Tyndall blue of the cell walls because of their relatively dark appearance by transmitted light. When the observer is on the same side as the illumination these cavities reflect part of the incident light back through the turbid medium to the eye, thus combining the yellow color of this light with the predominating blue color of the turbid medium of the cell walls, and giving a greenish blue appearance to the barbs. These effects are complicated by reflections from the outer surface of the barbs but since it is only necessary that there should be more light reflected back through the turbid medium to the eye in the second case than in the first, in order that the proper color change should be produced, the above explanation seems adequate.

It is also observed that the duller blues of feathers, when the illumination is on the opposite side from the eye, and the angle of incidence is large, appear almost grayish, by reflected

light the blue being much less intense. When the eye and the illumination are on the same side, the blue color shows plainly with the reflected light. This is shown very strikingly by *Andegena negrirostris*, *Cyanocorax*, and to a less degree by other dull blue feathers.

It may be explained by recalling that, while light which falls normally on a transparent surface is largely transmitted, if the angle of incidence is large the intensity of the reflected light becomes considerable, and that of the transmitted light is markedly decreased; for example, at normal incidence less than 5% of the light which falls upon the medium of refractive index 1.55, is reflected, the remainder being transmitted. At an angle of incidence of 75 degrees, 26% is reflected, while if the angle of incidence is 85 degrees, 62% of the incident light is reflected. As a result of this behavior, at large angles of incidence the greater portion of the light which falls on the blue feather is reflected from the surface and does not enter the turbid medium at all. Thus the blue is much reduced in intensity, while being obscured by the white light reflected from the outer surface of the feather. This combined with the dark barbules, results in a grayish, dull appearance of the feather; if the feather is in such a position that there is little reflection from its surface (illumination normal) or that this reflection does not reach the eye to detract from the strength of the blue (eye and illumination on same side of feather) the color appears at its maximum intensity.

This effect is mentioned here, because it influences the appearance of all feathers to a greater or less degree, and, in the case of structural blue, plays an important part in regulating the intensity of both the reflected and the scattered light.

Another remarkable property of blue feathers is that their color is, in general, rather easily affected by pressure, the lighter blues being darkened to deep blue or indigo as the barbs are compressed beneath a cover glass under the microscope. The darker blue appears first when the pressure is greatest, as when two barbs cross each other. Unless the pressure has

been very severe, the original color is restored on its removal. Crushing or hammering usually destroys the blue completely.

Since the indigo blue produced by pressure is a distinct color such as frequently occurs in blue feathers, rather than simply an admixture of black with the light blue, it must be caused by a variation in the structure in which the blue originates, namely, the walls of the color-cells. If it is admitted that the minute pores in the walls of these cells scatter the light with the production of blue color, various shades of blue may be ascribed to pores of different size; the deepest, purest blues being caused by smaller pores than those to which the whitish blues are due. If pressure affects these pores, it will tend to reduce their dimensions, and as a consequence of this decrease in size, a deeper blue will be be produced. The elasticity of the cell walls appears to be sufficient to restore them to their original condition and, when the pressure is removed, the original shade of blue is regained. Even the white tips of blue jay feathers show under the microscope a distinct blue when pressure is applied, indicating that they possess essentially the same structure as the blue portion of the feather, except for the larger size of the pores in the color cell-walls, which appear white for this reason. The change with pressure is shown best by barbs which are not armored by a thick sheath of keratin. Dark blue barbs under pressure appear black, since the pores of the color-cells are rendered too small to affect light and the cell walls become transparent, permitting the underlying layer of dark pigment to be seen.

As might be expected, swelling the color-producing structure of the feather has an effect just opposite to that of compressing it. The blues all tend to become lighter in tint, in all probability because of the enlargement of the pores in the walls of the color cells, as these cell walls are swelled by appropriate reagents. Swelling is most marked in those feathers, the barbs of which have a relatively thin keratinous sheath layer, because the color-cells are more exposed to the action of the reagent. Dilute sodium or ammonium hydroxide solutions, cresol, phenol vapor, ammonia, sodium hypochlorite,

hydrogen peroxide, and even water have marked swelling action on feathers. Of these, the solutions of the alkalies, and water appear to have the most pronounced effect on blue feathers. In all cases the original blue color of the feather is lightened; dark indigo blues become sky blue; light blues become almost white.

On removal of the swelling reagent, either by washing or by evaporation, the original color is restored. Pressure on the swelled barbs also restores their original color. Stronger pressure may even result in a darker blue than the original color of the untreated barbs, as explained above.

This change of color with swelling explains the frequently observed, perfectly reversible change from blue toward white when certain blue feathers are wetted. Those feathers which show the change in a striking manner generally are waxy in appearance, have prominent barbs with poorly developed barbules, only a thin outer layer of keratin being present. Among these are *Calliste lacuna, Procneas viridis.* An interesting illustration is afforded by *Procneas viridis;* a bright blue specimen of this bird was shot by a naturalist, whose dismay may be imagined when the bird, which fell in the water, was recovered and found to be practically white.

The effects caused by swelling are distinct from those due to permeation by liquids, for permeation by liquid always results in a greater transparency of the barb, while swelling tends rather to decrease the transparency, as well as to change the color. However, a single reagent may be the cause of changes by reason of its swelling action and also because it penetrates the pores in the walls of the color cells. For instance, cresol, as it acts progressively on the color cells of a barb, first swells them, giving a white, rounded appearance to the individual cells, and finally permeates the cell walls, tendering them transparent and colorless. The cell cavities may yet contain bubbles of air, which finally appear to dissolve in the cresol as it fills the cavities. Water or dilute ammonium hydroxide swells the color cell walls, causing white, and finally permeate these porous walls, but, on account of the low refractive index of

these liquids, the cell walls are rendered only partially transparent. By reflected light the empty bubble-like cavities of the color-cells may be seen appearing almost pinkish orange through the porous cell walls, through which the incident light passes twice before it reaches the eye, thus increasing the pinkish orange color which white of this nature transmits. It is possible that the dark brown color of the medullary cells aids in giving a brownish gray tinged with pink to the feather which has been subjected to long swelling and penetration by a liquid of refractive index markedly different from that of keratin. These peculiar appearances, observable only with special treatment, are of little significance, but an explanation of them in the light of the findings here presented seems necessary. It is not an essential part of the proof of the nature of the blue of feathers, however.

It is worth noting that when the light and dark blue adjoin each other in the same barb, one shade of blue graduates into the other cell by cell; that is, the individual color-cells are of one shade throughout, usually either light or dark blue, with few cells showing intermediate shades of color. The appearance is that of tiles in a floor, part of which is light blue, part composed of light and dark blue tiles, and part of dark blue tiles. Apparently the cells, developing as individuals, though side by side, have slightly different color-producing structure. This same character appears when several adjacent, apparently identical, cells are subjected to swelling. Some are affected much more rapidly than others, and appear markedly lighter in color, though uniform in themselves. This simply emphasizes the individual character of the cells, as units of the color-producing layer.

The general appearance of some blue feathers is influenced markedly by orientation alone. For example, the blue feathers of *Coracias indica* when viewed from a position inclined to the plane of the feather, appear brilliant blue when the barbs are seen crosswise of the line of vision and dull, darker blue, when they lie in the same direction as the line of vision. The same effect is noticed, to varying degrees, in other

blue feathers viewed in similar positions, and is striking enough to be worthy of mention, though the explanation is simple enough. When the barbs lie crosswise of the line of vision practically nothing but the blue color is visible; the barbules of darker color, are almost hidden by the blue barbs, which are thicker and form a series of parallel ridges. Maximum color is observed under these conditions. When the position of the feather is such that the observer sees between the ridges the general effect is much dulled by the appearance of dark barbules which are visible in this position. This is exactly the same effect one sees in "changeable" or "two-tone" silks, which are woven so that from one position the threads of one color are visible, while from another position the other color is more prominent.

The character of the barbules influences the blue color to a considerable extent. If these are white the blue appears pale and transparent, while if they are dark the blue gains strength, opacity, and brilliancy in some positions. If the barbules are only slightly developed, the blue feathers have a waxy, enameled appearance; while if the barbules are yellow or red the color of the feather as a whole will be modified by this admixture.

Dark bars across blue feathers, such as those of the jay, *Procneas viridis*, and others, are seen to differ from the blue portions only in the layer of color-cells which are constricted, ill-developed, pigmented, and apparently do not possess thick porous walls necessary to the production of blue.

Only one case in which the blue is not accompanied by underlying pigmentation was found. The blue tips of the feathers of *Procneas viridis* may be permeated by cresol so that they are perfectly transparent and colorless. No pigment is observed in the barbs of these feathers, though the barbules are dark. These barbs consist essentially of rods of turbid blue material (densely packed color-cells) with rows of bubbles (cavities of color-cells) down the central part of the barb. These bubbles play an important part in causing the blue-green to blue color change with angle, discussed above. Since

the blue of the barbs of the *Procneas viridis* feather is not inferior to other blues, it appears that the dark pigment is really not absolutely essential to production of a good blue, provided the color-cells have the proper structure, though it undoubtedly does intensify whitish or pale blues as well as lending opacity to the feather.

It has not been the aim in this investigation to examine all known blue feathers, but rather to develop methods by which any questioned blue may be studied and its character determined. The feathers examined were chosen without reference to their order or family, and include widely different types. Since the identical nature of the blues of birds of the different orders has never been questioned, and since no reason to doubt this has arisen in the course of this work, further study of this point was felt to be superfluous in the present investigation.

Blue feathers of the following birds have been examined and found to owe their color to the Tyndall blue: Blue jay, *Cissoloplia yucatanica, Procneas viridis, Sialia arctica, Pionus chalcopterus, Pitta cyanoptera, Callospiza thorasica, Cyanospiza ciris, Trichoglossus novae hollandae, Coracias indica, Cyanocorax, Irena puella, Ara, Blue and Yellow Macaw, Purple Gallinule, Indigo Bunting.*

## Green Feathers

Although dark brown pigment accompanies the Tyndall blue found in feathers, this pigment serves only as a dark background for the blue, and does not play a part in producing any other color. In non-iridescent green feathers, however, we have the Tyndall blue combined with pigment yellow, resulting in a color different from either alone.

With the exception of a green pigment *Turacoverdin*, found only in the *Musophagidae*, the non-iridescent greens of feathers are combinations of pigment and structural color. This view is the natural consequence of the recognition of the structural origin of the blues. Krukenberg[1] was unable to obtain any

[1] Vergleichend physiol. Studien, 1, V, 98 (1881).

green coloring matter from green feathers. Haecker[1] in addition to admitting that green may be caused by yellow pigment combined with Tyndall blue, points out that olive-green may be caused by yellow pigment combined with the dark brown pigment, melanin. Gadow[2] states that only dark brown and yellow pigments are to be found in green feathers, as Krukenberg had ascertained, but objects to the latter's statement that this yellow pigment, in conjunction with a structural blue, is the cause of the green color. With even less definiteness than in the case of blue, he attempts to connect the green color with ridges on the surface of the barbs, but offers no real explanation of its origin.

The color of green feathers is located in the barbs, and is not apparent when the feather is held against the light; only dark brown, almost opaque, pigment is observed under these conditions. The properties and structure of green feathers are the same as those of blue feathers as regards polygonal color-cells with porous walls, dark underlying pigment, yellowish color by transmitted light, color becoming more blue under pressure and less blue with swelling, partial polarization of scattered light, disappearance of color on penetration with liquid of proper refractive index, etc. In short, green feathers are identical with blue ones, except for one feature—the transparent outer sheath of keratin which surrounds the layor of color cells is yellow instead of colorless.

This outer layer of yellow keratin is the only essential difference between green and blue feathers, and its color superimposed on the blue of the color cells, gives the hue of the feather. If the color cells produce deep blue, either naturally, or because of pressure, this blue predominates and the green becomes almost blue, while if the color-cells are whitish, either naturally or because of swelling, the green becomes more yellowish. In a single barb some cells may appear almost blue while others are almost yellow, for this reason, while the color of the barbs of a feather may shade from greenish blue at one

[1] Archiv. mikr. Anatomie, 35, 68 (1890).
[2] Proc. Zoöl. Soc., London, 1882, p. 409.

end to yellow at the other, simply because the "blueness" of the color cells varies, while the yellow pigment remains the same. As a matter of fact, in such feathers the barbules and medullary portion of the barbs are usually free from dark brown pigment in the yellow parts of the feather, but the structure is the same throughout.

Such yellow feathers can be rendered distinctly green by painting on the back with India ink, just as the white tips of jay feathers are rendered blue by the same treatment, because the structure of a blue feather is present. Of course only the yellow feathers which possess this structure will become green under this treatment. Haecker points out that the same effect may be brought about by underlying black feathers on the bird, serving as a dark background, though this is more imperfect.

Penetration by cresol, or other liquid of the proper refractive index, renders the color cells transparent and colorless. The dark brown medullary pigment and the yellow of the outer layer are seen plainly. The original color is restored on washing and drying.

Prolonged extraction of green feathers with hot alcohol results in the removal of some or all of the yellow pigment, with the blue remaining as a structural color, unaffected by solvents.

The most simple way of showing that green feathers are only blue feathers with a yellow outer layer is by scraping, with a knife or scalpel, the colored barbs of the feather. Green feathers become blue under this treatment and examination with the microscope shows that a transparent yellow layer has been scraped off the outside of the barbs, leaving the blue color cells exposed. Sections, of course, show the same features.

Another striking demonstration of the entirely different nature of the yellow and the blue in green feathers is afforded by their behavior when faded. When blue feathers are exposed in a "Fadeometer" no loss of color results, but green feathers become blue in 20–40 hours' exposure (equivalent to

about 30–60 hours of direct sunlight). The pigment yellow of feathers is easily faded but the structural blue is unaffected.

It is possible to produce greens like those of feathers by covering a Tyndall blue medium (Jena glass, etc.) with a yellow varnish, while a blue feather, dyed with a yellow dye, which does not penetrate to the color cells, becomes a pronounced green.

Parrots furnish excellent examples of green feathers; Ara, Mexican Green Parrot; *Trichoglossus novae hollandae*, Blue and Yellow Macaw, all show greens which generally shade into yellow and blue. Other specimens studied include *Calliste lacuna*, *Callospiza thorasica*, *Purple Gallinule*, etc.

Some very pronounced and vivid greens, such as those of *Ptilopus puella*, *Ptilopus pulchellus*, *Green Heron*, etc., though lacking much of the brilliant lustre are nevertheless iridescent colors, and not related to blue feathers. Their different nature is apparent under the microscope; the green color is entirely in the barbules, and is highly lustrous under the microscope while any further study only shows that we have here an entirely different type of color, which will be discussed later. Newbigin discusses green in its relations to blue in kingfishers and other birds.

As far as other pigments are concerned, apparently they are not found in combination with Tyndall blue in feathers to any considerable extent, though the Blossom-headed Parakeet (*Paleornis cyanocephalis*) is said to have blue barbs combined with red barbules. In some parrot feathers, which shade from red, yellow, and green, to blue, the structure of the blue and green parts does not appear to have degenerated completely in the red portion of the barbs, though no hint of the blue appears to be produced by it, but only white. Chandler[1] makes a point of various devices which nature uses to produce similar color effects in feathers.

[1] Univ. of Cal. Pub. Zoöl., 13, No. 11 (1914–16).

## Conclusions

The conclusions of this paper are as follows:

1. Non-iridescent blues of feathers are due to the scattering of blue light by very fine pores in the walls of the outer layer of cells of the barbs of the feather. This is the blue described by Tyndall, which is commonly observed in turbid media.

2. No blue pigments, and no other structural causes of blue color have been observed in non-iridescent blue feathers.

3. Green feathers are essentially the same as blue feathers, except that the blue cells are overlaid by a transparent yellow layer.

*Cornell University*
*July 1, 1922*

# THE ANOMALOUS OSMOSE OF SOLUTIONS OF ELECTROLYTES WITH COLLODION MEMBRANES. II. THE EFFECT OF PORE DIAMETER

BY F. E. BARTELL AND D. C. CARPENTER

In a recent paper,[1] it was shown that the direction and magnitude of initial osmose of solutions of a large number of salts, also of acid and alkali, with collodion membranes were in accord with the anomalous osmose theory as previously outlined by Bartell and co-workers.[2] In the paper above referred to, attention was called to the change in shape of the osmose rate curve with time. A so-called straight line curve was obtained when the initial osmose values (two hour osmose readings) were plotted against the concentration, while a peculiar N shaped curve was obtained when the maximum osmose values (i. e., obtained after 12 hours or more) were plotted against concentration. The latter exhibited a minimum point at about 0.1 M concentration.

From the fact that the straight line initial osmose rate-concentration curve developed into the N shaped curve with time as the only apparent influencing factor, it was inferred that diffusion of electrolyte was the active factor directly responsible for the decided alteration of osmose rate through this concentration range.

In order to test this idea, collodion membranes of different degrees of permeability were prepared in the manner described in the previous paper. The number of capillary holes through a given area of membrane will be shown to be nearly the same

[1] Bartell and Carpenter: Jour. Phys. Chem., 27, 101(1923).

[2] Bartell and Hocker: Jour. Am. Chem. Soc., 38, 1029 (1916); Bartell and Madison: Jour. Phys. Chem., 24, 444, 593 (1920); Bartell and Sims: Jour. Am. Chem. Soc., 44, 289 (1922).

in all cases. The actual diameter of the capillaries was regulated at the time of setting and by the amount of evaporation of solvent which occurred before soaking in water.

### Permeability of the Membranes

The permeability of the membranes used in this work was determined by the hydrostatic method of Bigelow and Gemberling.[1] A known and constant hydrostatic pressure

TABLE I

Membrane Permeability (Very Permeable Membrane)

| Membrane no. | Pressure applied, mm $H_2O$ | Water passed, cu. mm | Time, sec. | Cu. mm $\times 10^{-4}$ water passing per sec. per sq. cm diaph. area |
|---|---|---|---|---|
| 1 | 385 | 18.48 | 337 | 319 |
| 2 | 385 | 19.50 | 355 | 319.3 |
| 3 | 385 | 23.16 | 421 | 320 |
| 4 | 385 | 18.90 | 344 | 319.5 |
| Average | | | | 319.45 |

Diaphragm Area = 171.2 sq. mm. Temperature = 20° C

was applied to water in contact with the membrane and the rate of passage of water through the membrane accurately noted on a calibrated capillary tube by means of a cathetometer. The cells were sealed with wax around the rubber stoppers, so that leakage was eliminated. They were then immersed in a thermostat. An idea of the reproducibility of the collodion membranes and the constancy of the effective membrane areas of the various cells may be gathered from the close agreement of the results. Absolute results involving correction for viscosity of water at 20° C were not attempted, as comparative data at the one temperature were all that was desired to establish relative permeability.

The following table was compiled from average values obtained in the same manner as shown in the foregoing table.

[1] Jour. Am. Chem. Soc., 29, 1576 (1907); 31, 1194(1909).

TABLE II

**Relative Membrane Permeability**
**Temperature = 20° C**

| Pressure applied, mm $H_2O$ | Cu. mm $\times 10^{-4}$ water passing per sec. per sq. cm. dia. area | Cu. mm $\times 10^{-4}$ water passing per sec. per sq. cm. area per mm pressure | Relative permeability |
|---|---|---|---|
| **Least permeable membrane** | | | |
| 485 | 54.76 | 0.1129 | |
| 385 | 42.93 | 0.1115 | |
| 285 | 31.84 | 0.1117 | |
| 185 | 21.37 | 0.1155 | |
| Ave. | | 0.1129 | 1 |
| **Medium permeable membrane** | | | |
| 492 | 109.32 | 0.2221 | |
| 392 | 87.82 | 0.2240 | |
| 292 | 64.84 | 0.2220 | |
| 192 | 43.29 | 0.2255 | |
| | | 0.2234 | 1.978 |
| **Very permeable membrane** | | | |
| 485 | 403.10 | 0.8311 | |
| 385 | 319.45 | 0.8297 | |
| 285 | 236.20 | 0.8288 | |
| 190 | 158.08 | 0.8320 | |
| | | 0.8304 | 7.355 |

From Poiseuille's Law for the flow of liquids through capillary tubes, we have the expression $Q = \frac{KnPD^4T}{L}$. Q represents the quantity of liquid passing through $n$, number of capillaries of diameter D and length L, in the time T, and under pressure P. K is a constant, the value of which is dependent upon the liquid used, the temperature, etc. It is assumed that the length of the capillary pore in the various membranes is a function of the thickness of the membrane. Under the conditions of the experiment, K, P, and T may be combined into a single constant $k$ and the equation rewritten $Q = \frac{knD^4}{L}$. If we assume for the time being that $n$ is a constant for all three membranes,

we are able to compare the relative pore diameters of the membranes.

The actual thicknesses of the three membranes were, respectively, 0.08 mm, 0.15 mm, and 0.31 mm.

The relative diameters of the pores of the three membranes, calculated as above, give the values 1 : 1.38 : 2.31.

### Measurement of Membrane Pore Size

The membrane pore size was measured directly by the method, based on Jurin's Law, as used by Bigelow and Bartell.[1] This gives us information relative to the assumption made concerning the number of pores in each of the membranes used. In case the relative pore diameters as measured by the two independent methods agree, we are justified in the previous assumption that the number of pores in a given area of membrane is the same for all three membranes.

The membrane was supported in a holder by a fine-mesh wire screen. Owing to the nature of the membrane, which was somewhat elastic, and which stretched under the pressure necessary to force water out of the pores, the values here reported must be considered as representing pores which have been slightly stretched. Results obtained follow:

TABLE III
Membrane Pore Size

| | K. Gms pressure per sq. cm. | Pore diameter, microns | Relative Pore Diameter | |
|---|---|---|---|---|
| | | | Jurin's Law | Poiseuille's Law |
| Least permeable membrane | 4.23 | 0.701 | 1.00 | 1.00 |
| Medium permeable membrane | 3.17 | 0.934 | 1.33 | 1.38 |
| Very permeable membrane | 1.76 | 1.681 | 2.39 | 2.31 |

The above agreement between the values for relative pore diameter, as determined by the two different methods, indi-

[1] Jour. Am. Chem. Soc., 31, 1194 (1909).

cates the validity of the assumption that the number of pores in a given cross-sectional area of the various membranes is very nearly the same, at least within 3 to 4%. We shall throughout this paper, distinguish between these three membranes by referring to them as (*a*) least permeable, (*b*) medium permeable, and (*c*) very permeable.

### Osmose through Membranes of Different Degrees of Permeability

The validity of the hypothesis that diffusion was responsible for the change in shape of the osmose rate-concentration curve, may be tested by comparing the osmose through the membranes of different permeabilities. The membrane of least permeability should show an initial rate-concentration curve which approaches more nearly a straight line than do the curves obtained with the other membranes of greater permeability. The membrane of medium permeability should show less of the straight line effect, and should rapidly develop the N type of curve, while the very permeable membrane should probably show no straight line effect at all, but should give instead the N shaped curve from the beginning.

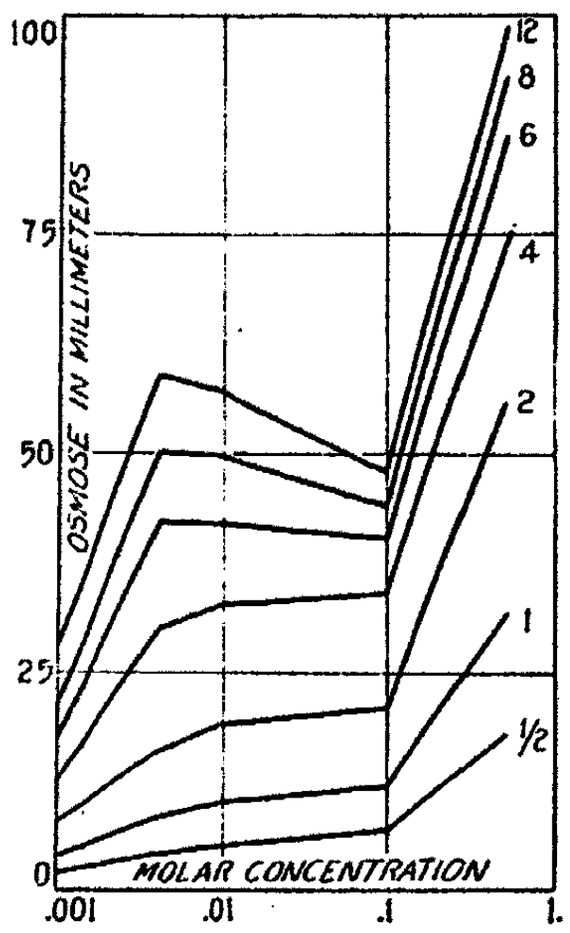



Fig. 1

Development of N shaped Osmose Curve as influenced by time in case of KCl. Least permeable membrane. Time in hours

In all of the work described in this paper, very carefully selected osmometer tubes of 2.5 mm internal bore were used. These were selected

from among over four hundred tubes and the volumes of given lengths of them varied not more than one percent. This uniformity was considered satisfactory. The duplicability of osmose experiments with these refinements and with good temperature control was close to one percent.

Inasmuch as it was desired to obtain results when membranes of different permeabilities were used, both with representative potassium salts with anions of different valencies

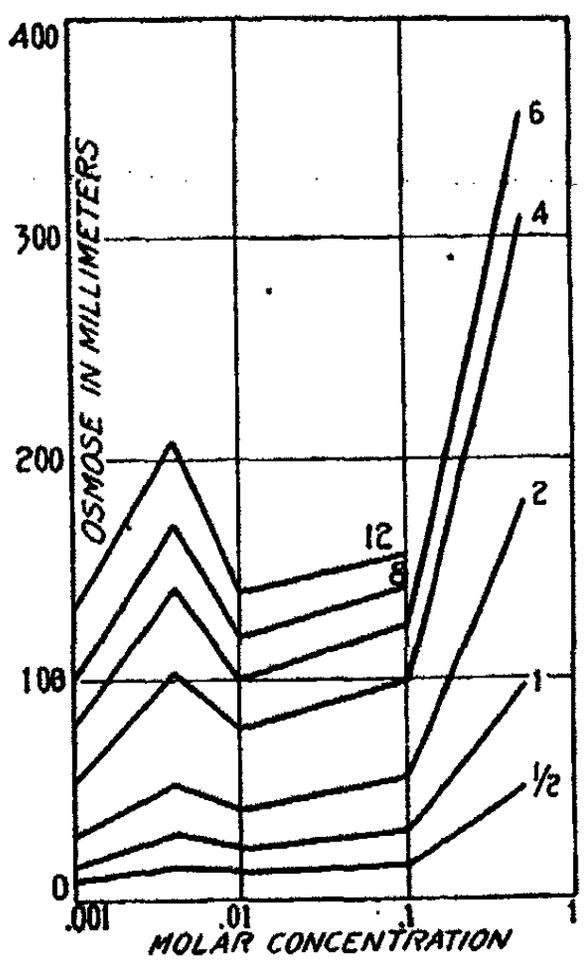



Fig. 2

Development of N shaped Osmose Curve as influenced by time in case of $K_2SO_4$. Least permeable membrane. Time in hours

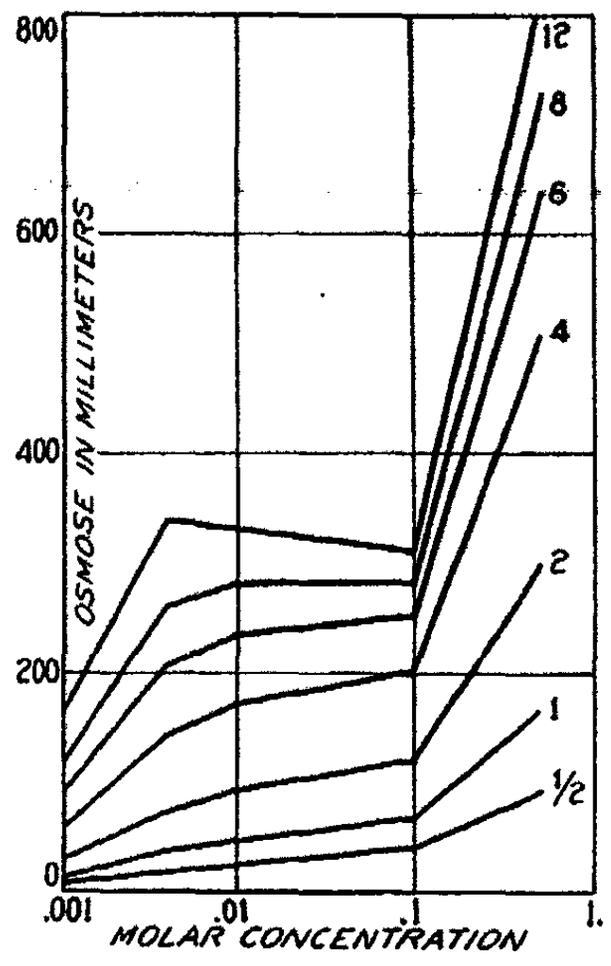



Fig. 3

Development of N shaped Osmose Curve as influenced by time in case of $K_3Fe(CN)_6$. Time in hours

and with salts of bivalent and trivalent metals, the following were used: KCl, $CaCl_2$, $AlCl_3$, $K_2SO_4$, and $K_3FeC_6N_6$. In addition, sucrose was also used in order to ascertain how the osmose of a substance supposed to give a normal osmose rate was affected by permeability. One concentration in addition

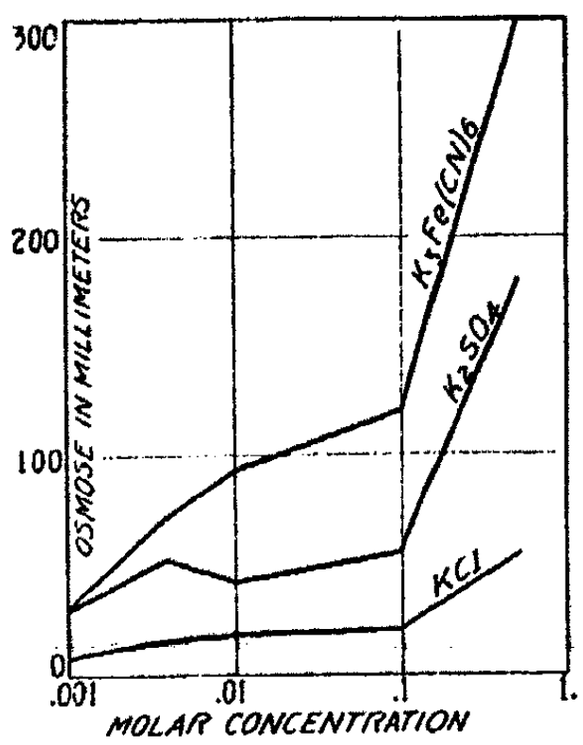



Fig. 4

Initial Osmose Rate (2 Hrs) of Potassium Salts.
With least permeable membrane

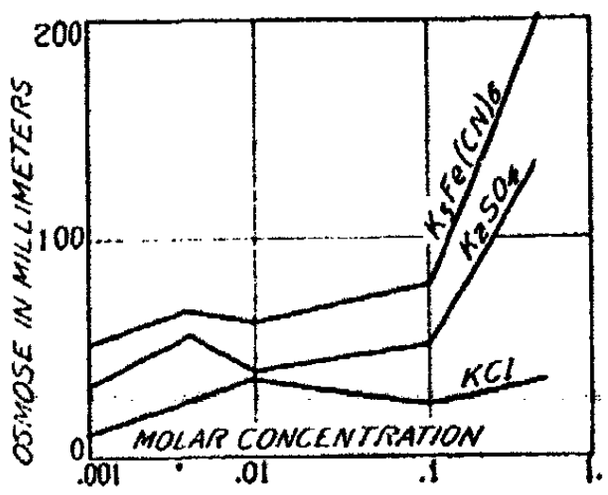



Fig. 5

Initial Osmose Rate (2 Hrs) of Potassium Salts.
With medium permeable membrane

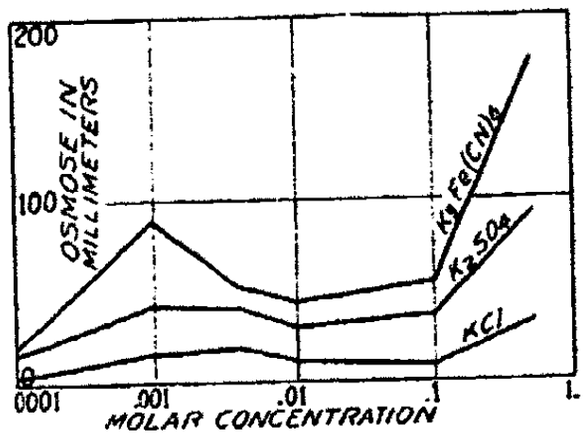



Fig. 6

Initial Osmose Rate (2 Hrs) of Potassium Salts.
With very permeable membrane

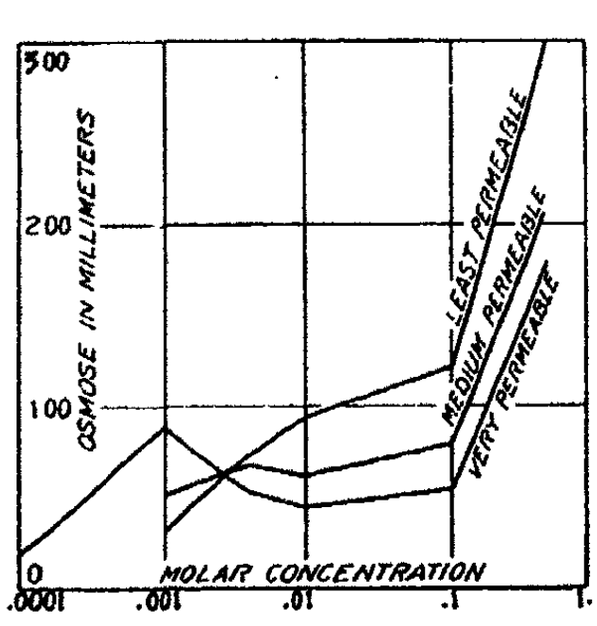



Fig. 7

Initial Osmose Rate (2 Hrs) of $K_4Fe(CN)_6$
With membranes of different permeabilities

to those used in the previous work was introduced, namely, 0.004 M. The recession in the N shaped curve started to develop with potassium salts at about 0.004 M concentration. In place of 1 M concentration 0.5 M was substituted, the osmose in this region of concentration was of the positive type, and proved to be of no special import in this investigation. The hydrostatic pressure was read at thirty minute intervals for the first two hours, after which two hour readings were generally made. Close watch, however, was kept on the experiments as they neared the maximum, so that the extreme pressure developed would be known. The accompanying Table IV for KCl contains data such as was obtained for all solutions investigated. In order to economize space, only values read at the end of 2 hr., 12 hr., and at maximum osmose will be given. The development of the N shaped curve with time is shown for potassium salts in Figures 1, 2, and 3, the time being expressed in hours. The effect of increasing the membrane pore diameter on the initial osmose rate-concentration curve is shown in Figures 4, 5, and 6. Figure 7 shows the initial (2 hr.) osmose rate-concentration curve for $K_3FeC_6N_6$ with all three membranes.

TABLE IV

Osmose of KCl (Least Permeable Membrane)

| Osmose period, hrs. | 0.001 M | 0.004 M | 0.01 M | 0.1 M | 0.5 M |
|---|---|---|---|---|---|
| 0.5 | 2 | 4 | 4 | 7 | 18 |
| 1 | 4 | 8.5 | 10 | 12 | 32 |
| 1.5 | 6 | 12 | 15 | 16.5 | 44.5 |
| 2 | 8 | 16 | 19 | 21 | 56 |
| 4 | 13 | 30 | 33 | 34 | 74 |
| 6 | 17.5 | 42 | 42.2 | 40 | 86 |
| 8 | 21.5 | 50 | 49.5 | 44 | 93 |
| 10 | 25 | 55 | 54.5 | 46.5 | 98 |
| 12 | 28.5 | 59 | 57 | 48 | 98 |
| 14 | 28.5 | 62 | — | 49.5 | — |
| 16 | — | — | 59 | — | — |
| 18 | — | 67 | — | — | — |
| 20 | — | — | 59 | — | — |
| 22 | — | 67 | — | — | — |

TABLE V

Osmose Values in Millimeters at the End of 2 Hr. and 12 Hr. Periods with Membranes of Different Permeabilities

| Salt | 2 Hr. Period Concentration | | | | | 12 Hr. Period Concentration | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Least permeable membrane** | 0.001 M | 0.004 M | 0.01 M | 0.1 M | 0.5 M | 0.001 M | 0.004 M | 0.01 M | 0.1 M | 0.5 M |
| KCl | 8 | 16 | 19 | 21 | 56 | 28.5 | 59 | 57 | 48 | 98 |
| $CaCl_2$ | 1.5 | −2 | −3 | 6.8 | 83 | 7.3 | −2 | −11 | 24 | 262 |
| $AlCl_3$* | 5 | 20.5 | 36.5 | 112.5 | 562 | 16 | 80 | 133.5 | 378 | — |
| $K_2SO_4$ | 30 | 53 | 42 | 56 | 180 | 133 | 208 | 140 | 158 | — |
| $K_3Fe(CN)_6$ | 32 | 73 | 94.5 | 122 | 300 | 166 | 339 | 331 | 311 | 806 |
| Sucrose | — | 0 | 1 | 21.2 | 106 | — | .5 | 8.2 | 97.5 | 500 |
| **Medium permeable membrane** | | | | | | | | | | |
| KCl | 11.2 | 26 | 36 | 23.5 | 35 | 37.2 | 94 | 120 | 55 | 75 |
| $CaCl_2$ | 5 | −2 | −9 | −6 | 53 | 15.5 | −4.5 | −25.8 | −17.8+ | 170 |
| $AlCl_3$* | 12 | 2 | 9.5 | 68 | 362 | 25 | 7 | 27 | 180 | 1004 |
| $K_2SO_4$ | 33 | 56 | 40.2 | 51 | 140 | 142 | 210 | 136 | 136.2 | 400 |
| $K_3Fe(CN)_6$ | 52 | 67 | 62 | 79 | 206 | 240 | 279 | 206 | 195 | 496 |
| Sucrose | 0 | — | 4 | 25 | 106 | 0 | — | 9 | 86 | 407 |
| **Very permeable membrane** | | | | | | | | | | |
| KCl | 15.5 | 20 | 12.2 | 8.5 | 32.5 | 28.5 | 38 | 22 | 14 | 47 |
| $CaCl_2$ | 0 | −9 | −14.5 | −5.5 | 56.2 | 0 | −15.5 | −23 | −7.2 | 88.2 |
| $AlCl_3$* | 4 | 3 | 8 | 59 | 285 | 7 | 4 | 12 | 96.5 | 554 |
| $K_2SO_4$ | 42 | 41.5 | 31 | 36.5 | 92 | 71 | 60.5 | 39 | 43 | 119 |
| $K_3Fe(CN)_6$ | 88.5 | 52.5 | 44 | 54 | 174 | 145 | 85 | 56 | 73 | — |
| Sucrose | — | — | 0 | 16 | 118 | — | — | 0.5 | 30 | 196 |

*Concentrations for $AlCl_3$ were as follows: 0.002 M, 0.008 M, 0.02 M, 0.2 M, 1 M.

TABLE VI

Maximum Osmose Values obtained with Salt Solutions of Different Concentrations with Membranes of Different Permeabilities

| Salt | Concentration | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Least permeable membrane | 0.001 M Time in hrs. | Osmose | 0.004 M Time in hrs. | Osmose | 0.01 M Time in hrs. | Osmose | 0.1 M Time in hrs. | Osmose | 0.5 M Time in hrs. | Osmose |
| KCl | 12 | 28.5 | 18 | 67 | 16 | 59 | 14 | 49.5 | 12 | 98 |
| $CaCl_2$ | 12 | 7.3 | 24 | −2 | 20 | −13.5 | 14 | 26.5 | 18 | 287 |
| $AlCl_3$* | 14 | 17.5 | 18 | 89 | 16 | 142 | 20 | 407 | 6 | 1210 |
| $K_2SO_4$ | 28 | 185 | 18 | 236 | 16 | 150 | 16 | 161 | 6 | 355 |
| $K_3Fe(CN)_6$ | 48 | 380 | 36 | 512 | 20 | 359 | 14 | 314 | 13 | 809 |
| Sucrose | — | — | 42 | 2 | 30 | 14 | 30 | 125 | 33 | 695 |
| Medium permeable membrane | | | | | | | | | | |
| KCl | 16 | 39.5 | 20 | 105 | 14 | 123 | 12 | 55 | 12 | 75 |
| $CaCl_2$ | 12 | 15.5 | 18 | −5.5 | 16 | −27.6 | 12 | −17.8 | 16 | 176 |
| $AlCl_3$* | 10 | 25 | 18 | 9 | 12 | 27 | 12 | 180 | 14 | 1006 |
| $K_2SO_4$ | 18 | 156 | 18 | 223 | 14 | 140 | 12 | 136.2 | 14 | 405 |
| $K_3Fe(CN)_6$ | 16 | 260 | 18 | 297 | 12 | 206 | 12 | 195 | 12 | 496 |
| Sucrose | 24 | 0 | — | — | 12 | 9 | 24 | 90 | 24 | 463 |
| Very permeable membrane | | | | | | | | | | |
| KCl | 8 | 30.5 | 8 | 41 | 6 | 22 | 6 | 14 | 6 | 47 |
| $CaCl_2$ | 6 | 0 | 6 | −15.5 | 6 | −23 | 6 | −7.2 | 6 | 88.2 |
| $AlCl_3$* | 10 | 8.5 | 8 | 4.5 | 6 | 12 | 6 | 96.5 | 8 | 586 |
| $K_2SO_4$ | 6 | 71 | 6 | 60.5 | 4 | 40 | 4 | 44 | 4 | 120 |
| $K_3Fe(CN)_6$ | 8 | 149 | 6 | 85. | 6 | 56 | 6 | 73 | 4 | 224 |
| Sucrose | — | — | — | — | 6 | .5 | 8 | 33 | 8 | 205 |

*$AlCl_3$ concentrations were as follows: 0.002 M, 0.008 M, 0.02 M, 0.2 M, 1 M.

The following generalizations may be drawn from the foregoing data:

1. The *least permeable membranes*, i. e., the ones with pore diameters less than 0.7 microns, during the first five hours showed a tendency to give only positive osmose with all the salts used with the exception of $CaCl_2$, which gave a negative osmose. At no time during the first few hours did the N shaped curve become pronounced. ($K_2SO_4$ solutions gave a slight N shape with this membrane.) These facts indicate that the phenomenon of negative osmose is not entirely dependent upon the specific salt used, neither is it dependent entirely upon concentration, but its appearance is dependent also, and to a large degree, upon the diameter of the membrane pores. It seems probable that negative osmose does not occur until the diameter of the membrane pore reaches a certain limiting value, which is definite for a given salt solution. In this work we have noted that when negative tendencies prevail, the negative effects became greater as the pore diameters are increased.

2. With *medium permeable membranes* (pore diameters less than 0.9 microns), the N shaped curve was fairly pronounced, though not obtained throughout the entire period of osmose, with the potassium salt solutions, KCl, $K_2SO_4$ and $K_3FeC_6N_6$. The repression in the curve occurred between 0.004 M and 0.1 M concentration.

3. With *very porous membranes* (pore diameters less than 1.6 microns), the N shaped curve became pronounced and was maintained throughout the entire period of osmose, from the initial to the final reading.

4. It should be pointed out that the N shaped curve was obtained even with the slightly permeable membranes, provided the experiment was allowed to continue for a sufficient length of time before osmose readings were taken. When readings were made at the end of a twelve hour period, a repressing effect was noted with all three potassium salts, this repression occurred between the concentrations of 0.004 M and 0.1 M.

5. With the least permeable membranes, the initial osmose rate of the concentrated solutions was greater than that obtained when the very permeable membranes were used. On the other hand, the rather surprising observation was made that the initial osmose rate of dilute solutions was less with the least permeable membranes than with the very permeable membranes.

6. The time required to reach maximum osmose was less with the very permeable membranes than with the less permeable membranes. Also, the maximum osmose attained with potassium salts was progressively less with increasing membrane porosity (an exception in the case of KCl with medium permeable membranes is to be noted).

7. The range of concentration over which repression of osmose occurred was greater with very permeable membranes than with the less permeable membranes.

8. The osmose of a substance of supposedly normal osmotic tendencies, such as sucrose, showed a decreasing maximum value as the porosity of the membrane was increased. No N shaped curve was obtained with sucrose solutions.

**Diffusion of Solute into Water Compartment during Osmose**

It has been known since dialyzers of collodion were first used by Fick[1] that they were permeable to crystalloids. For this reason, the exosmotic current during an osmose experiment must be of considerable magnitude. A study of the exosmotic current has received but little attention from recent investigators in osmosis.

The passage of solute into the water compartment may be regarded as taking place in some one or more of the following ways:

1. Filtration, the passage of solute through the membrane pores due to hydrostatic pressure.

2. Diffusion, the passage of solute particles through the membrane pores due to their own motion and according to

[1] Pogg Ann., **99**, 59 (1855).

Fick's Law, dependent largely on the salt, the concentration gradient and the temperature.

3. Dissolving of solute in the membrane material itself, the membrane then giving up solute to the water compartment according to the partition law.

4. Adsorption of solute from the contents of the solution compartment by the walls of the membrane capillary and then the subsequent giving off of solute by the membrane to the contents of the water compartment, in order that the adsorption process between membrane and water may come to equilibrium according to the partition law.

In the case of collodion, all of the factors may be active simultaneously, hence the question arose which of these factors are the predominating ones. That this was a very intricate problem can be seen from the fact that diffusion, solution, and adsorption are quite interdependent, also diffusion and filtration effects are not easily distinguishable from each other.

## Effect of a Given Salt and of the Pore Diameter of Membrane on Exosmotic Current or Salt Diffusion

The collodion membranes of different degrees of porosity which had already been used in the foregoing osmotic studies were used in this work. In these stationary cells, the osmotic experiment was stopped at the end of two hours and the contents of the water compartment removed and analyzed. Then another identical experiment was started and allowed to run to its maximum value, and the contents of the water compartment analyzed as before, so that not only the initial rate (2 hour period) would be known, but also the total amount of electrolyte which diffused from the cell by exosmose during the maximum osmose period.

Analyses of KCl, $CaCl_2$ and $K_3FeC_6N_6$ solutions were done volumetrically, the chlorides by Mohr's method[1] and the ferricyanide by Muller and Diefenthaler's method.[2]

[1] Mohr: Zeit. anorg. Chem., **63**, 330 (1909).

[2] Muller and Diefenthaler: Zeit. anorg. Chem., **67**, 418 (1910).

$AlCl_3$ and $K_2SO_4$ solutions were analyzed gravimetrically by evaporations and ignition; also by precipitation and ignition of $Al(OH)_3$ and $BaSO_4$, respectively.

Direct comparison of the total amounts of salt which passed through the various membranes during the maximum osmose period was a difficult matter, inasmuch as the time period of reaching maximum osmose depended not only on the specific salt and its concentration, but also, and more particularly, on the membrane porosity. For this reason, the amount of salt which passed through the membrane in a given time, say in two hours, must be considered a fairer means of comparing actual diffusion rates. Even then, comparisons of the diffused salts will be subject to some error, especially when made between the less porous and the very porous membranes, since in a two hour period, the osmose will have progressed rela-

TABLE VII

Millimols of Salt which passed through Membranes of Different Permeability during Two Hour Osmose Period

| Stationary Cells | | | | |
|---|---|---|---|---|
| Salt | Millimols of salt which passed through | | | |
| | Initial molar conc. in salt compartment | Very permeable (pore diam. about 1.6 micron) | Med. permeable (pore diam. about 0.93 micron) | Least permeable (pore diam. about 0.7 micron) |
| $K_3FeC_6N_6$ | 0.004 | 0.0045 | 0.0020 | 0.00155 |
| | 0.01 | 0.0129 | 0.0096 | 0.0090 |
| | 0.1 | 0.175 | 0.169 | 0.164 |
| $K_2SO_4$ | 0.004 | 0.00193 | 0.00345 | 0.0034 |
| | 0.01 | 0.01205 | 0.0109 | 0.0144 |
| | 0.1 | 0.1584 | 0.155 | 0.1803 |
| KCl | 0.004 | 0.0032 | 0.0018 | 0.0020 |
| | 0.01 | 0.0115 | 0.0112 | 0.0107 |
| | 0.1 | 0.219 | 0.190 | 0.207 |
| $CaCl_2$ | 0.004 | 0.00396 | 0.00264 | 0.00275 |
| | 0.01 | 0.01385 | 0.00835 | 0.01225 |
| | 0.1 | 0.173 | 0.097 | 0.199 |
| $AlCl_3$ | 0.008 | 0.0137 | 0.0098 | 0.00587 |
| | 0.02 | 0.0234 | 0.02736 | 0.0234 |
| | 0.2 | 0.311 | 0.311 | 0.282 |

tively further with the more porous membranes than with the less porous membranes. Since the time interval for maximum osmose is nearly the same with the two least permeable membranes, no appreciable error of the type above

TABLE VIII

Millimols of Salt which passed through Membranes of Different Permeability during Maximum Osmose Period

| | Stationary Cells | | | |
|---|---|---|---|---|
| Salt | Millimols of salts which passed through | | | |
| | Initial molar conc. in salt compartment | Very permeable | Medium permeable | Least permeable |
| $K_3FeC_6N_6$ | 0.001 | 0.0028 | 0.0037 | 0.0048 |
| | 0.004 | 0.0138 | 0.0163 | 0.0188 |
| | 0.01 | 0.0344 | 0.0431 | 0.0551 |
| | 0.1 | 0.434 | 0.529 | 0.665 |
| | 0.5 | 2 216 | 3.042 | 3.444 |
| $K_2SO_4$ | 0.001 | 0.005 | 0.0025 | 0.0038 |
| | 0.004 | 0.016 | 0.022 | 0.0237 |
| | 0.01 | 0.036 | 0.055 | 0.073 |
| | 0.1 | 0.460 | 0.626 | 0.808 |
| | 0.5 | 2.450 | 3.467 | 1.964 |
| KCl | 0.001 | trace | trace | 0.0021 |
| | 0.004 | 0.0175 | 0.0235 | 0.0329 |
| | 0.01 | 0.0479 | 0.0641 | 0.0790 |
| | 0.1 | 0.610 | 0.688 | 0.836 |
| | 0.5 | 3.112 | 3.77 | 4.265 |
| $CaCl_2$ | 0.001 | 0.0014 | 0.0010 | 0.0014 |
| | 0.004 | 0.0764 | 0.0241 | 0.0261 |
| | 0.01 | 0.0476 | 0.0647 | 0.0837 |
| | 0.1 | 0.520 | 0.565 | 0.682 |
| | 0.5 | 2.651 | 3.596 | 4.30 |
| $AlCl_3$ | 0.002 | 0.0070 | 0.0070 | 0.0080 |
| | 0.008 | 0.0293 | 0.0311 | 0.0332 |
| | 0.02 | 0.0315 | 0.104 | 0.275 |
| | 0.2 | —— | 1.010 | 1.582 |
| | 1.0 | 5.5 | 6.38 | 4.01 |

indicated will be probable when comparisons are made between them. Such comparisons will be more justifiable than when comparisons are made between the least permeable and the very permeable membranes.

**Summary**

The foregoing data brought out the following conclusions:

1. The rate at which $K_3FeC_6N_6$ and $AlCl_3$ passed through the membrane was increased at all concentrations as the pore diameter was increased. On the other hand, relative diffusion values of $K_2SO_4$ and $CaCl_2$ decreased materially as the pore diameter was increased. The diffusing rate of KCl remained about the same with the different membranes.

2. In dilute solutions $K_2SO_4$, $CaCl_2$ and $AlCl_3$ appeared to pass through the membrane at a relatively greater rate than the other salts.

3. Comparisons of the rate of passage of potassium salts through the *least porous membranes* (i. e., with pore diameters of about 0.7 microns) in the case of dilute solutions gave the following anion order $SO_4'' > Cl' > FeC_6N_6'''$. For concentrated solutions the order for the least porous membrane was $Cl' > SO_4'' > FeC_6N_6'''$. This latter order was the inverse of the order of magnitude of maximum osmose. Comparison of the rates of passage of chlorides into the water compartment showed the cation order in dilute solution to be $Al > Ca > K$. Exactly the opposite order $K > Ca > Al$ was found for concentrated solutions. The order for magnitude of osmose with dilute solutions, bore no apparent relation to the cation diffusion order, however, the order of magnitude of osmose with concentrated solutions was the inverse of the cation diffusion order.

4. With *medium porous membranes* (i. e., with pore diameters of about 0.93 microns) the anion order for rate of diffusion of potassium salts from dilute solutions was $SO_4'' > Cl' > FeC_6N_6'''$ and with concentrated solutions was $Cl' > SO_4'' > FeC_6N_6'''$. This was again the inverse of the order of maximum osmose for concentrated solutions. The cation order for rate of diffusion was $Ca > K > Al$ in dilute solutions, and $Ca > Al > K$ in concentrated solutions.

5. For *very permeable membranes* (i. e., with pore diameters of about 1.6 microns), comparison of the amounts of potas-

sium salts diffused during the period of maximum osmose, showed the anion order to be $Cl > SO_4 > FeC_6N_6'''$ for both dilute and concentrated solutions. This order is the inverse of the order of maximum osmose. For chlorides, the cation order with the most porous membrane was $K > Ca > Al$ in both dilute and concentrated solutions. This order was the same as the maximum osmose order in very dilute solutions, but was the converse of the order of maximum osmose in concentrated solutions.

6. If the pore diameter of an unstretched membrane, i. e., one not subjected to the high pressures such as were used in measuring pore diameters, is as we believe, slightly less than the diameter as measured with the stretched membrane, these membranes then have pore diameters of just about the same magnitudes as the copper ferrocyanide membranes investigated by Bartell[1] which were on the border line between osmotic effect and no osmotic effect.

7. Tinker[2] made a microscopic study of copper ferrocyanide gels and found: "The structure seems to be that of a somewhat irregular network having a mesh of the order 0.5 to 1.0 microns. In this respect, it seems to be similar to most of the other ordinary gels, such as gelatine, silicic acid, etc., which have been examined with great thoroughness by Bütschli, Hardy, van Bemmelen, von Weimarn, Quincke, Zsigmondy, Pauli and others. There seems to be a general agreement at the present time that most gels consist of a lattice work system in which a solid or semi-solid phase encloses a more liquid phase." The results of this investigation tend to corroborate the above view. The lattice work of the collodion membrane may be formed in such a manner that the net work forms a mesh of the order 0.5 to 1.0 microns. If the liquid phase is replaced by water when the lattice work is of this order the lattice work remains unaltered for months even though constantly subjected to filtration tests.

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[1] Bartell: Jour. Phys. Chem., **16**, 318 (1912).
[2] Tinker: Proc. Roy. Soc., **92A**, 357 (1916).

8. The work of this paper has clearly brought out the fact that the pore diameter of an osmotic membrane is a highly important factor in determining the exact nature of osmose. Furthermore, it seems probable that the phenomena of anomalous osmose and the attending salt diffusion is governed largely by the precise pore diameter of the osmotic membrane.

In our next paper, results will be given which will show to what extent osmose and diffusion of solute are affected by stirring the solutions bathing the membrane.

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# PRODUCTION AND CHARACTERISTICS OF THE CARBIDES OF TUNGSTEN

BY MARY R. ANDREWS

As is well known, the commercial method of exhausting lamps involves the use of rotary oil pumps. The problem has often arisen as to the effect of residual vapors from the oil on the characteristics of the lamps. Under normal operating conditions any such traces of residual gases are "cleaned up" by the phosphorus or other reagent which is volatilized for this purpose when the lamp is flashed.[1] But, under imperfect manufacturing conditions, it is possible that an amount of hydrocarbon vapor may remain in the lamp which is greater than that which can be cleaned up during flashing.

It therefore appeared that the results of an investigation of the reaction between hydrocarbon vapors and an incandescent tungsten filament might throw some light upon possible sources of trouble in lamp manufacture. As ordinary oil vapor consists of a mixture of aliphatic hydrocarbons whose composition changes with the history of the oil it was decided to work with a pure hydrocarbon. Since as has been pointed out by Langmuir[2] "there are many advantages in studying heterogeneous reactions at very low pressures" it appeared desirable to work with very low pressures of hydrocarbon vapor.

## Vapor Pressure of Naphthalene

Naphthalene, $C_{10}H_8$, possesses properties which made it especially suitable for the purposes of the present investigation and it was used chiefly in the work described in this paper. Vapor pressure measurements for this substance have been published for temperatures above its melting point by Nelson

[1] S. Dushman: "Methods for the Production and Measurement of High Vacua," Gen. Electric Rev., 24, 676 et seq. (1921).

[2] Jour. Ind. Eng. Chem., 7, 350 (1915).

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and Senseman[1] and for lower temperatures by Barker[2] and by Allen.[3] Data at still lower temperatures were obtained some time ago in this laboratory by Miss Mary Daly by means of the ionization gage.[4] These latter determinations are here published for the first time.

| Temp. °C | Pressure in mms. Hg. | Pressure in bars |
|---|---|---|
| 18 | $63.5 \times 10^{-3}$ | 84.5 |
| 14 | $51.5 \times 10^{-3}$ | 68.5 |
| 11 | $39.4 \times 10^{-3}$ | 52.4 |
| 6 | $24.3 \times 10^{-3}$ | 32.3 |
| 5 | $27.5 \times 10^{-3}$ | 36.6 |
| 0.5 | $15.7 \times 10^{-3}$ | 20.9 |
| 0 | $15.8 \times 10^{-3}$ | 21.0 |
| 0 | $14.6 \times 10^{-3}$ | 19.4 |
| − 2.5 | $11.7 \times 10^{-3}$ | 15.6 |
| − 5 | $9.7 \times 10^{-3}$ | 12.9 |
| − 6 | $8.9 \times 10^{-3}$ | 11.8 |
| − 6.5 | $8.0 \times 10^{-3}$ | 10.5 |
| − 7 | $7.7 \times 10^{-3}$ | 10.2 |
| − 9.5 | $5.7 \times 10^{-3}$ | 7.59 |
| −10.5 | $5.5 \times 10^{-3}$ | 7.32 |
| −11 | $4.8 \times 10^{-3}$ | 6.38 |

Plotting the logarithms of the pressures against the reciprocals of the absolute temperatures, and giving weight to the values obtained at the extreme temperatures it is found that within the limits of experimental error all the data are best represented by the two straight lines shown in Fig. 1. This corresponds to a vapor-pressure relation of the form

$$P = P_0 e^{\frac{-Q}{RT}}$$

As a matter of fact most vapor pressure data at low pressures are found to be very satisfactorily represented by an equation of this form.

[1] Jour. Ind. Eng. Chem., 14, 58 (1922).
[2] Zeit. phys. Chem., 71, 235 (1910).
[3] Jour. Chem. Soc., 77, 410 (1900).
[4] Dushman and Found: Phys. Rev., [2] 17, 7 (1921).

By means of this plot (extrapolated for low temperatures) the following vapor-tension data are obtained for the range of temperatures used in the present investigation.

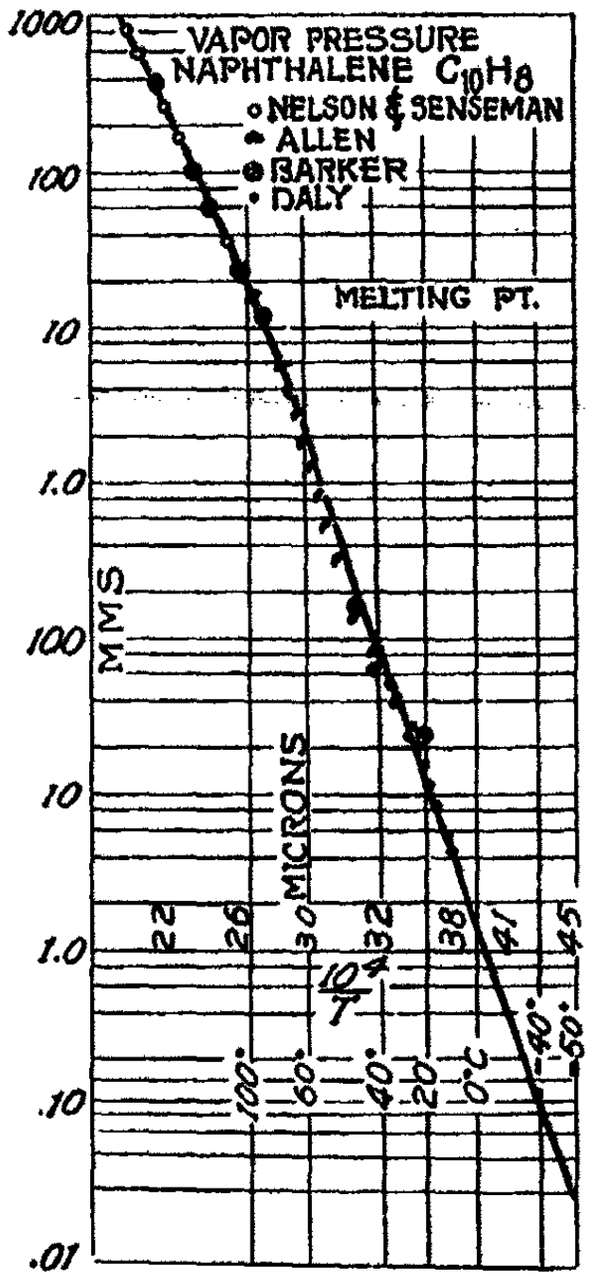



Fig. 1

| Temp. ° C | Pressure in mm Hg. | Pressure in bars |
|---|---|---|
| 0 | $15 \times 10^{-3}$ | 20 |
| −10 | $5.0 \times 10^{-3}$ | 7.3 |
| −20 | $1.55 \times 10^{-3}$ | 2.4 |
| −30 | $.48 \times 10^{-3}$ | 0.77 |
| −40 | $.12 \times 10^{-3}$ | 0.23 |
| −50 | $.03 \times 10^{-3}$ | 0.06 |

## Apparatus and Method

Most of the experiments were carried out in an apparatus of the type shown in Fig. 2. The system could be exhausted to less than half a bar by a Langmuir condensation pump backed up by suitable mechanical pumps. During exhaustion and baking out of the lamp (A) the naphthalene reservoir (B)

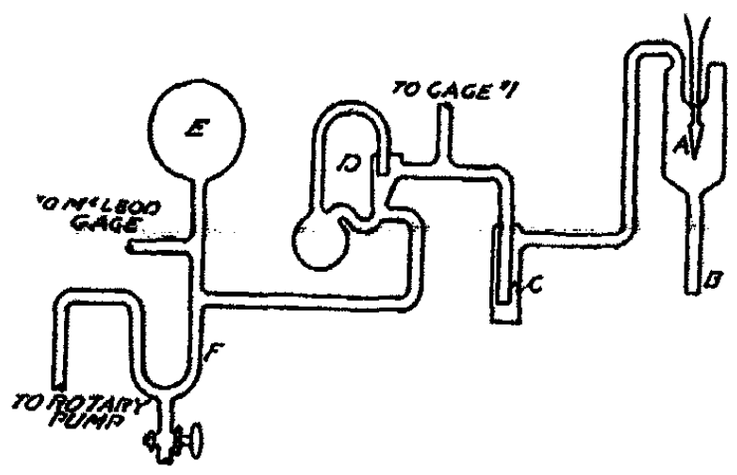



Fig. 2

A—Lamp containing tungsten filament.
B—Reservoir of hydrocarbon.
C—Liquid air trap.
D—Mercury pump.
E—Bulb for collecting hydrogen.
F—Mercury seal.

was usually warmed to eliminate moisture and adsorbed gases. This was followed by aging of the filament at about 2400° K to constant resistance, meanwhile keeping the naphthalene trap in liquid air. Resistance measurements at room temperature were made in the usual way with a Wheatstone bridge and galvanometer, care being taken that the current passing through the filament was too small to heat it appreciably. With the four mil filaments ordinarily used in these experiments this meant less than five milliamperes.

The vapor pressure at which the reaction was to be investigated was obtained by submerging the naphthalene reservoir (B) in acetone kept at the desired temperature by adding liquid air. The residual naphthalene vapor after passing through the lamp (A) was condensed in the liquid air trap (C).

The filament was lighted for a measured time and the hydrogen evolved was determined by closing the trap (E) and observing the rise in pressure in the bulb (D) by a McLeod gage. Filament temperatures were estimated by color matching with a tungsten lamp standardized in this laboratory.

### Reaction between Tungsten and Naphthalene

At the surface of an incandescent tungsten filament at a temperature of 1600° K or higher naphthalene is decomposed into hydrogen and carbon, the latter forming carbide as it diffuses into the metal.

Chemical analysis of carbonized filaments and determinations of the hydrogen evolved during carbonization showed that the decomposition of naphthalene into carbon and hydrogen was quantitative, the carbon being entirely taken up by the tungsten. Conductance at room temperature was measured at intervals during carbonization. The following are two typical determinations.

Filament A

| Conductance* percent | % C calculated from $H_2$ evolved | % C found by analysis |
|---|---|---|
| 74.5 | 0.806 | — |
| 35.3 | 2.05 | — |
| 7.1 | 3.12 | — |
| 8.1 | 3.27 | — |
| 17.6 | 4.28 | — |
| 20.9 | 4.5 | 4.0 |

Filament B

| Conductance* percent | % C calculated from $H_2$ evolved | % C found by analysis |
|---|---|---|
| 68. | 1.26 | — |
| 31. | 2.14 | — |
| 7.6 | 3.11 | — |
| 34.8 | 5.2 | 5.9 |

* Reported as percent of the conductance of the original uncarbonized filament.

Since both hydrogen and conductance measurements are subject to appreciable error and since analytical determinations on such extremely small samples are very difficult the agreement between calculated and determined values for carbon are as good as could be expected.

Figure 3 shows the relation between conductance and the percent of carbon in the filament. It will be observed that the conductance decreases linearly with increased carbon content until a minimum of about six percent of the original conductance is reached at a composition of 3.16 percent carbon. As this corresponds exactly to the formula of $W_2C$ it is

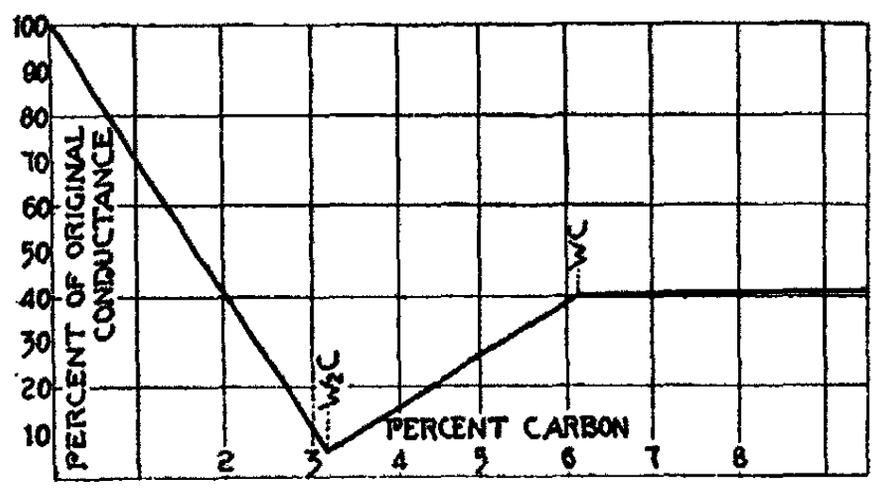



Fig. 3

Change of conductance with carbon content of carbonized tungsten

reasonable to conclude that at this point the filament is completely converted into a carbide of the above composition. As the carbon content is increased beyond this minimum the conductance increases linearly again until a composition of 6.12 percent carbon is obtained, corresponding to the complete conversion of the filament into the carbide WC. Further heating in hydrocarbon vapor results in the slow deposition of a shell of carbon on the filament, the conductance being affected only inappreciably.

As a check on this curve which was derived as an average of several determinations such as are shown above, two fila-

ments were carbonized beyond the minimum conductance and their carbon content determined by their conductance. These filaments were then analyzed. The results were as follows:

| | Carbon by conductance | C by analysis |
|---|---|---|
| Filament 11 | 3.6 | 3.9 |
| Filament 12 | 6.2 | 6.2 |

It should be noted that there is no indication of the formation of a carbide of the formula $W_3C$. Ruff and Wunsch[1] in their experiments with carbon and tungsten heated in the electric furnace or the arc thought they identified such a compound, as well as WC and probably $W_2C$. Moissan[2] in his early work with the electric furnace had prepared $W_2C$, and Williams[3] prepared WC and from it $W_2C$ in the same way, but neither of these authors found the tri-tungsten carbide.

### Microscopic Structure. Mechanics of Carbonization

Cross-sections of filaments partially carbonized to $W_2C$ show, under the microscope, the compound as a ring surrounding a core of pure tungsten. The outer ring was brittle and would not take a polish; the core could be given a mirror surface. In carbonizing, carbon must penetrate the layer of carbide already formed and react with the tungsten at the outer surface of the core. It is the rate of diffusion of carbon through this ring of carbide which limits the rate of carbonization unless a high filament temperature and a very low pressure of hydrocarbon vapor are maintained, in which case the speed of carbonization may be limited by the rate of decomposition of the hydrocarbon at the surface of the filament. For example, with a four mil filament running at 2300° K in a pressure of naphthalene greater than three bars, carbonization is limited by the rate of diffusion. This is apparent if conductance is

[1] Zeit. anorg. Chem., **85**, 292 (1914).
[2] Comptes rendus, **123**, 15 (1896).
[3] Ibid., **126**, 1722 (1898).

plotted against the time during which the filament has been lighted (Curve A—Fig. 4). In this case as the shell of tungsten carbide, $W_2C$, becomes thicker the rate of penetration of carbon to the tungsten core becomes less and the rate of decrease in conductance becomes less and less, though the pressure of hydrocarbon vapor remains constant. If the temperature of the filament be increased, diffusion of carbon will occur much more rapidly and carbonization will proceed at a constant rate (Curve B—Fig. 4), if the temperature be high enough, being limited in this case only by the rate of decomposition of hydrocarbon at the surface of the filament. It was found that decomposition of hydrocarbons (at least in the case of naphthalene and toluene) proceeded much more rapidly while the filament was being carbonized from pure tungsten to $W_2C$ than while it was being converted from $W_2C$ to WC. Apparently decomposition is more rapid at a surface of $W_2C$ than at one of WC or carbon. To test this idea we lighted a pure carbon filament in naphthalene and found the reaction (measured in this case by the hydrogen evolved) to be very slow and of about the same order of magnitude as when a filament corresponding to the composition of WC is lighted under the same conditions. It may be that decomposition on a surface of WC is as rapid as on one of $W_2C$, but that diffusion of carbon through the former compound is slower than through the latter at the temperature used so that a carbon coating is formed on the filament which cuts down the rate of decomposition to that on carbon. This rate being very low, the carbon coating would

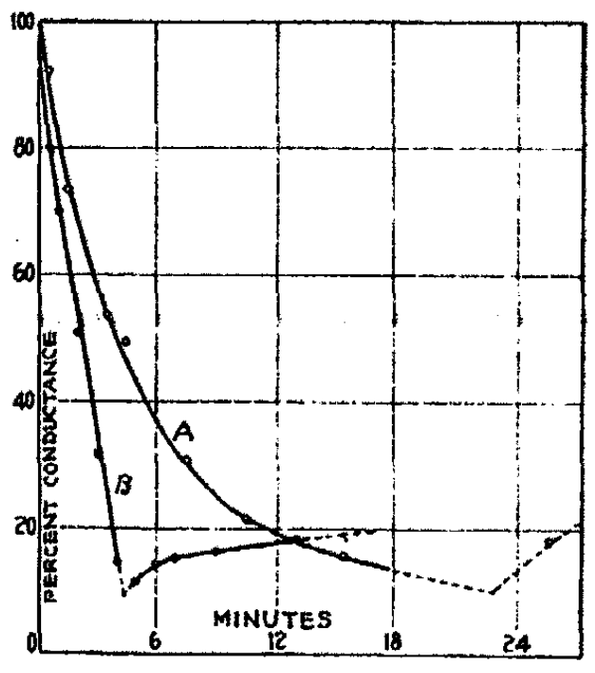



Fig. 4

Carbonization in 2.15 microns of naphthalene ($C_{10}H_8$), 4 mil. tungsten filaments. A—at 2300° K, B—at 2500° K

tend to thicken up very slowly, probably more slowly than carbon would diffuse into the filament. The coating would therefore remain of negligible thickness and the effective rate of decomposition would be the rate at which carbon is absorbed by the filament. This idea is borne out by the decreasing rate of reaction as a filament is carbonized (at constant temperature and pressure) from $W_2C$ to WC. (See the second arm of Curve B—Fig. 4.)

In carbonizing with acetylene the gas was allowed to flow from a large reservoir through the lamp to the liquid air trap. The rate of flow and the pressure in the lamp were controlled by the length and size of tubing between reservoir and lamp, and between lamp and trap. We found that at a given initial pressure in the lamp the rate of carbonization varied directly as the rate of flow of the gas. In other words, all of the acetylene reaching the lamp was decomposed. In our work with naphthalene, using the type of bulb shown in Fig. 1, carbonization progressed with a speed of only three or four percent of the rate to be expected from the calculation of the amount of gas striking the filament per second. We assumed at first that only this proportion of the molecules which struck the filament reacted; but when in later experiments we used a lamp in which the naphthalene reservoir was larger and affording a greater area of the solid for evaporation, the rate of carbonization increased to three-tenths of the rate calculated from the vapor pressure of the naphthalene. Possibly the filament decomposed the gas faster than it evaporated from the solid, so that, during any time the filament was lighted, the pressure of hydrocarbon in the lamp was considerably below the normal vapor-pressure corresponding to the temperature of the reservoir. This point of view is indirectly supported by data given by Barker in his determination of the vapor pressure of naphthalene.[1] He found great difficulty in obtaining saturation of the gas which he caused to flow over the naphthalene even at a very slow rate. He suggested that the surface of the naphthalene may become covered with a layer of the gas

[1] Loc. cit.

or an impurity. Langmuir[1] has found that reactions between tungsten or molybdenum vapors and the simple gases take place, if they occur at all, at every collision. But in the case of solids reacting with vapors, as when tungsten is attacked by oxygen or by a mixture of oxygen and carbon monoxide, he finds the conditions much more complex.[2] In these cases only a fraction of the molecules of oxygen which strike the filament reacts with it. This fraction he calls "E." Apparently monomolecular layers of gas adsorbed on the surface of the filament play an important part in the value of "E" for many such reactions. In the case of naphthalene this may also be the case as it is quite conceivable that there may be a monomolecular layer of carbon atoms adsorbed on the surface. We have, moreover, in the case of naphthalene a large molecule which in decomposing to carbon and hydrogen must deposit ten carbon atoms on the filament from the two rings of its structure—a complicated condition. While we have no proof as yet that every molecule of naphthalene that strikes the tungsten of $W_2C$ surface is not decomposed, it seems probable from data given in the earlier part of this article that not all molecules striking a carbon surface (possibly also a surface of WC) react, since the rate of carbonization of a $W_2C$ filament is less than that for a less carbonized one. There must be considered, also the large volumes of hydrogen formed at the surface of the filament, through which fresh naphthalene must pass to reach the metal. Further work is being undertaken on this phase of the subject, particularly with a view to determining the value of "E."

A few experiments were made, using pure ethyl alcohol as the carbonizing agent. With this gas flowing from a reservoir, carbonization was one to two-tenths as rapid as with acetylene at the same pressure and rate of flow. This would indicate that not every molecule striking the filament was successfully

[1] "Chemical Reactions at Low Pressures," Jour. Am. Chem. Soc., **41**, 167 (1919).

[2] Ibid., **35**, 105 (1913); **37**, 1139 (1915).

decomposed. The presence of the oxygen atom probably accounts for this slowing down of the carbonization of alcohol.

### Physical Characteristics: Conductance and Temperature Coefficient

Both carbides are brittle. Due probably to the difference in the coefficient of expansion between tungsten and $W_2C$ highly carbonized filaments invariably show radial cracks.

While the cold resistivity of $W_2C$ is about fifteen times that of tungsten the temperature coefficient of resistance is very much less. The following table gives the resistivity and the ratio of hot to cold resistivity ($R_H/R_c$) for $W_2C$ for various temperatures, and for comparison the ratio for pure tungsten at the same temperatures. These figures, however, are only approximate as they are based on measurements of a single filament of $W_2C$ which may not have been entirely homogeneous.

| Color temperature | Resistivity of $W_2C$ | $R_H/R_c$ for $W_2C$ | $R_H/R_c$ for W |
|---|---|---|---|
| 298° K | $.81 \times 10^{-4}$ | — | — |
| 1655° K | $1.05 \times 10^{-4}$ | 1.26 | 8.47 |
| 1800° K | $1.10 \times 10^{-4}$ | 1.33 | 9.43 |
| 1930° K | $1.15 \times 10^{-4}$ | 1.40 | 10.30 |
| 2060° K | $1.20 \times 10^{-4}$ | 1.46 | 11.17 |
| 2215° K | $1.25 \times 10^{-4}$ | 1.51 | 12.30 |

Figure 5 shows temperature-conductance curves for filaments of pure tungsten of $W_2C$ and of filaments partially carbonized to $W_2C$. A partially carbonized filament shows at any temperature a conductance which is in agreement with the conductance calculated from the amount of tungsten and of $W_2C$ present. The coefficient of resistance, therefore, of any partially carbonized filament is calculable from its composition and the temperature coefficients of the two components. We are

indebted to Dr. W. E. Forsythe, of the Research Laboratory at Nela Park, for the pyrometric data on which these curves and the preceding table are based. He finds also that the

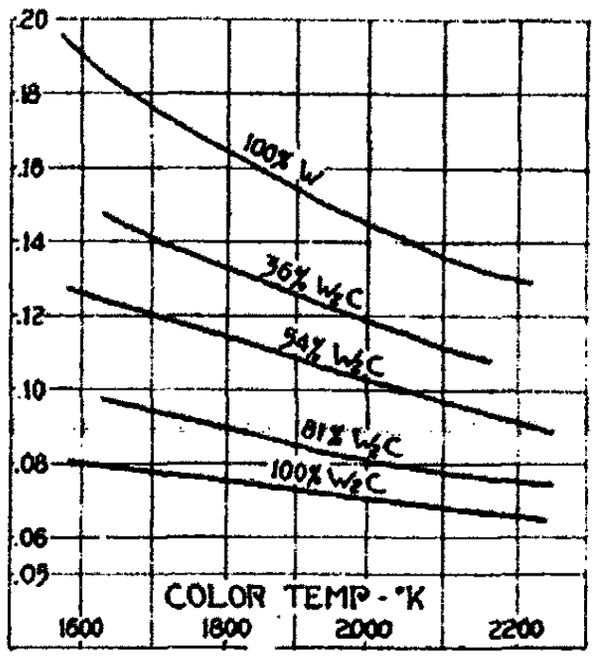



Fig. 5

Effect of varying $W_2C$ content on conduction of tungsten filaments as function of temperature. Filaments 10 cm long and 0.01 cm in diameter. From Forsythe's data

emissivity of $W_2C$ is practically the same as of pure tungsten. Measurements made by Mr. G. M. J. Mackay, of this laboratory, confirm this observation.

## Carbonizing Agents

Among the hydrocarbons other than naphthalene, which have been used by the author or by associates in this laboratory are benzene, toluene,[1] anthracene, acetylene, methane and

[1] In using toluene we found it necessary to determine its vapor pressure. This was done with the ionization gage. The points determined were:

| Temp. °C | Pressure |
|---|---|
| −90 | 3 bars |
| −80 | 31 „ |
| −70 | 49 „ |

The freezing point is roughly −90° C.

illuminating gas. Undoubtedly almost any hydrocarbon vapor will react with incandescent tungsten to form tungsten carbides.[1]

### Decarbonization

Carbonized filaments heated in vacuum decompose at rates depending on the temperature. Below 2400° K the rate of decomposition is extremely low, but as the temperature is raised the rate is increased. Carbon is volatilized without loss of tungsten. It is possible to drive out the carbon completely and obtain a tungsten filament of the same conductance as before carbonization. In 8 hours at about 2700° K a 4 mil filament which had been carbonized to $W_2C$ was entirely decarbonized, and the conductance increased to the same as that of the original tungsten filament. The magnified cross-section of a filament which had been carbonized almost entirely to $W_2C$ and then heated in vacuum until the cold conductance has risen to about fifty percent of the original tungsten showed a ring structure. The outer ring consists of pure tungsten, the core is undecomposed carbide. Carbon can also be taken out very quickly by flashing the filament in a considerable pressure of hydrogen.

In conclusion, I wish to express my sincere thanks to Dr. Saul Dushman for his enthusiastic interest and help in the work presented here, to Dr. Irving Langmuir for his valuable suggestions and criticisms, and to Mr. C. G. VanBrunt for the careful analytical work done in determining carbon in the minute samples available.

### Summary

The reaction between incandescent tungsten and naphthalene vapor has been studied. The existence of two compounds $W_2C$ and WC is shown by points of inflection of the resistance-composition curve. The mechanics of the reaction are discussed,

[1] Tungsten can also be carbonized by coating the cold filament with carbonaceous material such as dextrine, lamp-black, glycerine, graphite etc., and then heating it in vacuum to incandescence.

the factors being rate of diffusion of carbon through tungsten carbide as a function of temperature, the vapor pressure and the value of "E." Approximate resistivities of $W_2C$ at different temperatures are given and the conductance of a partially carbonized tungsten filament is shown to be the sum of the conductances of its two components. Various carbonizing agents are mentioned. A complete vapor-pressure curve for naphthalene from —50° to +200° is shown, and a few values for the vapor-pressure of toluol at low temperatures given. Decarbonization is discussed briefly.

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# BASIC ALUMINUM SULPHATE

BY F. S. WILLIAMSON

It has been claimed by Knecht, Rawson and Loewenthal[1] that, when the amount of potash alum exceeds five percent of the weight of the wool, a basic aluminum sulphate is taken up by the wool. There is no proof of this, as they themselves admit, because the experiments show merely that alumina and sulphuric acid are both adsorbed by the wool.[2] On the other hand, there is nothing in these experiments which disproves the formation of a basic sulphate. As a preliminary to deciding this question, it seemed desirable to check Schlumberger's statement that one basic sulphate of aluminum, and only one, is formed by the action of caustic soda or potash on potash alum. Schlumberger[3] added 4.5, 5.0, and 6.0 mols of KOH to solutions each containing one mol of aluminum sulphate as alum. The supernatant liquid was distinctly acid in the first case; in the second case it was neutral and contained no salt of aluminum. The third solution was alkaline and contained some aluminum, presumably as potassium aluminate. Since the precipitate from the second solution analyzed $(Al_2O_3)_2$-$SO_3.7H_2O$, Schlumberger wrote the formula of the basic salt as $(Al_2O_6H_6)_2.H_2SO_4$. He analyzed only the precipitate thrown down by adding five mols of caustic potash to one of alum and consequently had no proof that he was really dealing with a compound. There was nothing in his experiments to prove that the precipitate, formed on adding two, three, or four mols of caustic potash had the same composition.

The following experiments were made to test this point. Forty-six grams of potassium alum were dissolved in distilled water to make two liters and this was divided equally between

[1] "A Manual of Dyeing," 58 (1910).
[2] Bancroft: Jour. Phys. Chem., **26**, 512 (1922).
[3] Bull. Soc. chim. France, [3] **13**, 41 (1895).

two two-liter beakers. To the first was added a quantity of sodium hydroxide equivalent to two mols, and to the second an amount equivalent to four mols. It is of course of no importance whether the sodium hydroxide was or was not exactly equivalent to two and four mols. The sodium hydroxide was added slowly at room temperature with constant stirring. The precipitates were allowed to settle and were washed by decantation with distilled water, the wash water being tested for sulphates. It was found that the precipitates went into colloidal suspension before the last small trace of sulphate was removed. Since it was desired to have some material left for analysis, the precipitates were not washed until the wash water gave no test for sulphate. The washing was discontinued just before the state of complete colloidal suspension occurred; but the amount of free sulphate remaining can be considered as negligible. Schlumberger washed less than this and also left in traces of removable sulphate. After the washing the precipitates were filtered and then dried to constant weight in an electric oven at 100°–110°. The dry precipitates were placed in clean, dry, labelled, sample bottles and were analyzed for $Al_2O_3$ and $SO_4$.

The $Al_2O_3$ content was determined, as Schlumberger did, by heating a weighed sample in a weighed porcelain crucible to constant weight over a blast lamp.

The $SO_4$ content was determined by precipitating the sulphate as barium sulphate by means of barium chloride. A weighed portion of the finely powdered sample was dissolved in 500 cc of a fairly concentrated solution of hydrochloric acid. It is important to be certain that all of the sample is dissolved. The solution was then diluted and boiled for several minutes, after which a solution of barium chloride, sixty grams per liter, was added slowly and with constant stirring as long as any precipitate was formed. The precipitated barium sulphate was digested for thirty minutes at a temperature just below boiling, the solution being stirred frequently. The precipitate was then allowed to settle completely and the clear supernatant liquid was then decanted

through an ashless filter paper. The precipitate was washed by decantation until the wash water gave no test for chlorides, after which it was transferred completely to the filter paper.

The moist precipitate and filter paper cone were placed, with the apex of the latter up, in a weighed porcelain crucible which was heated carefully until all the moisture had been expelled, after which it was heated at a low red heat in a Bunsen burner until the ash became white. The crucible was allowed to cool, and a drop of concentrated sulphuric acid was added to change back to barium sulphate any barium sulphide that might have been formed by reduction of the barium sulphate. The crucible was then heated very carefully until the excess sulphuric acid had been driven off and finally at a low red heat for ten minutes. It was then cooled in a desiccator and weighed.

All determinations were made in duplicate. The results of the analyses are given in Table I

TABLE I

| Run no. | Mols NaOH added | Average % $Al_2O_3$ | Average % $SO_3$ | % $H_2O$ by difference |
|---|---|---|---|---|
| 1. | 2 | 51.2 | 23.6 | 25.2 |
| 2. | 4 | 51.3 | 23.8 | 24.9 |

It was found that a lower percentage of alumina is obtained (49.54%) if the sample taken for analysis is pulverized. Apparently it is not easy to drive off the last traces of sulphate if the material is at all coarse. While this seems to point to a still lower value as the true one, there may be a balancing of errors, as there might easily be some alumina going off as smoke if the particles were extremely fine. Since the problem was not to determine the best method of analyzing for alumina, it was decided to take 50.0% as the true value, which, with 23.7% for $SO_3$, gives us 26.3% by difference for the water. This corresponds well enough to the formula $5Al_2O_3.3SO_3.15H_2O$ or $Al_2(SO_4)_3.(Al_2O_6H_6)_4.3H_2O$ as is shown in Table II.

TABLE II

| | $Al_2O_3$ | $SO_3$ | $H_2O$ |
|---|---|---|---|
| Calculated for $(Al_2O_3)_5.(SO_3)_2.15H_2O$ | 50.0 | 23.5 | 26.4 |
| Found by analysis | 50.0 | 23.7 | 26.3 |

If one prefers to take 49.5% for alumina and consequently 26.8% for water, the results can be represented approximately by the formula $8Al_2O_3.5SO_3.25H_2O$ as shown in Table III.

TABLE III

| | $Al_2O_3$ | $SO_3$ | $H_2O$ |
|---|---|---|---|
| Calculated for $(Al_2O_3)_8.(SO_3)_5.25H_2O$ | 49.0 | 24.0 | 27.0 |
| Found by analysis | 49.5 | 23.7 | 26.8 |

The important thing is not the actual composition; but that, when the analyses are made in the same way, we get the same composition regardless whether two or four mols of caustic soda are added. This shows that the precipitate is a phase of practically constant composition over this range of precipitation. When the precipitation was made at 60°, the results were the same.

Schlumberger's data are given in Table IV.

TABLE IV

| | $Al_2O_3$ | $SO_3$ | $H_2O$ |
|---|---|---|---|
| Calculated for $(Al_2O_3)_2.SO_3.7H_2O$ | 49.76 | 19.51 | 30.73 |
| Found by analysis | 49.95 | 18.75 | 31.30 |

The molecular ratio of $Al_2O_3$ to $SO_3$ is 2.0 with Schlumberger and either 1.66 or 1.6 in the work reported here. If either of the latter figures is right, Schlumberger added too much alkali and consequently had some alumina mixed with his basic salt. That would bring his sulphate determination low. Since he did not check his results in any way, beyond saying that the supernatant liquid was neutral when he had added five mols of caustic soda, this is probably where he went wrong. If there were a slight adsorption of alkali by the basic salt, that would account for all his results.

Since the ratio of alumina to sulphate is constant over a range of concentration and of temperatures, we must call the precipitate a basic salt for the present, because the constancy of composition is our criterion when dealing with non-volatile constituents. We can apply another test, however, to the water. The original plan was to determine the rate of evaporation[1] by putting the finely powdered material on a weighed watch-glass in a desiccator over concentrated sulphuric acid and observing the rate of loss in weight. This experiment failed because the precipitate lost only about 2.5% of its weight instead of approximately 26%. This means that, after the first small loss, the vapor pressure is lower than that of concentrated sulphuric acid.

A sample of finely powdered material was next placed in an open bottle and heated in a sand bath at 200° for an hour. The loss of weight was 25.8% which means that all the water was driven off. A second experiment was tried at 150°, weighing the sample every fifteen minutes. Most of the water—over 90% of the total—was driven off in the first quarter of an hour, and 25.6% was lost in two hours heating, which is not what one would expect from a definite chemical compound. Instead of repeating this experiment at 125° for instance, the sample which had been dried at 150° was moistened with distilled water and then dried in the electric oven at 100°–110° to see whether it went back to the original value. The sample would not take up as much moisture as it had lost. After moistening and drying several times, the sample had gained only 7.4 mg, whereas it had lost 25.6 mg. We are therefore not dealing with a reversible hydrate and it seems simpler to postulate that the water is adsorbed water and not water of crystallization. If the product sinters somewhat on drying it would not take up as much water as it had lost. We have a similar case with hydrous cupric oxide, which analyzes pretty closely for $CuO.H_2O$, and has a negligible vapor pressure at ordinary temperature; but which sinters spontaneously even under water and changes to black cupric oxide. The

[1] Richards: Zeit. anorg. Chem., **17**, 165 (1898).

conclusion that we are dealing with adsorbed water is not necessarily binding because it has been shown that the definite hydrate, $Al_2O_3.3H_2O$, is not formed again after dehydration; but takes up water[1] by adsorption. While it would have been very interesting to have settled this point one way or the other, this lay outside the scope of the present investigation.

The fact that a basic sulphate is formed under these conditions with a molecular ratio of $Al_2O_3$ to $SO_3$ of about 5:3 does not prove that this basic sulphate is adsorbed by wool and the experiments by Paddon[2] show no signs of it; but he found that more sulphate was adsorbed than alumina so that it is not impossible that the wool may have taken up a basic sulphate plus sulphuric acid instead of alumina plus sulphuric acid. Some method will have to be devised which will enable us to distinguish between these two cases.

This work has been carried on under the direction of Professor Bancroft and was made possible by a grant from the Chemical Foundation.

The general results of this paper are as follows:

1. When 2–4 mols of caustic soda are added to one mol of potash alum, the precipitate has a constant composition, corresponding about to the formula $Al_2(SO_4)_3.(Al_2O_3)_4.15H_2O$.

2. The substance $(Al_2O_6H_6)_2.H_2SO_4$, obtained by Schlumberger on adding five mols of caustic potash to one mol of potash alum is a mixture because he added too much potash.

3. The substance $Al_2(SO_4)_3.(Al_2O_3)_4.15H_2O$ loses less than ten percent of its water over concentrated sulphuric acid at ordinary temperature. Practically all the water is driven off by heating at 150°; but less than a third of it is taken up again at lower temperatures, so the substance is not a reversible hydrate.

*Cornell University*

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[1] Milligan: Jour. Phys. Chem., 26, 247 (1922).

[2] Jour. Phys. Chem., 26, 790 (1922).

# NEW BOOKS

**Oxidations and Reductions in the Animal Body.** *By H. D. Dakin. Second edition. 25 × 16 cm; pp. ix + 176. New York and London: Longmans, Green and Co., 1922. Price: $2.00.*—In the preface to the first edition the author said "the statements that fats and sugars are oxidized in the body to carbon dioxide and water, while proteins yield urea in addition, are no longer considered all-sufficient explanations of the chemical rôle of these substances in animal economy. The study of chemical structure is rapidly changing the whole aspect of biological science, and we may look forward confidently to the time when the orderly succession of chemical reactions constituting the activities of the living cell will be resolved into their individual phases."

In the preface to the second edition he says: "It has become increasingly clear in recent years that the oxidations and reductions occurring in the living body are interwoven so closely with other types of reaction, especially condensation and hydrolysis, that it would seem that their consideration apart from other metabolic changes was becoming unduly artificial and could not be justified much longer."

The chapters are entitled: introduction; the nature of the oxidizing and reducing agents of the body; methods of investigation; the normal, saturated, fatty acids; the unsaturated acids; the fatty acids with branched chains; the dibasic acids; the $\alpha$-amino acids, $\alpha$-hydroxy acids, and $\alpha$-ketonic acids; phenylalanine, tyrosine, tryptophan, and other related substances; the oxidation and reduction of amino acids by micro-organisms; the carbohydrates; the purine derivatives; hydrocarbons, phenols, alcohols, aldehydes, amines, and indole derivatives.

There are many passages in the book which will be of great interest to the chemist who is not directly interested in physiology. The appeal is therefore to a much larger audience than one might happen to think from the title.

"Three independent studies on the oxidation of paraffins and especially paraffin wax have recently been published by Kelber, Fischer and Schneider, and by Grün. The results appear of great significance from many points of view. It is found that paraffin wax which is so resistant to most oxidising reagents is readily oxidised at temperatures varying from 140°–170° by ordinary air or oxygen. Catalysts are apparently unnecessary and many of them have a negative action, though manganese and iron appear to favour the change. The reaction is of course strongly exothermic and if it is not carefully controlled the carbon atoms are burned successively away so that a whole series of fatty acids are formed from those of high molecular weight down to acetic and formic acids and finally carbon dioxide. Fischer and Schneider obtained principally normal fatty acids with an odd number of carbon atoms, $C_{13}H_{26}O_2$, $C_{15}H_{30}O_2$, $C_{17}H_{34}O_2$ and $C_{19}H_{38}O_2$, while Kelber obtained mostly acids with even numbers of carbon atoms. The successive burning away of pairs of carbon atoms illustrated by Fischer and Schneider's results is of extraordinary interest in connection with fatty acid catabolism in the body. It should be noted also that hydroxyl acids and also acetone are products of the reaction just as they are found to occur in animal fatty acid

metabolism. Kelber states that the same type of oxidation may be carried out starting with stearic acid instead of paraffin; and it is eminently desirable that experiments along these lines should be extended for they promise to throw much light on the analogous oxidation of fatty acids *in vivo*." p. 5.

"Largely owing to the work of Bach and Chodat it has been commonly assumed that the oxidases concerned with biochemical oxidations represent systems composed of a superoxide formed by the union of ordinary oxygen with an 'oxygenase' together with a catalyst (peroxidase) capable of acting upon it with production of active oxygen of high potential. The marked individuality of the animal as well as some of the vegetable oxidases makes it appear likely that both the peroxide and peroxidase must bear a special relation to the substance undergoing change. The specific character of animal oxidations is most remarkable, especially when phenomena such as those presented by diabetes and alcaptonuria are concerned. In these conditions oxidation of a single readily oxidizable product of metabolism (glucose, homogentisic acid) may be completely restrained without in the least impairing the capacity of the body for effecting the oxidation of other substances.

"Within recent years other evidence has been secured in favour of the belief of the formation of unstable superoxides as the active oxidizing reagents of the body. If the hypothesis of superoxide formation is correct, one would expect a certain similarity between the oxidations effected in the body and those brought about by the simplest superoxide, namely hydrogen peroxide. As a matter of fact, an extraordinarily close similarity as regards the types of reaction exists between the two sets of phenomena. Thus the normal saturated fatty acids in the body undergo oxidation in the $\beta$-position, butyric acid yielding acetoacetic acid—a truly remarkable change.

"Hydrogen peroxide alone of all the various chemical oxidizing agents brings about precisely the same reaction:

$$\underset{\text{(Butyric acid)}}{CH_3.CH_2.CH_2.COOH} \longrightarrow \underset{\text{(Acetoacetic acid)}}{CH_3.CO.CH_2.COOH}$$

"Hydroxy acids, such as lactic acid and $\beta$-hydroxybutyric acid, are oxidized to ketonic acids, both in the body and by hydrogen peroxide:

$$\underset{\text{($\beta$-Hydroxybutyric acid)}}{CH_3.CHOH.CH_2.COOH} \longrightarrow \underset{\text{(Acetoacetic acid)}}{CH_3.CO,CH_2.COOH}$$

"Amino acids and ketonic acids, such as leucine and phenylpyruvic acid, are oxidized to lower fatty acids with liberation of carbon dioxide and either ammonia or water:

$$\underset{\text{(Leucine)}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH_2.CH_2.CH(NH_2).COOH} \longrightarrow \underset{\text{(Isovaleric acid)}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH_2.CH_2.COOH} + NH_3 + H_2O$$

"Glycerol may be oxidized by hydrogen peroxide to glyceric aldehyde or dihydroxyacetone. The same reaction is believed to occur in the body:

$$\underset{\text{(Glycerol)}}{CH_2(OH).CH(OH).CH_2(OH)} \longrightarrow \underset{\text{(Glyceric aldehyde)}}{CH_2(OH).CH(OH).CHO}$$

"Glucose may be oxidized in the body to glucuronic acid, while hydrogen peroxide is the only reagent capable of effecting this change outside the body:

$$\underset{\text{(Glucose)}}{CH_2OH.(CHOH)_4.CHO} \longrightarrow \underset{\text{(Glucuronic acid)}}{COOH.(CHOH)_4.CHO}$$

"Benzene is oxidized in the body to phenol, catecohl, and quinol, and precisely the same change is brought about by hydrogen peroxide, but by scarcely any other reagent. Indole is oxidized to indoxyl in the body while no reagent other than hydrogen peroxide has been observed to bring about this change *in vitro*.

"A great many other biochemical reactions of less strikingly characteristic types such as the oxidation of simple alcohols, aldehydes, acids, etc., may be reproduced *in vitro* by means of hydrogen peroxide.

"An additional point of similarity between the types of oxidation effected by the animal tissues and by hydrogen peroxide is seen in the behaviour of the saturated and unsaturated acids. In the animal body the unsaturated acids, e. g., oleic acid, occur along with the corresponding saturated acids, and there does not appear to be a very profound difference in the ease with which the two types of acids undergo oxidation in the living organization. Indeed, in the case of some of the simpler acids the saturated acids appear to be more readily oxidized in the body. When these saturated and unsaturated acids are subjected to oxidation with most of the common laboratory reagents, the unsaturated acids are, of course, infinitely more readily oxidized than are the saturated acids, which appear remarkably stable. But if hydrogen peroxide be chosen as oxidizing agent, and is allowed to act on the neutral salts of the saturated and unsaturated acids under comparable conditions, it is found that they both undergo oxidation to not widely different extents," p. 10.

"Thunberg (1920) made some highly suggestive studies on the oxidation or rather dehydrogenation of intermediary products of metabolism. He found that when the finely chopped muscle of a freshly killed frog is thoroughly washed with water it loses its power to reduce methylene blue in the absence of oxygen. When, however, certain metabolites which do not themselves reduce the dye are added to the washed muscle the power to decolorize the methylene blue is restored wholly or in part. The change is represented by Thunberg as due to the action of specific enzymes which have the power to effect the removal of hydrogen from the metabolite and transfer it to the methylene blue which is then reduced. The ferments are given the generic name of 'Hydrogentransportases.' Under normal conditions the hydrogen is supposed to be burned to water or used for the reduction of other compounds. The specificity of the enzymes is rather unconvincingly inferred from their unequal resistance to thermal changes. Thunberg regards all food substances as essentially 'hydrogen donators' and hydrogen is regarded as the common fuel of tissue combustions. Dehydrogenation, the addition and removal of water and the splitting off of carbon dioxide are regarded as the fundamental catabolic changes undergone by substances containing carbon, oxygen and hydrogen. The fact that many metabolites react with washed muscle tissue in the way described is certainly an interesting phenomenon; but whether, as Thunberg appears to suggest all substances so reacting are thereby of necessity to be regarded as intermediary metabolites with specific 'hydro-

gentransportases' to act upon them, appears much more doubtful. Indeed an inspection of Thunberg's results with analogously constituted substances only serves to increase the reviewer's hesitation in accepting the method as a means of deciding whether a substance is an intermediary metabolite or not. But whatever the outcome may be it is clear that Thunberg has hit upon an interesting mode of experimentation which should lead to further results of value," p. 18.

"The direct formation of an unsaturated acid from a saturated one requires the removal of two atoms of hydrogen. Such a reaction today appears much less extraordinary since the clear proof afforded by Wieland that many oxidations involve not an activation of oxygen but rather of hydrogen which is then taken up by a suitable acceptor or catalyser. Wieland's theory of dehydrogenation fits in admirably with the idea that unsaturated acids may be formed by the oxidation of saturated ones, although directly analogous reactions have not yet been carried out in the laboratory. The change appears, however, to have been shown to occur in the body. Battelli and Stern in 1910 showed that some animal tissues, especially muscle, in contact with oxygen, could rapidly effect the oxidation of succinic acid. They identified malic acid as a product of the reaction. Later investigations by Einbeck have shown with a considerable degree of certainty that fumaric acid is first produced and that this acid secondarily takes up water with formation of malic acid. The production of fumaric acid appears to be quantitative, while its subsequent conversion into malic acid takes place to the extent of about seventy-five percent. The reaction may be represented as follows.

$$COOH.CH_2.CH_2.COOH \longrightarrow COOH.CH{=}CH.COOH \rightleftharpoons COOH.CHOH.CH_2COOH$$

"The ease with which succinic acid is oxidised by muscle tissue is the more remarkable when its great resistance to ordinary chemical oxidising reagents is considered," p. 40.

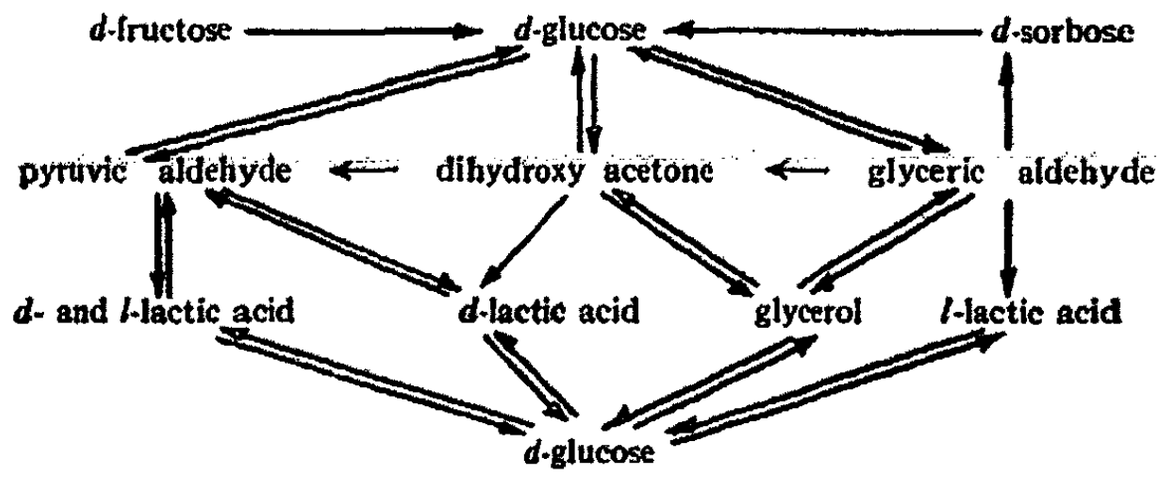
"Leathes and Meyer Wedell have shown that on feeding animals with oils or fats containing unsaturated acids, fats accumulate in the liver, the fatty acids of which, judged by their iodine values, are even more unsaturated than those contained in the food. But there are two possible explanations of this phenomenon. Either new double linkages are introduced into the fatty acid molecule by oxidation, or structurally isomeric unsaturated acids which absorb iodine more readily are formed by intramolecular rearrangement," p. 41.

"Lactic and malic acids are the only hydroxy acids which are known to give glucose in the animal body and it is not improbable that malic is converted into lactic as a first step. The fact that both *d*- and *l*-lactic acids, as well as *d*- and *l*-alanines are transformed quantitatively into glucose in the diabetic organism lends support to the hypothesis that some common, optically inactive, intermediate product, such as pyruvic aldehyde or dihydroxyacetone, is concerned in the process. The discussion of these possibilities is reserved for the section on carbohydrates," p. 77.

"It has long been recognised that the hexoses containing six carbon atoms could be converted into substances containing three carbon atoms by a variety of processes, while conversely the synthesis of certain hexoses could be effected by condensation of two molecules of certain substances containing three carbon

atoms. The formation of lactic acid by the action of alkali upon glucose and the synthesis of fructose and sorbose by the action of dilute alkali upon glyceric aldehyde (Schmitz) may be cited as examples of these changes. It appears that reactions of this type are of great importance in carbohydrate metabolism," p. 108.

"By combining the results obtained by experiments *in vitro* and *in vivo*, especially those occurring in the perfused liver or the diabetic organism it appears that the equilibria or reactions shown in the following diagram have been fairly satisfactorily demonstrated. The actual isolation of glyceric aldehyde and dihydroxyacetone from glucose has not been accomplished; but their formation, transitorily at any rate, can hardly be doubted from the results of the experiments on the action of alkali on glucose already referred to.




"The above representation is non-committal as regards the actual course of glucose metabolism. For this purpose the reader will be able to construct a diagram according to his own predilection showing any or all of the possible metabolites or may reject any such attempts at rigid representation," p. 114.

*Wilder D. Bancroft*

**A Dictionary of Applied Chemistry.** *By Sir Edward Thorpe. Vol. IV. 23 × 16 cm; pp. viii + 740. New York and London: Longmans, Green and Co., 1923. Price $20.00.*—The editor keeps up the surprising rate of publication and the fourth volume is now ready. Among the subjects included in it are: lac dye, lacquer, lactic acid, lakes, lampblack, lanthanum, lard, lead, leather, lecithin, lichens, linseed oil, lipase, liquefaction of gases, liqueurs, lithium, litmus, logwood, lubricants, madder, magnesium, malonic acid, manganese, margarine, matches, meat extract, melting point, mercaptans, mercerising, mercury, metallography, methyl, methyl anthracene, methylene blue, mica, milk, molybdenum, mustard, naphthalene, neodymium, nephelometry, nickel, niton, nitrogen, octyl, odour, oils, oleo-resins, olive oil, opal, opium, oxalic acid, oxydases.

Although one knows that lakes do not have anything to do with water, there is always a thrill when one reads that the word comes from the Indian 'lac' or 'lakh' which means a hundred thousand and refers to the immense numbers in which the lac insects appear at certain seasons on the trees infested with them.

It is rather interesting to learn, p. 126, that the essential difference between linseed oils from different localities is one of impurities and is not primarily a question of soil or climate. "Two qualities of Russian seed are recognised in the

trade, known according to their source as Baltic and Black Sea seed; hence the terms 'Baltic linseed oil' and 'Black Sea linseed oil.' The oil expressed from Indian seed is known as 'East India oil.' The Baltic linseed yields the best drying oil; this is explained by the fact that the Baltic seed is the purest, whereas in Black Sea seed five percent (and more) of hemp seed and (or) ravison seed are usually present. Indian seed is frequently mixed with mustard, rape, and cameline seed, owing to the plants yielding the latter being grown along with the flax plant. It has been proved that, when the Indian linseed is separated carefully from the foreign seeds and then expressed, the oil possesses as good drying properties as the best Russian oil."

"Madder is the ground root of the *Rubia tinctorium* (Linn.), which has been cultivated for dyeing purposes from a remote antiquity, so remote indeed that one is unable to say with certainty in which countries it originated. It is known to have been employed by the ancient Egyptians, Persians, and Indians, probably by the last in the first instance, and more recently by the ancient Greeks and Romans. About the time of the Crusades the cultivation of madder was introduced into Italy and probably also into France. The Moors cultivated it in Spain, and it was brought to Holland during the sixteenth century. Colbert introduced it into Avignon in 1666, Frantzen into Alsace in 1729; but only towards 1760–1790 did it become important. During the wars of the Republic, its cultivation was largely abandoned, and only after 1815 did this again become regular.

"Owing to the beauty and fastness of the tints it yields, and the range in colour that can be produced from it by a variation in the mordant, it was considered until recently as perhaps the most important of all dyestuffs. Although its commercial value has been reduced greatly through the introduction of artificial alizarin, it has still considerable scientific interest, " p. 176.

Few of us know about the early history of matches, p. 228. "In 1816, friction matches tipped with a composition containing phosphorus are stated to have been manufactured in Paris by Francois Derosne, who by Gintl and others is regarded as the first maker of the phosphorus friction-match. The year 1823 is marked by the invention of the Döbereiner lamp, already referred to. About this time, too, were used, at Erfurt in Prussia, small glass tubes containing equal quantities of phosphorus and sulphur carefully fused together, into which thin sticks or splints of wood were introduced, easily inflamed afterwards by friction. The early attempts to make friction matches in Paris and elsewhere appear to have failed completely; and the honour of having invented, in 1827 or earlier, the first practical and useful matches ignitable by friction, indisputably rests with an Englishman, John Walker, of Stockton-on-Tees, Durham (d. 1859). Walker was an apothecary, who had been apprenticed to a local surgeon before starting in business as a druggist. He was much interested in experimental chemistry, and for some years prior to 1827 had been preparing and selling, under the name of 'percussion powder,' dried mixtures of potassium chlorate and antimony sulphide, made up with gum water. Eventually it occurred to him to dip splinters of wood into such a composition, and to supply these matches in tin boxes, together with a piece of folded glass-paper, under the name of friction-lights."

Under metallography we read that another method for determining cooling-curves, "which has been worked out and adopted at the National Physics Laboratory, avoids any attempt to control the rate of cooling or heating a furnace but

utilises a furnace consisting of a long tube which is kept hot at one end and cold at the other; the specimen under observation is moved along this tube by mechanical means at a constant rate and is thus heated or cooled at a correspondingly constant rate. These 'gradient furnaces' have given very good results, and they have the considerable advantage that the rate of heating or cooling can be varied at will so as to suit different purposes."

One is always interested in any theory in regard to the hardening of steel whether one agrees with it or not, p. 299. "The simplest and most logical explanation of the phenomena of hardening in quenched steel is based on what has come to be known as the 'amorphous theory' of metals. This theory is based on the hypothesis first put forward by Beilby that metals, while ordinarily crystalline, may under certain conditions exist in a non-crystalline or amorphous state in which their properties resemble those of hard, brittle vitreous bodies such as glass or fused silica. Such amorphous metal never exists in considerable masses, but is formed as the result of mechanical disturbance of crystalline arrangement or remains as a very thin residual layer where adjacent growing crystals meet, acting—in the latter case—as an intercrystalline cement holding the crystals together. The strength and hardness of this cementing layer accounts for the fact that in pure metals the crystal junctions are stronger than the crystals themselves, so that the metal becomes stronger and harder the greater the number of junctions, i. e., the smaller the scale of the crystal structure. In the extreme case, where the crystals themselves are little more than incipient nuclei, we should have the maximum amount of junction area and—according to the amorphous theory—the largest amount of hard, amorphous metal, so that the metal would attain its maximum hardness in that condition. Now this is precisely the condition which may be expected to arise during the quenching of steel. The transformation from $\gamma$ iron to $\alpha$ iron takes place, during slow cooling, but the development of a number of small $\alpha$ crystals which grow larger and absorb more and more of the $\gamma$ iron. When cooling becomes very rapid, however, there is no time for the growth of these $\alpha$ crystals, and in these circumstances a very much larger number of $\alpha$ nuclei would come into existence, but each would remain little more than a nucleus, surrounded by its layer of amorphous cement. The fullest hardness would thus be attained if the rate of cooling and other conditions were such that the whole volume of the steel was finally occupied by these minute or incipient $\alpha$ crystals merely separated from one another by films of amorphous metal. In any actual case, however, the size of the developed $\alpha$ crystals, and the number of nuclei formed, would vary even in different parts of a single original $\gamma$ crystal, thus giving rise to the acicular structure of martensite, which is undoubtedly related to the crystalline planes of the austenite from which it is derived. On this theory, the hardness of quenched steel is ascribed to the presence in it of a relatively large amount of amorphous metal, thus correlating the hardness obtained by quenching with the hardness produced by plastic deformation ('cold work') and with the hardness of such substances as glass. It is interesting to note that both quench-hardened and work-hardened metals are softened by tempering and annealing, and that when hardness of either kind is extreme it is liable to undergo slight changes even at the ordinary temperature ('ageing'). Finally, it may be pointed out that the magnetic properties of hardened steel are readily accounted for by the 'amorphous' theory; the nuclear crystals of $\alpha$ iron

are the seat of permeability and 'remanence,' while the high coercive force or magnetic hardness is due to the fact that the magnetic atoms (or molecules) of $\alpha$ iron lie tightly embedded in the hard and unyielding amorphous cement which hinders re-arrangement of any kind, whether under the action of mechanical forces (hardness) or under the action of magnetic forces ('coercivity')."

Some unfamiliar facts in regard to mica are to be found on p. 361. "The mica of commerce comes mostly from India, the United States, and Canada; the Canadian being the brownish magnesian mica phlogopite, known in the trade as 'amber.' Large sheets of sufficient purity to be profitably worked are of very limited occurrence; they are usually found in veins of pegmatite or giant granite, where the constituents crystallise on a large scale, and are often associated with rare minerals such as beryl and columbite. In India the chief mica-mining districts are those of Hazaribagh in Bengal and of Nellore in Madras; from the former the mica (muscovite) is usually of a pale ruby tint, and from the latter of a greenish shade. In the Inikurti mine, Nellore, 'books' of mica measuring 10 feet across the basal plane and up to 15 feet across the folia have been found. Rectangular sheets measuring 30 × 24 inches and free from flaws have frequently been obtained. A single mica crystal from North Carolina has been known to weigh nearly 2000 pounds. Mica has been worked at Alstead, in New Hampshire, where sheets have been found measuring 4 feet across."

Under milk the conclusion is drawn, p. 364, that it is certain that the only membrane is a liquid layer condensed round the fat globules by surface tension. This does not seem to mean anything. The flaw in the reasoning is that Mr. Richmond does not realize that one can emulsify liquids with finely divided particles, such as carbon black. His only alternatives appear to be a coherent, solid sheath and an unspecified liquid film.

Under odours, p. 627, we read that "in order that an odoriferous substance may be detected by the nose, it is essential that the substance should be volatile. Although the conditions which produce odour and volatility are frequently the same, it is possible to have a volatile substance, such as water, entirely without smell, so that it is clear that the conditions which produce odour and volatility are not identical. Since ammonia, with a molecular weight less than that of water, is odorous, the lack of odour in water cannot be explained by assuming that the molecular weight of water is below a limiting value necessary to produce odour; the nasal nerve endings being soaked in water are probably unaffected by it. It is possible that a substance, apparently odourless, might possess a chemical constitution which would condition odour if the substance could be obtained in a volatile state at a temperature suitable for examination. The limits of sensitiveness of odours and emanations were investigated by Berthelot, who found that the odour of iodoform is detectable when 1 gram of the substance loses $^1/_{10}{}^{12}$ gram per hour; in one hundred years the loss from 1 gram under the conditions of the experiment would be less than 1 mg, and with musk the loss of weight associated with the perception of odour is 1000 times less."

"Turkey-red oil is a fatty substance used in the preparation of the cotton fibre for dyeing and printing Turkey-red. The part which the Turkey-red oil plays is not fully understood; opinions differ as to whether it exercises a physical or a chemical action. The advocates of the former explanation assume that the oil protects the lake formed on the fibre, much as boiled linseed oil serves to

protect a painted surface. The supporters of the chemical theory hold that the Turkey-red oil combines with alumina and finally with the colouring matter to form a compound lake. In those cases, however, where chemical combination with formation of a lake is excluded on account of the chemical constitution of the colouring matter, the physical theory appears to commend itself. Hence Turkey-red oil is not a mordant proper, but acts as a fixing agent in so far as it imparts to the dyed fabric a better and superior lustre, which does not belong to the unoiled fibre. The sulphonated oils would appear to the author to be absorbed by the fibre in the same manner as glycerol (from soft soaps) is fixed on the fibre on washing woollen goods."

The reviewer was not aware that "the outer skins of onion bulbs which are of a brownish orange colour have long been used in Germany for dyeing Easter eggs yellow, and, in conjunction with alum, for dyeing woollen, line, and cotton materials. From Kurrer's observations onion skins are very suitable for dyeing cotton, on which they give a cinnamon-brown with acetate of alumina, a fawn with alumina and iron salt, and a variety of shades with other conditions."

On p. 739 we read that "peroxydases and catalases are so widely distributed in living tissues that their presence might almost be used as a test for vital activity. They are characterised by great stability: thus the peroxydase of horse-radish is not entirely destroyed when its solution is boiled for a short time. The activity of a weak oxydase is increased greatly by a peroxydase, more especially by that from the same source as itself. They gradually lose their activity during the oxidations which they bring about.

"Peroxydases appear invariably to contain manganese and Bertrand has shown that the oxidising power of laccase is proportional to the amount of manganese present; further, that the addition of a small amount of manganese increased greatly the oxidising power of lucerne laccase. He therefore regards manganese as the co-ferment of laccase in the same way as hydrochloric acid is the co-ferment of pepsin. The manganese cannot be replaced by other metals in the case of laccase, but iron and other metals have similar functions with other enzymes. Colloidal suspensions and solutions of these metals have been shown to form artificial peroxydase systems. The subject is a complex one."

The article on leather is almost a monograph in itself and, at that, it only takes sixteen pages as against one hundred and seven for naphthalene. The reviewer believes that under lacmoid and litmus the pH values for the color changes should have been given. *Wilder D. Bancroft*

**Histoire de la Chimie.** *By Maurice Delacre. 23 × 14 cm; pp. xv + 632. Paris: Gauthier-Villars et Cie, 1920. Price: 24 francs.*—Except for the last few pages the book does not come down beyond 1860, so that it is really a history of the early development of chemistry. The point of view is rather that of Carlyle. If you know about the great men that is sufficient. The author's other striking characteristic is given explicitly by himself in the preface. "I have made war on hypotheses. I have forced myself always to worship the facts. I have lived so much *myself in* the midst of theories and have had to teach them so much that I have acquired an irresistible aversion to them. I felt this aversion without being able to justify it. Now that my book is finished, I am completely satisfied because my scepticism is justified by history."

Speaking of dualism, p. 409, the author says that "one cannot upset an established theory, no matter how poor it is, by words no matter how good they are. New facts are necessary." The reviewer believes that a theory can never be upset by facts but only by another theory. The phlogiston theory was overthrown by the oxygen theory and not by the facts. Until a new and better theory makes its appearance, most people hope that the discrepant facts will eventually be harmonized and they are right in this. Chaos is a hopeless state, though the author does not agree. He will not admit that a theory is valuable so long as it is fruitful. He considers the phlogiston theory as thoroughly bad, because it was wrong; but most people will consider that the phlogiston theory was a distinct step forward at one time.

The subject is divided into fifteen chpaters: antiquity and philosophy; the Middle Ages and alchemy; the experimental reformation; Stahl's phlogiston; the chemistry of Lavoisier; the law of definite proportions; the period of Davy and the laws of state; the period of Dumas; substitution, the nuclei of Laurent, and the types of Dumas; the reforms of Gerhardt and Laurent; Williamson, Kolbe, and Frankland; Gerhardt's theory of types; valence; definitive chemical formulas; organic chemistry since 1860.

The book is written in an entertaining fashion and gives a number of brief but interesting biographical sketches. The personal bias comes out very strongly in the epilogue, p. 617. "Wurtz has told us that we should cling to a hypothesis so long as it enables us to interpret the facts faithfully, to group them, to tie them together, and to predict new facts; in other words, as long as it proves fruitful. Such a hypothesis rises to the rank of a theory... He believes theories necessary to the progress of science. What great discovery has not been the result of theoretical ideas and has not given rise to new ones?"

The author then asks what theories have shown their fruitfulness. "Greek science was nothing but theory; so were the doctrines of the Middle Ages; purely theoretical was phlogiston, a conception of a deep and general truth; but systematized in a detestable and obstructive manner, which annulled logic on the part of most of the chemists for over fifty years. Where is the theory or even the theoretical idea which served as the starting point for the magnificent experiments of Black? There is none. There is no theoretical idea unless one is willing to give this name to the logical relations which the experimenter tries to establish between the facts which he has proved by his results, in other words to the display of initiative characteristic of all experimental minds."

According to the author Cavendish relied on his superb technique, Priestley made experiments haphazard, and Lavoisier worked from fact to fact. Dalton's atomic weights did not represent either a hypothesis or a theory. They were an idea which was so serviceable to science that it at once became a fact, whereas Berthollet's idea was a theory and did not prove of any value for over fifty years. Berzelius disclaimed all preconceived ideas, p. 620, and Davy was strong against theories. Liebig, like Berthollet, was a theorist and his contributions to science are therefore negligible. Gerhardt and Laurent based their conclusions on good experimental evidence, as did also Ste. Claire Deville. In this way one can prove anything.

Throughout the book the feeling against Germany and German scientific

men is very strong; but one can scarcely criticize the author for that because this book was written in 1916 in Ghent while the city was held by the Germans and is dedicated to M. Fanyan who died in prison at Lille that same year.

*Wilder D. Bancroft*

**The Formation of Colloids.** *By The Svedberg. 19 × 13 cm; pp. viii + 127. New York: D. Van Nostrand Company, 1921. Price: $2.00.*—This is apparently the first of a series of short monographs, this particular one giving "a survey of the processes which cause the formation of colloids. . . .especially with regard to the conditions that determine the degree of subdivision of the systems formed." The author discusses the subject under the three general heads: formation of disperse systems *in vacuo;* formation of disperse systems in gases; and formation of disperse systems in liquids and in solids. To the reviewer the chapter on condensation in a vacuum was practically new. "It is determined to a great extent by the temperature of the walls and of the gas just before condensation takes place. According to Knudson, is seems that a metal molecule which encounters a surface of the same substance always adheres to it. If the surface consists of another material, there is a critical temperature dividing the domain of temperature into two parts. Below this point the molecule adheres to the surface, above it the molecule is reflected. For a glass wall and mercury molecules Knudson found the critical temperature to be about —135°, for glass and silver it is above +575°. Thus mercury vapor adheres without reflection to a glass surface colder than —135°, and silver when it is colder than +575°. . . . .If the glass wall on which condensation is to take place is covered beforehand with a thin film (for example, 10$\mu\mu$ thick) of some salt, no coherent film is formed. . . .In order to prevent the darkening of electric incandescent lamps, the makers have recently begun to cover the inside of the glass globes with very thin films of certain salts, and the result has been very good indeed."

On p. 91 it is reported that a solution of nickel carbonyl in benzene apparently dissociates when boiled, forming a colloidal solution of nickel. As might be expected there is an admirable general presentation of Bredig's arc method of making colloidal metals and of Svedberg's own improvements on it, p. 24. These few references will show that the book is interesting though small.

*Wilder D. Bancroft*

**Übungsbeispiele aus der unorganischen Experimentalchemie.** *By Heinrich Biltz and Wilhelm Biltz. Third and fourth edition. 24 × 16 cm; pp. xii + 242. Leipzig: Wilhelm Engelmann, 1920. Price: 37 marks, paper.*—An earlier edition was reviewed fifteen years ago (12, 140). We now have the third and fourth editions simultaneously. According to the authors there have been changes in No. 31 on cuprous oxide and in No. 39 on iodine from iodide residues. The experiments on complex platinum salts, Nos. 141–143, have been replaced by experiments on hexamminocobaltous chloride and on the two isomers of diamminodichlorocobalt. There is a new experiment on the dissociation of nitrogen peroxide and a new one on the preparation of potassium iodide tetrachloride, $KICl_4$.

*Wilder D. Bancroft*

# RELATIONS CONCERNING THE INTERNAL HEAT OF VAPORIZATION[1]

BY J. E. MILLS AND P. K. SMITH

Under the heading "The Internal Heat of Vaporization" one of the authors discussed, some years ago,[2] the following equations for calculating the internal heat of vaporization:—

1. $\lambda = 0.0_431833 \left(\frac{dP}{dT} T - P\right) (V - v)$ calories.

2. $\lambda = \mu'(\sqrt[3]{d} - \sqrt[3]{D})$ calories.

3. $\lambda = CRT\, ln\, \frac{V}{v} = C\, \frac{4.577}{m}\, T \log \frac{d}{D}$ calories.

Here $\lambda = L - E29 = L - 0.0_431833\ P(V - v)$ calories.

In these equations:

L is the total heat of vaporization of one gram of the liquid.

$\lambda$ is the internal heat of vaporization of one gram of the liquid.

$E_R$ is the energy spent in pushing back the external pressure during the change from liquid to vapor.

T is the absolute temperature.

P is the vapor pressure in millimeters of mercury.

V is the volume of one gram of the saturated vapor.

$v$ is the volume of one gram of the liquid.

$d$ is the density of the liquid.

D is the density of the saturated vapor.

$\mu'$ is a constant for any particular substance. These constants are given in Table 2, under the heading "Average $\mu'$" in the paper cited.

C is a constant for any particular substance. These constants are given in Table 2, under the heading "Average

[1] From a thesis submitted by P. K. Smith in partial fulfillment of the requirements for the degree of Master of Science at the University of South Carolina.

[2] Jour. Am. Chem. Soc., 31, 1099 (1909).

C'' in the paper cited. R is the constant of the gas equation $PV = RT$, and is equal to $1.9878/m$ in units used.

$m$ is the molecular weight of the substance.

Equation 1 is the well known Clausius-Clapeyron thermodynamical equation. Equation 2 is an equation derived by Mills on the supposition that the molecular attraction varies directly as a constant and inversely as the square of the distance apart of the molecules. Equation 3 is an empirical equation discovered by Dieterici. These equations have been studied for thirty-eight substances in the paper above mentioned and in numerous articles there cited. Additional studies have appeared in the articles cited below.[1]

Equation 1 is universally believed to be absolutely accurate per se. Errors are introduced in the measurements of the quantities involved, particularly in obtaining the $\frac{dP}{dT}$ at the end-points of the vapor-pressure curve. Practically, therefore, the equation may give less accurate values than can be obtained from equations 2 and 3.

Equation 2 seems to hold within the limits of the errors of measurement for normal non-associated liquids (theoretically it should not hold for associated liquids) at all temperatures within the saturated vapor-liquid region. Mills believes that it holds true outside of this region but sufficient proof has not yet been obtained to enable such a statement to be made with any certainty.

Equation 3 gives apparently very accurate results for all temperatures within the saturated vapor-liquid region, *except at very low vapor pressures.* At such low vapor pressures the results obtained are too high. The equation is not true for other than the saturated vapor-liquid region.

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[1] Mills: Jour. Phys. Chem., **15**, 417 (1911); **18**, 101 (1914); **19**, 257 (1915); **19**, 650 (1915); **21**, 101 (1917); **21**, 345 (1917); **21**, 623 (1917); Phil. Mag., Oct., 1910; July, 1911; Oct., 1912. Sydney Young: Tabulation and discussion of data in Sci. Proc. Roy. Dublin Society, **12**, 374 (1910). Dieterici: Ann. Phys., (4) **35**, 220 (1911). Steinhaus: Dissertation, Kiel, 1910. Kendall: Meddellanden från K. Vetenskapsakademiens Nobelinstitut, **2**, No. 29, No. 36; Jour. Am. Chem. Soc., **36**, 1620 (1914).

Many relations existing between these equations (and other equations) have been studied in the papers cited. The object of this paper is to throw additional light upon the relation between equations 2 and 3 above. Combining them, we get;

$$4. \quad \mu'(\sqrt[3]{d} - \sqrt[3]{D}) = CRT\ ln\ \frac{d}{D} = CRT\ ln\ \frac{V}{v}.$$

Steinhaus first transformed this equation into the form:

$$5. \quad \mu'\sqrt[3]{d} + CRT\ ln\ v = \mu'\sqrt[3]{D} + CRT\ ln\ V.$$

and studied it for isopentane and benzol in the article already cited. The right-hand side of the equation refers entirely to the liquid and the left-hand side entirely to the saturated vapor. The equation is remarkably accurate, *and gave the entirely unexpected result that the values obtained on both sides of the equation were constant with change in temperature.* Mills published[1] an additional study of the equation for isopentane using revised data. Mills similarly calculated the values for normal pentane and for stannic chloride, but the values have not previously been published. These calculations and similar calculations for nine additional substances made by one of the present authors (Smith) are given in the Tables I–XII.

In inspecting the tables it should be remembered that $2.3026 \log x = ln\ x$. The data used have been taken from the article by Young already cited. The accuracy of equation 5, except at the lowest temperature, as shown by the last two columns in each table is remarkable. There are few divergences from the mean values greater than 0.3%, and none greater than 0.7% except at the very lowest vapor pressure and explanation is offered later of these divergences. A careful study of the equation is important and shows the following facts:—

1. Since the individual values of $\mu'$ and C given in

[1] Jour. Phys. Chem., 19, 268 (1915).

TABLE I
Ethyl Oxide

| Temperature | $\mu'\sqrt[3]{d}$ | $\mu'\sqrt[3]{D}$ | log $v$ | log V | 2.3026 CRT | CRT $ln\,v$ | CRT $ln$ V | $\mu'\sqrt[3]{d}$ + CRT $ln\,v$ | $\mu'\sqrt[3]{D}$ + CRT $ln$ V, |
|---|---|---|---|---|---|---|---|---|---|
| 0° C | 93.68 | 9.73 | 0.1330 | 3.0825 | 29.055 | 3.86 | 89.56 | 97.54 | 99.29 |
| 20 | 92.71 | 12.78 | 0.1466 | 2.7281 | 31.184 | 4.57 | 85.07 | 97.28 | 97.85 |
| 40 | 91.66 | 16.09 | 0.1615 | 2.4281 | 33.312 | 5.38 | 80.88 | 97.04 | 96.98 |
| 60 | 90.60 | 19.63 | 0.1767 | 2.1694 | 35.441 | 6.26 | 76.88 | 96.86 | 96.51 |
| 80 | 89.43 | 23.44 | 0.1937 | 1.9375 | 37.569 | 7.28 | 72.79 | 96.71 | 96.23 |
| 100 | 88.01 | 27.52 | 0.2143 | 1.7288 | 39.698 | 8.51 | 68.63 | 96.52 | 96.15 |
| 120 | 86.34 | 31.99 | 0.2393 | 1.5326 | 41.827 | 10.01 | 64.11 | 96.35 | 96.10 |
| 140 | 84.41 | 36.87 | 0.2688 | 1.3479 | 43.955 | 11.82 | 59.25 | 96.23 | 96.12 |
| 160 | 82.06 | 42.58 | 0.3056 | 1.1605 | 46.084 | 14.08 | 53.48 | 96.14 | 96.06 |
| 180 | 78.12 | 50.24 | 0.3698 | 0.9452 | 48.213 | 17.83 | 45.57 | 95.95 | 95.81 |
| 190 | 74.23 | 56.55 | 0.4362 | 0.7904 | 49.277 | 21.49 | 38.95 | 95.72 | 95.50 |
| 193 | 71.69 | 60.80 | 0.4814 | 0.6964 | 49.596 | 23.88 | 34.54 | 95.57 | 95.34 |
| 193.8 | 66.41 | 66.41 | 0.5814 | 0.5814 | 49.681 | 28.88 | 28.88 | 95.29 | 95.29 |

$m=74.08$, $\mu'=103.76$, C=1.724, 2.3026 R=.06174

TABLE II
Di-isopropyl

| Temperature | $\mu'\sqrt[3]{d}$ | $\mu'\sqrt[3]{D}$ | log $v$ | log $V$ | 2.3026 CRT | CRT $ln\,v$ | CRT $ln$ V | $\mu'\sqrt[3]{d}$ + CRT $ln\,v$ | $\mu'\sqrt[3]{D}$ + CRT $ln$ V |
|---|---|---|---|---|---|---|---|---|---|
| 0° C | 85.75 | 7.09 | 0.1678 | 3.4156 | 25.031 | 4.20 | 85.50 | 89.95 | 92.59 |
| 60 | 83.36 | 14.78 | 0.2046 | 2.4585 | 30.532 | 6.25 | 75.06 | 89.61 | 89.84 |
| 80 | 82.44 | 17.75 | 0.2190 | 2.2201 | 32.366 | 7.09 | 71.86 | 89.53 | 89.61 |
| 100 | 81.44 | 20.96 | 0.2350 | 2.0035 | 34.199 | 8.04 | 68.51 | 89.48 | 89.47 |
| 120 | 80.34 | 24.34 | 0.2526 | 1.8082 | 36.033 | 9.10 | 65.15 | 89.44 | 89.49 |
| 140 | 79.10 | 27.99 | 0.2730 | 1.6263 | 37.867 | 10.34 | 61.58 | 89.44 | 89.57 |
| 160 | 77.66 | 31.97 | 0.2968 | 1.4533 | 39.701 | 11.78 | 57.70 | 89.44 | 89.67 |
| 180 | 75.86 | 36.44 | 0.3275 | 1.2826 | 41.535 | 13.60 | 53.27 | 89.46 | 89.71 |
| 200 | 73.47 | 41.72 | 0.3691 | 1.1062 | 43.367 | 16.01 | 47.97 | 89.48 | 89.69 |
| 220 | 69.16 | 49.67 | 0.4479 | 0.8791 | 45.201 | 20.25 | 39.74 | 89.41 | 89.41 |
| 225 | 66.70 | 53.49 | 0.4951 | 0.7828 | 45.659 | 22.60 | 35.74 | 89.30 | 89.23 |
| 227.35 | 60.70 | 60.70 | 0.6178 | 0.6178 | 45.874 | 28.34 | 28.34 | 89.04 | 89.04 |

$m=86.112$, $\mu'=97.53$, C = 1.725, 2.3026 R = 0.05315

TABLE III
Di-isobutyl

| Temperature | $\mu'\sqrt[3]{d}$ | $\mu'\sqrt[3]{D}$ | log $v$ | log V | 2.3026 CRT | CRT $ln\, v$ | CRT $ln$ V | $\mu'\sqrt[3]{d}$ + CRT $ln\, v$ | $\mu'\sqrt[3]{D}$ + CRT $ln$ V |
|---|---|---|---|---|---|---|---|---|---|
| 0° C | 78.14 | 3.17 | 0.1486 | 4.3222 | 19.847 | 2,95 | 85.78 | 81.09 | 88.95 |
| 100 | 74.82 | 12.66 | 0.2051 | 2.5205 | 27.117 | 5,56 | 68.35 | 80.38 | 81.01 |
| 120 | 74.06 | 15.20 | 0.2185 | 2.2824 | 28.571 | 6,23 | 65.21 | 80.29 | 80.41 |
| 140 | 73.21 | 17.90 | 0.2335 | 2.0686 | 30.025 | 7,01 | 62.11 | 80.22 | 80.01 |
| 160 | 72.27 | 20.70 | 0.2503 | 1.8791 | 31.479 | 7,88 | 59.15 | 80.15 | 79.85 |
| 180 | 71.25 | 23.60 | 0.2690 | 1.7084 | 32.933 | 8,86 | 56.26 | 80.11 | 79.86 |
| 200 | 70.05 | 26.83 | 0.2910 | 1.5416 | 34.387 | 10,01 | 53.01 | 80.06 | 79.84 |
| 220 | 68.62 | 30.45 | 0.3179 | 1.3766 | 35.841 | 11,39 | 49.33 | 80.01 | 79.78 |
| 240 | 66.79 | 34.71 | 0.3532 | 1.2060 | 37.295 | 13,17 | 44.98 | 79.96 | 79.69 |
| 260 | 64.06 | 40.24 | 0.4076 | 1.0133 | 38.749 | 15,79 | 39.26 | 79.85 | 79.50 |
| 270 | 61.61 | 44.60 | 0.4580 | 0.8791 | 39.476 | 18,08 | 34.70 | 79.69 | 79.30 |
| 274 | 59.83 | 47.27 | 0.4965 | 0.8035 | 39.767 | 19,75 | 31.95 | 79.58 | 79.22 |
| 276.8 | 62.93 | 62.93 | 0.6260 | 0.6260 | 39.971 | 25,01 | 25.01 | 79.18 | 79.18 |

$m$=114.144, $\mu'$=87.58, C=1.813, 2.3026 R=0.04010

TABLE IV
Isopentane

| Temperature | $\mu'\sqrt[3]{d}$ | $\mu'\sqrt[3]{D}$ | log $v$ | log V | 2.3026 CRT | CRT $ln\, v$ | CRT $ln$ V | $\mu'\sqrt[3]{d}$ + CRT | $\mu'\sqrt[3]{D}$ + CRT $ln$ V |
|---|---|---|---|---|---|---|---|---|---|
| 0° C | 90.83 | 10.85 | 0.1944 | 2.9626 | 29.246 | 5.69 | 86.64 | 96.52 | 97.49 |
| 20 | 89.90 | 14.00 | 0.2079 | 2.6300 | 31.389 | 6.52 | 82.54 | 96.42 | 96.54 |
| 40 | 88.89 | 17.35 | 0.2227 | 2.3510 | 33.532 | 7.47 | 78.83 | 96.36 | 96.18 |
| 60 | 87.79 | 20.94 | 0.2389 | 2.1059 | 35.675 | 8.52 | 75.13 | 96.31 | 96.07 |
| 80 | 86.61 | 24.71 | 0.2565 | 1.8904 | 37.818 | 9.70 | 71.49 | 96.31 | 96.20 |
| 100 | 85.22 | 28.72 | 0.2775 | 1.6946 | 39.961 | 11.09 | 67.72 | 96.31 | 96.44 |
| 120 | 83.64 | 33.15 | 0.3018 | 1.5079 | 42.102 | 12.71 | 63.49 | 96.35 | 96.64 |
| 140 | 81.65 | 38.13 | 0.3333 | 1.3253 | 44.245 | 14.74 | 58.64 | 96.39 | 96.77 |
| 160 | 79.01 | 44.03 | 0.3761 | 1.1373 | 46.388 | 17.45 | 52.76 | 96.46 | 96.79 |
| 180 | 74.30 | 52.84 | 0.4562 | 0.9004 | 48.531 | 22.14 | 43.70 | 96.44 | 96.54 |
| 185 | 71.70 | 56.95 | 0.5028 | 0.8031 | 49.063 | 24.67 | 39.40 | 96.37 | 96.35 |
| 187 | 69.45 | 59.91 | 0.5441 | 0.7368 | 49.277 | 26.81 | 36.31 | 96.26 | 96.22 |
| 187.8 | 65.01 | 65.01 | 0.6302 | 0.6302 | 49.360 | 31.11 | 31.11 | 96.12 | 96.12 |

$m = 72.10$, $\mu' = 105.46$, C = 1.688, 2.3026 R = 0.06347

TABLE V
Normal Pentane

| Temperature | $\mu'\sqrt[3]{d}$ | $\mu'\sqrt[3]{D}$ | log $v$ | log V | 2.3026 CRT | CRT $ln\, v$ | CRT $ln$ V | $\mu'\sqrt[3]{d}$ + CRT $ln\, v$ | $\mu'\sqrt[3]{D}$ + CRT $ln$ V |
|---|---|---|---|---|---|---|---|---|---|
| 0° C | 95.01 | 10.10 | 0.1902 | 3.1102 | 29.577 | 5.63 | 91.99 | 100.64 | 102.09 |
| 40 | 93.04 | 16.47 | 0.2174 | 2.4735 | 33.911 | 7.37 | 83.88 | 100.41 | 100.35 |
| 60 | 91.94 | 20.00 | 0.2328 | 2.2204 | 36.077 | 8.40 | 80.10 | 100.34 | 100.10 |
| 80 | 90.74 | 23.77 | 0.2500 | 1.9948 | 38.244 | 9.56 | 76.29 | 100.30 | 100.06 |
| 100 | 89.40 | 27.85 | 0.2694 | 1.7889 | 40.411 | 10.89 | 72.29 | 100.29 | 100.14 |
| 120 | 87.87 | 32.16 | 0.2918 | 1.6015 | 42.578 | 12.42 | 68.19 | 100.29 | 100.35 |
| 140 | 86.00 | 37.16 | 0.3199 | 1.4133 | 44.745 | 14.31 | 63.24 | 100.31 | 100.40 |
| 160 | 83.57 | 42.82 | 0.3571 | 1.2284 | 46.911 | 16.75 | 57.62 | 100.32 | 100.44 |
| 180 | 80.08 | 49.90 | 0.4126 | 1.0290 | 49.078 | 20.25 | 50.50 | 100.33 | 100.40 |
| 195 | 74.12 | 59.80 | 0.5136 | 0.7934 | 50.703 | 26.04 | 40.23 | 100.16 | 100.03 |
| 197.15 | 68.99 | 66.03 | 0.6070 | 0.6642 | 50.936 | 30.92 | 33.83 | 99.91 | 99.86 |
| 197.2 | 67.59 | 67.59 | 0.6340 | 0.6340 | 50.942 | 32.30 | 32.30 | 99.89 | 99.89 |

$m = 72.10$, $\mu = 109.94$, C = 1.707, 2.3026 R = 0.06347

TABLE VI
Normal Hexane

| Temperature | $\mu'\sqrt[3]{d}$ | $\mu'\sqrt[3]{D}$ | log $v$ | log V | 2.3026 CRT | CRT $ln\, v$ | CRT $ln$ V | $\mu'\sqrt[3]{d}$ + CRT $ln\, v$ | $\mu'\sqrt[3]{D}$ + CRT $ln$ V |
|---|---|---|---|---|---|---|---|---|---|
| 0° C | 90.27 | 6.27 | 0.1694 | 3.6443 | 25.420 | 4.32 | 92.64 | 94.59 | 98.91 |
| 60 | 87.76 | 13.93 | 0.2061 | 2.6042 | 31.007 | 6.39 | 80.75 | 94.15 | 94.68 |
| 80 | 86.81 | 16.92 | 0.2202 | 2.3502 | 32.869 | 7.24 | 77.25 | 94.05 | 94.17 |
| 100 | 85.80 | 20.16 | 0.2355 | 2.1229 | 34.732 | 8.18 | 73.73 | 93.98 | 93.89 |
| 120 | 84.68 | 23.55 | 0.2527 | 1.9201 | 36.594 | 9.25 | 70.26 | 93.93 | 93.81 |
| 140 | 83.42 | 27.29 | 0.2722 | 1.7292 | 38.456 | 10.47 | 66.50 | 93.89 | 93.79 |
| 160 | 81.93 | 31.34 | 0.2956 | 1.5478 | 40.318 | 11.92 | 62.40 | 93.85 | 93.74 |
| 180 | 80.21 | 35.82 | 0.3232 | 1.3738 | 42.181 | 13.63 | 57.95 | 93.85 | 93.77 |
| 200 | 77.99 | 40.97 | 0.3600 | 1.1987 | 44.044 | 15.86 | 52.79 | 93.85 | 93.77 |
| 220 | 74.52 | 47.89 | 0.4191 | 0.9952 | 45.906 | 19.24 | 45.69 | 93.76 | 93.58 |
| 230 | 71.24 | 53.44 | 0.4777 | 0.8525 | 46.837 | 22.37 | 39.93 | 93.61 | 93.37 |
| 233 | 69.12 | 56.48 | 0.5171 | 0.7803 | 47.117 | 24.36 | 36.77 | 93.48 | 93.25 |
| 234 | 67.91 | 58.11 | 0.5402 | 0.7431 | 47.210 | 25.50 | 35.08 | 93.41 | 93.19 |
| 234.8 | 63.38 | 63.38 | 0.6302 | 0.6302 | 47.284 | 29.80 | 29.80 | 93.18 | 93.18 |

$m = 86.112$, $\mu' = 102.80$, C = 1.752, 2.3026 R = 0.05315

TABLE VII
Normal Heptane

| Temperature | $\mu'\sqrt[3]{d}$ | $\mu'\sqrt[3]{D}$ | log $v$ | log V | 2.3026 CRT | CRT $ln\ v$ | CRT $ln$ V | $\mu'\sqrt[3]{d}$ + CRT $ln\ v$ | $\mu'\sqrt[3]{D}$ + CRT $ln$ V |
|---|---|---|---|---|---|---|---|---|---|
| 0° C | 87.60 | 4.01 | 0.1546 | 4.1723 | 22.637 | 3.50 | 94.43 | 91.10 | 98.44 |
| 80 | 84.61 | 12.43 | 0.1999 | 2.6990 | 29.270 | 5.85 | 78.99 | 90.46 | 91.42 |
| 100 | 83.77 | 15.11 | 0.2130 | 2.4440 | 30.929 | 6.59 | 75.59 | 90.36 | 90.70 |
| 120 | 82.86 | 18.00 | 0.2272 | 2.2164 | 32.586 | 7.40 | 72.22 | 90.27 | 90.23 |
| 140 | 81.84 | 21.10 | 0.2433 | 2.0094 | 34.244 | 8.33 | 68.81 | 90.17 | 89.91 |
| 160 | 80.73 | 24.38 | 0.2611 | 1.8209 | 35.902 | 9.37 | 65.37 | 90.09 | 89.75 |
| 180 | 79.48 | 27.82 | 0.2813 | 1.6493 | 37.560 | 10.57 | 61.95 | 90.05 | 89.77 |
| 200 | 78.04 | 31.65 | 0.3052 | 1.4810 | 39.221 | 11.97 | 58.09 | 90.01 | 89.74 |
| 220 | 76.23 | 36.07 | 0.3358 | 1.3105 | 40.879 | 13.73 | 53.57 | 89.96 | 89.64 |
| 240 | 73.73 | 41.50 | 0.3791 | 1.1281 | 42.538 | 16.14 | 47.99 | 89.87 | 89.49 |
| 260 | 69.23 | 49.80 | 0.4613 | 0.8904 | 44.196 | 20.39 | 39.35 | 89.62 | 89.15 |
| 264 | 67.23 | 52.85 | 0.4995 | 0.8129 | 44.528 | 22.24 | 36.20 | 89.47 | 89.05 |
| 266 | 65.35 | 55.48 | 0.5366 | 0.7501 | 44.694 | 23.98 | 33.53 | 89.33 | 89.01 |
| 266.5 | 64.68 | 56.66 | 0.5500 | 0.7226 | 44.735 | 24.60 | 32.33 | 89.28 | 88.99 |
| 266.85 | 60.79 | 60.79 | 0.6306 | 0.6306 | 44.764 | 28.23 | 28.23 | 89.02 | 89.02 |

$m=100.13$, $\mu'=98.64$, C=1.814, 2.3026 R=0.04571

TABLE VIII
Normal Octane

| Temperature | $\mu'\sqrt[3]{d}$ | $\mu'\sqrt[3]{D}$ | log $v$ | log V | 2.3026 CRT | CRT $ln$ $v$ | CRT $ln$ V | $\mu'\sqrt[3]{d}$ + CRT $ln$ $v$ | $\mu'\sqrt[3]{D}$ + CRT $ln$ V |
|---|---|---|---|---|---|---|---|---|---|
| 0° C | 83.44 | 2.51 | 0.1436 | 4.7117 | 20.340 | 2.92 | 95.83 | 86.36 | 98.34 |
| 120 | 79.30 | 13.80 | 0.2099 | 2.4885 | 29.281 | 6.14 | 72.86 | 85.44 | 86.66 |
| 140 | 78.46 | 16.35 | 0.2238 | 2.2672 | 30.771 | 6.88 | 69.76 | 85.34 | 86.11 |
| 160 | 77.56 | 19.09 | 0.2387 | 2.0659 | 32.261 | 7.70 | 66.65 | 85.26 | 85.74 |
| 180 | 76.59 | 21.99 | 0.2553 | 1.8808 | 33.751 | 8.61 | 63.48 | 85.20 | 85.47 |
| 200 | 75.47 | 25.14 | 0.2743 | 1.7067 | 35.241 | 9.67 | 60.15 | 85.14 | 85.29 |
| 220 | 74.20 | 28.53 | 0.2964 | 1.5416 | 36.731 | 10.89 | 56.62 | 85.09 | 85.15 |
| 240 | 72.60 | 32.47 | 0.3250 | 1.3729 | 38.221 | 12.42 | 52.47 | 85.02 | 84.94 |
| 260 | 70.62 | 36.92 | 0.3608 | 1.2060 | 39.711 | 14.33 | 47.89 | 84.95 | 84.81 |
| 280 | 67.59 | 43.00 | 0.4181 | 1.0073 | 41.201 | 17.23 | 41.50 | 84.82 | 84.50 |
| 290 | 64.80 | 47.74 | 0.4730 | 0.8710 | 41.947 | 19.84 | 36.54 | 84.64 | 84.28 |
| 296.2 | 57.30 | 57.30 | 0.6332 | 0.6332 | 42.409 | 26.85 | 26.85 | 84.15 | 84.15 |

$m = 114.144$, $\mu' = 93.16$, C = 1.858, 2.3026 R = 0.04010

TABLE IX
Benzene

| Temperature | $\mu'\sqrt[3]{d}$ | $\mu'\sqrt[3]{D}$ | log $v$ | log V | 2.3026 CRT | CRT $ln\ v$ | CRT $ln$ V | $\mu'\sqrt[3]{d}$ + CRT $ln\ v$ | $\mu'\sqrt[3]{D}$ + CRT $ln$ V |
|---|---|---|---|---|---|---|---|---|---|
| 0° C | 105.49 | 5.41 | 0.0457 | 3.9154 | 27.055 | 1.24 | 105.93 | 106.73 | 113.34 |
| 80 | 102.04 | 15.27 | 0.0891 | 2.5635 | 34.983 | 3.12 | 89.68 | 105.16 | 104.95 |
| 100 | 101.12 | 18.31 | 0.1009 | 2.3276 | 36.965 | 3.73 | 86.04 | 104.85 | 104.35 |
| 120 | 100.11 | 21.56 | 0.1139 | 2.1149 | 38.947 | 4.44 | 82.37 | 104.55 | 103.93 |
| 140 | 99.00 | 24.84 | 0.1284 | 1.9294 | 40.929 | 5.25 | 78.97 | 104.25 | 103.81 |
| 160 | 97.85 | 28.28 | 0.1436 | 1.7610 | 42.911 | 6.16 | 75.57 | 104.01 | 103.85 |
| 180 | 96.57 | 31.89 | 0.1608 | 1.6043 | 44.893 | 7.22 | 72.02 | 103.79 | 103.91 |
| 200 | 95.14 | 35.89 | 0.1801 | 1.4502 | 46.875 | 8.44 | 67.98 | 103.58 | 103.87 |
| 220 | 93.44 | 40.29 | 0.2037 | 1.2997 | 48.856 | 9.95 | 63.50 | 103.39 | 103.79 |
| 240 | 91.38 | 45.32 | 0.2328 | 1.1464 | 50.838 | 11.83 | 58.28 | 103.21 | 103.60 |
| 260 | 88.58 | 51.35 | 0.2735 | 0.9838 | 52.820 | 14.44 | 51.96 | 103.02 | 103.31 |
| 280 | 83.81 | 60.05 | 0.3454 | 0.7800 | 54.802 | 18.93 | 42.75 | 102.74 | 102.80 |
| 288.5 | 73.51 | 73.51 | 0.5164 | 0.5164 | 55.646 | 28.73 | 28.73 | 102.24 | 102.24 |

$m=78.05$, $\mu'=109.26$, C=1.690, 2.3026 R=0.05864

TABLE X
Iodobenzene

| Temperature | $\mu'\sqrt[3]{d}$ | $\mu'\sqrt[3]{D}$ | log $v$ | log V | 2.3026 CRT | CRT $ln\, v$ | CRT $ln$ V | $\mu'\sqrt[3]{d}$ + CRT $ln\, v$ | $\mu'\sqrt[3]{D}$ + CRT $ln$ V |
|---|---|---|---|---|---|---|---|---|---|
| 30° C | 52.90 | 0.51 | −0.2588 | 4.7867 | 11.471 | −2.97 | 54.91 | 49.93 | 55.43 |
| 180 | 50.52 | 7.28 | −0.1987 | 2.3249 | 17.150 | −3.41 | 39.87 | 47.11 | 47.15 |
| 200 | 50.16 | 8.41 | −0.1895 | 2.1380 | 17.907 | −3.40 | 38.29 | 46.76 | 46.70 |
| 220 | 49.77 | 9.58 | −0.1794 | 1.9680 | 18.644 | −3.35 | 36.73 | 46.42 | 46.31 |
| 240 | 49.37 | 10.82 | −0.1692 | 1.8082 | 19.421 | −3.29 | 35.11 | 46.08 | 45.93 |
| 260 | 48.97 | 12.15 | −0.1579 | 1.6575 | 20.178 | −3.19 | 33.44 | 45.78 | 45.59 |
| 270 | 48.71 | 12.85 | −0.1514 | 1.5843 | 20.556 | −3.11 | 32.57 | 45.60 | 45.42 |
| 448 | 36.20 | 36.20 | 0 2355 | 0.2355 | 27.297 | 6.48 | 6.43 | 42.63 | 42.63 |

$m = 203.89$, $\mu' = 43.37$, C = 1.687, 2.3026 R = 0.02245

TABLE XI
Carbon Tetrachloride

| Temperature | $\mu'\sqrt[3]{d}$ | $\mu'\sqrt[3]{D}$ | log $v$ | log V | 2.3026 CRT | CRT $ln\,v$ | CRT $ln$ V | $\mu'\sqrt[3]{d}$ + CRT $ln\,v$ | $\mu'\sqrt[3]{D}$ + CRT $ln$ V |
|---|---|---|---|---|---|---|---|---|---|
| 0° C | 51.82 | 2.94 | −0.2129 | 3.5252 | 13.543 | −2.89 | 47.74 | 48.93 | 50.68 |
| 80 | 50.11 | 8.03 | −0.1692 | 2.2159 | 17.512 | −2.96 | 38.80 | 47.15 | 46.83 |
| 100 | 49.63 | 9.57 | −0.1566 | 1.9886 | 18.504 | −2.90 | 36.80 | 46.73 | 46.37 |
| 120 | 49.12 | 11.18 | −0.1431 | 1.7853 | 19.496 | −2.79 | 34.80 | 46.33 | 45.98 |
| 140 | 48.58 | 12.87 | −0.1287 | 1.6021 | 20.488 | −2.64 | 32.82 | 45.94 | 45.69 |
| 160 | 48.01 | 14.60 | −0.1133 | 1.4378 | 21.481 | −2.43 | 30.86 | 45.58 | 45.46 |
| 180 | 47.37 | 16.48 | −0.0959 | 1.2799 | 22.473 | −2.15 | 28.76 | 45.22 | 45.24 |
| 200 | 46.62 | 18.49 | −0.0751 | 1.1297 | 23.465 | −1.76 | 26.51 | 44.86 | 45.00 |
| 220 | 45.74 | 20.70 | −0.0503 | 0.9832 | 24.457 | −1.23 | 24.05 | 44.51 | 44.75 |
| 240 | 44.65 | 23.20 | −0.0189 | 0.8344 | 25.449 | −0.48 | 21.23 | 44.17 | 44.43 |
| 260 | 43.12 | 26.35 | 0.0265 | 0.6684 | 26.442 | 0.70 | 17.67 | 43.82 | 44.02 |
| 280 | 40.22 | 31.30 | 0.1173 | 0.4440 | 27.434 | 3.22 | 12.18 | 43.44 | 43.48 |
| 283.15 | 36.22 | 36.22 | 0.2536 | 0.2536 | 27.442 | 6.96 | 6.96 | 43.18 | 43.18 |

$m=153.8$, $\mu'=44.01$, C = 1.667, 2.3026 R = 0.02976

TABLE XII
Stannic Chloride

| Temperature | $\mu'\sqrt[3]{d}$ | $\mu'\sqrt[3]{D}$ | log $v$ | log V | 2.3026 CRT | CRT $ln\, v$ | CRT $ln$ V | $\mu'\sqrt[3]{d}$ + CRT $ln\, v$ | $\mu'\sqrt[3]{D}$ + CRT $ln$ V |
|---|---|---|---|---|---|---|---|---|---|
| 0° C | 34.89 | 1.19 | −0.3577 | 4.0459 | 8.342 | −2.98 | 33.74 | 31.91 | 34.93 |
| 100 | 33.49 | 4.75 | −0.3050 | 2.2405 | 11.398 | −3.47 | 25.54 | 30.02 | 30.29 |
| 120 | 33.19 | 5.70 | −0.2931 | 2.0035 | 12.009 | −3.52 | 24.06 | 29.67 | 29.76 |
| 140 | 32.87 | 6.70 | −0.2804 | 1.7910 | 12.620 | −3.54 | 22.59 | 29.33 | 29.29 |
| 160 | 32.52 | 7.76 | −0.2667 | 1.5999 | 13.231 | −3.53 | 21.17 | 28.99 | 28.93 |
| 180 | 32.16 | 8.86 | −0.2522 | 1.4273 | 13.842 | −3.49 | 19.76 | 28.67 | 28.62 |
| 200 | 31.76 | 10.06 | −0.2361 | 1.2629 | 14.453 | −3.41 | 18.25 | 28.35 | 28.31 |
| 220 | 31.32 | 11.29 | −0.2172 | 1.1119 | 15.064 | −3.27 | 16.74 | 28.05 | 28.03 |
| 240 | 30.79 | 12.64 | −0.1950 | 0.9652 | 15.675 | −3.06 | 15.13 | 27.73 | 27.77 |
| 260 | 30.15 | 14.15 | −0.1687 | 0.8182 | 16.286 | −2.75 | 13.32 | 27.40 | 27.47 |
| 280 | 29.38 | 15.91 | −0.1344 | 0.6656 | 16.900 | −2.27 | 11.25 | 27.11 | 27.16 |
| 318.7 | 24.00 | 24.00 | 0.1297 | 0.1297 | 18.081 | 2.34 | 2.34 | 26.34 | 26.34 |

$m=260.8$, $\mu'=26.51$, C=1.741, 2.3026 R=0.01755

previous papers were obtained from equations 2 and 3, $\mu' = \frac{\lambda}{\sqrt[3]{d} - \sqrt[3]{D}}$, and $C = \frac{\lambda}{RT\ ln\frac{V}{v}}$, it follows that if these individual values are used in equation 5, the equation reduces always to an identity, irrespective of all errors in theory or measurement. The equation also reduces to an identity at the critical temperature.

But $\frac{\lambda}{\sqrt[3]{d} - \sqrt[3]{D}}$ and $\frac{\lambda}{RT\ ln\frac{V}{v}}$ are constants for saturated vapor equilibrium conditions irrespective of the values of $\lambda$ and $d$, D, etc., and irrespective even of the particular temperatures. Therefore the relation presented in equation 5 shows a physical relation between the quantities involved and does not simply conceal a mathematical identity. The two sides of equation 5 must be equal if equations 2 and 3 are true, but there is no reason to expect either side to remain constant with change in temperature. In six of the twelve substances examined the variation of the "constant" unexpectedly obtained throughout the entire range of temperature is *less than one percent* and in two of the others less than 1.5%. Steinhaus thought that he had a real constant for all substances.

Moreover equation 5 gives a direct comparison of equations 2 and 3 from a different point of view.

2. When constant values are assigned to $\mu'$ and C, if this constant value of $\mu'$ is greater than the individual value of $\mu'$, then the values on both sides of the equation will be increased but the *left-hand side of the equation will be increased by the greatest amount.*

If the constant value of C is greater than the individual value, then the values on both sides of the equation will be increased but the *right-hand side of the equation will be increased by the greatest amount.* Thus the effect at 0° C (30° for iodobenzene), of using an average C which is of greater value than the individual C at 0° (30°), in increasing the value given by the right-hand side of the equation is very noticeable.

An unpublished theory by one of the authors (Mills) led to the belief that the form of the (incomplete) curve followed by the molecules changed when $\mu' \sqrt[3]{D}$ was equal to $^3/_2 RT$ and that equation 3 above was not true when $^3/_2 RT$ was greater than $\mu' \sqrt[3]{D}$. A comparison of these values was therefore made, gram molecular weights being used, and the results are given in Table XIII. The results confirm the idea that equation 3 breaks down below the point indicated.

Except at the lowest temperatures, for the probable reason just indicated, the equality shown by the two sides of equation 5 is most excellent and leads to the conclusion that the values of $\mu'$ and C used are correct values. (Equality would of course also be obtained if $\mu'$ and C changed proportionately from their true values.)

3. No reason is known why equation 5 should give constant values with changing temperature, and that it does with isopentane, and to only a slightly less degree with some of the other substances, is remarkable. When there is a change in the value of the constant such change is fairly regular with increasing temperature. Efforts to connect these facts with the Cailletet and Mathias law of rectilinear diameter have failed.

Also these facts do not seem to be connected with possible hitherto overlooked progressive changes in $\mu'$ and C. For if C has steadily *decreased* with rising temperature and an average value for C has been taken, then the right-hand side of the equation will be too small at 0° C and too large later. If C has steadily *increased* and an average value for C has been used, then the right-hand side of the equation will be too large at 0° C and too small later. $\mu'$ bears a similar relation to the left-hand side of the equation.

In other words, a decrease in the values shown on both sides of equation 5 with increasing temperature could be due to ignoring an increase in the value of $\mu'$ and C with the temperature and erroneously considering them constant. Previous studies have shown no clearly defined increase in values of $\mu'$ or C with normal non-associated substances, though

TABLE XIII

| Temperature | ½ RT | Ethyl oxide | Di-iso-propyl | Di-iso-butyl | Iso-pentane | Normal pentane | Normal hexane | Normal heptane | Normal octane | Benzene | Iodo-benzene | Carbon tetra-chloride | Stannic chloride |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0° C | 813.3 | 721 | 610 | 362 | 782 | 728 | 540 | 402 | 286 | 422 | | 452 | 310 |
| 20 | 872.9 | 943 | | | 1009 | | | | | | 30° C | | |
| 40 | 932.5 | 1192 | | | 1251 | 1187 | | | | | 104 | | |
| 60 | 992.1 | 1454 | 1273 | | 1510 | 1442 | 1199 | | | | | | |
| 80 | 1051.7 | 1736 | 1528 | | 1781 | 1714 | 1457 | 1245 | | 1192 | | 1235 | |
| 100 | 1111.2 | 2039 | 1805 | 1445 | 2071 | 2008 | 1736 | 1513 | | 1429 | | 1471 | 1239 |
| 120 | 1170.8 | 2370 | 2096 | 1734 | 2390 | 2319 | 2028 | 1802 | 1575 | 1683 | | 1719 | 1486 |
| 140 | 1230.4 | 2731 | 2410 | 2043 | 2749 | 2679 | 2350 | 2113 | 1862 | 1937 | | 1979 | 1747 |
| 160 | 1290.0 | 3154 | 2753 | 2342 | 3174 | 3087 | 2699 | 2441 | 2179 | 2206 | | 2245 | 2024 |
| 180 | 1349.6 | 3722 | 3138 | 2670 | 3810 | 3598 | 3084 | 2786 | 2510 | 2487 | 1485 | 2534 | 2311 |
| 200 | 1409.1 | | 3593 | 3035 | | | 3528 | 3169 | 2869 | 2794 | 1714 | 2844 | 2623 |
| 220 | 1468.7 | | 4277 | 3445 | | | 4124 | 3612 | 3257 | 3143 | 1953 | 3184 | 2944 |
| 240 | 1528.3 | | | 3962 | | | | 4155 | 3706 | 3527 | 2206 | 3578 | 3296 |
| 260 | 1587.9 | | | 4552 | | | | 4986 | 4214 | 4005 | 2477 | 4053 | 3690 |
| 280 | 1647.4 | | | | | | | | 4908 | 4684 | | 4814 | 4149 |
| $T_c$ | | 4920 | 5227 | 6183 | 4687 | 4873 | 5458 | 6087 | 6540 | 5734 | 7381 | 5571 | 6259 |
| $mE_c$ | | 7059 | 7667 | 9038 | 6930 | 7202 | 8024 | 8913 | 9605 | 7980 | 8692 | 6640 | 6869 |
| $mE_c/T_c$ | | 15.12 | 15.32 | 16.44 | 15.04 | 15.32 | 15.80 | 16.51 | 16.87 | 14.21 | 12.06 | 11.94 | 11.61 |

there is a possibility of its existence with some substances. In the case of stannic chloride, where equation 5 shows a well marked decrease in the value of the constant with rise in temperature, the values of both $\mu'$ and C show no evidence whatever of any progressive temperature change.

It would seem therefore that the reason for the constant value given by equation 5 with increasing temperature with some substances, and the lack of constancy with other substances, *must be sought in progressive changes in the density relations*.

4. Equation 5 gives when $v = 1$, $CRT\,ln\,v = 0$ and 6, $\mu'\sqrt[3]{d} + CRT\,ln\,v = \mu'\sqrt[3]{d} = \mu'$.

This condition is fulfilled for carbon tetrachloride between 240° and 260° C and for stannic chloride between 280° and 318.7° C and for iodobenzene between 270° and 448° C as will be seen upon reference to the respective tables.

After $v$ becomes equal to one as T decreases, $CRT\,ln\,v$ becomes negative, and finally again becomes zero when T = 0° absolute. The left-hand member of equation 5 then reduces to $\mu\sqrt[3]{d}$. It follows therefore that the left hand member of equation 5 could not remain a constant during the changes described. With most of the substances examined $v$ does not become equal to one until $^3/_2$ RT has become greater than $\mu'\sqrt[3]{D}$ and equation 3 has ceased to apply.

5. A graph of equation 5 for isopentane has been published.[1] The two lower branches of the graph should be designated $\mu'\sqrt[3]{D}$ and $CRT\,ln\,v$, respectively.

Referring to Fig. 1 given on page 259 of the above article, it is clear that if the ideas there given concerning negative internal pressure are correct, $\mu'\sqrt[3]{d}$ represents the area between the ordinate (pressures are ordinates) at $v$, the volume axis, and the curve G–H prolonged to the point where the volume is equal to infinity. The term $CRT\,ln\,v$ represents the area between the ordinate at $v$, the curve M–N–O, the volume axis, and the line P–Q drawn at volume $v = 1$.

[1] Jour. Phys. Chem., 19, 270 (1915), Fig. 2.

*It then becomes clear that the absolute size of the values given by either side of equation 5 are determined by an arbitrary constant of integration due to the fact that the integration proceeds from volume $v=1$, and that such values would have no direct physical significance.*

6. Other forms of equations 4 and 5 can readily be derived. Thus from 4,

$$7.\quad \frac{\mu'}{3CRT} = \frac{ln\ \frac{\sqrt[3]{d}}{\sqrt[3]{D}}}{\sqrt[3]{d}-\sqrt[3]{D}} \text{ or } \frac{ln\ \sqrt[3]{\frac{d}{D}}}{\sqrt[3]{d}-\sqrt[3]{D}}\ T = \text{Constant.}$$

If $s_1$ and $s_2$ are the relative distance apart of the molecules of liquid and vapor, respectively, then $s_1 = \sqrt[3]{\frac{m}{d}}$ and $s_2 = \sqrt[3]{\frac{m}{D}}$ and

$$8.\quad \frac{\mu'\sqrt[3]{m}}{3\,CRT} = \frac{ln\ \frac{s_2}{s_1}}{\frac{1}{s_1}-\frac{1}{s_2}},$$

At the critical temperature $\frac{ln\ \sqrt[3]{\frac{d}{D}}}{\sqrt[3]{d}-\sqrt[3]{D}}$ has the value $\frac{1}{\sqrt[3]{dc}}$ and equation 7 becomes,

$$9.\quad \frac{\mu'\sqrt[3]{dc}}{3CRT\,c} = 1 = \frac{m\mu'\sqrt[3]{dc}}{5.9634\,Tc}.$$

This equation was first published and studied by Mills[1] and the values are given in Table 2 of the paper cited under the heading $\frac{C'}{C}$. The average value obtained for 28 substances is 1.025. The divergence of 2.5% from the value one, predicted by equation 9, probably is caused by slight association in some of the substances examined. (The worst diver-

[1] Jour. Am. Chem. Soc., **31**, 1099 (1909).

gence is with the esters where reasons for supposing association have been found by others.)

7. The values obtained from Equation 5 at the critical temperature were multiplied by the molecular weight and are given in Table 13 on the line designated $mE_c$. Also there are given the values of $\frac{mE_c}{T_c}$. No relationship between these values is noted.

Equation 5 was also investigated for isopentane at 180°C for the unsaturated region. Constant results were not given by the term $\mu'\sqrt[3]{D} + CRT\, ln\, V$.

8. The value of C is connected with the slant of the Cailletet and Mathias line of rectilinear diameter as will be shown in a future article. Also it would seem to be connected with the pressure exerted by a molecule in such way that for saturated vapor liquid equilibrium conditions the total pressure $P_T$, is equal to the external pressure plus $\frac{CRT}{V}$ that is,

$$10. \quad P_T = P_E + \frac{CRT}{V}.$$

All attempts to explain or derive this relation from kinetic considerations have failed.

**Summary**

The equation $\mu'\sqrt[3]{d} + CRT\, ln\, v = \mu'\sqrt[3]{D} + CRT\, ln\, V$ has been tested for twelve substances from 0° C to the critical temperature and has been found to be a remarkably exact equation whenever $\mu'\sqrt[3]{D}$ is greater than $^3/_2\, RT$.

*University of South Carolina*
*Columbia, S. C.*
*November 24, 1920*

# THE PROBLEM OF NEGATIVE CATALYSIS. I*

BY HUGH S. TAYLOR

In contrast to the marked attention which has been devoted to positive catalysis and to the theoretical bases of such accelerations of reaction, the subject of negative catalysis has been but little studied and no well-defined opinion is prevalent as to the causes, or, in some cases, the existence even, of negative catalytic action. This cannot be attributed to lack of interesting and as yet unsolved problems of chemical theory in connection therewith. Nor does the subject lack the practical aspect since the negative catalyst is employed in the prevention of hydrogen peroxide decomposition both thermal and photochemical; it intrudes in various photochemical oxidation and halogenation problems of technical importance, it is of use in a variety of ways in the prevention of autoxidation.

In heterogeneous reactions, many of the cases of retardation may be accounted for on the assumption of interaction of the negative catalyst with, or adsorption of the inhibitor on, the positive catalyst. Much recent work has given good experimental support to such a viewpoint. This is undoubtedly the explanation of many cases of "poisoning" in the catalysis of gas reactions on both the laboratory and the industrial scale. The explanation holds true also in many of the cases of poisoning of the catalytic action of colloidal particles. In this latter case, however, agglomeration of the colloidal particles by the added agents may at times account for such inhibitions, since the extent of interfacial surface may thereby be considerably varied.

Such assumptions do not, however, cover the cases of retardation exhibited in homogeneous media. In commenting recently[1] on the tendency of theory to account for negative

* Contribution from the Laboratory of Physical Chemistry, Princeton University.

[1] "Catalysis in Theory and Practice," Macmillan, p. 33 (1919).

catalysis, the writer pointed out that this lay in two directions. Either the negative catalyst could act by suppressing a positive catalyst or by interaction with one of the constituents of the reaction under investigation. Luther is credited by Titoff with the concept of negative catalysis involving the suppression of a positive catalyst. Titoff,[1] as a result of a most thorough and quantitative investigation of the rate of oxidation of solutions of sodium sulphite by dissolved oxygen in presence of a variety of positive catalysts and of inhibitors, concluded that the negative catalysis in this case consisted in the suppression by the inhibitor of the activity of positive catalysts. Titoff was able to show that the presence of 0.000,000,000,000,1 $NCuSO_4$ solution is sufficient to produce a perceptible acceleration of the rate of oxidation of an aqueous solution of sodium sulphite. The suppression of such minute amounts of positive catalysts even by the minimal quantities of a wide variety of inhibitors such as was indicated by the researches of Bigelow[2] and of Young,[3] was, in Titoff's view, not improbable. The phenomenon of negative catalysis is not found with concentrated solutions of sulphites.[4] Ostwald,[5] dealing with the kinetics of reactions, formulated the expression for a monomolecular reaction in which one of the products retarded the reaction, namely, negative autocatalysis, by means of the equation,

$$\frac{dx}{dt} = k_1 (a - x) - k_2 x(a - x)$$

where $x$ is the quantity of negative catalyst produced at time $t$. This expression, however, does not hold good. For example it is possible that with certain values for $k_1$ and $k_2$ the value of $dx/dt$ would change sign, i. e., the reaction would reverse itself—which has never been observed. The experiments of

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[1] Titoff: Zeit. phys. Chem., **45**, 641 (1903).
[2] Bigelow: Zeit. phys. Chem., **26**, 493(1898).
[3] Young: Jour. Am. Chem. Soc., **23**, 119, 450(1901); **24**, 297(1902).
[4] Milbauer and Pazourek: Bull. Soc. chim. France, **31**, 676 (1922).
[5] Allgemeine Chem., **2**, II, 270.

Müller[1] on the hydrolysis of bromsuccinic acid showed that an equation

$$\frac{dx}{dt} = k\frac{a - x}{x}$$

more nearly represented the effect of the concentration $x$ of the anti-catalyst, hydrobromic acid, on the rate of the reaction.

Senter and Porter[2] dealing with the influence of the hydrogen halides on the hydrolysis of the several halogen acids of acetic, propionic, and butyric acids, with the anti-catalytic action of nitric acid on the reaction between bromo-substituted aliphatic acid and silver nitrate in alcoholic solutions, and with the problem of negative auto-catalysis in general showed that the term involving the inhibitor concentration normally appears in the denominator. They showed that, in the reactions of the halogen-substituted acids, both the undissociated molecule and the anion of the acid undergo hydrolysis at rates definite and distinct for each acid and each ion. Retardation is produced by the halogen acid formed in those cases in which the rate of hydrolysis of the ion is faster than that of the undissociated acid molecule, e. g., brompropionic anion and acid. The inhibition is, therefore, due to the function of the strong hydrogen halide in altering the relative ratios of the more active anion and the less active molecule of the weaker acid. They developed the mathematical equations expressing this explanation and showed that the concentration of inhibitor appeared in the denominator of the equations in agreement with their experimental observations.

On Titoff's view, the rate of reaction being inversely proportional to the anti-catalyst is to be attributed to the capacity of the negative catalyst B to remove the positive catalyst A by formation of a complex AB,

$$A + B = AB,$$

whence, by the Law of Mass Action,

$$(A) = K\frac{(AB)}{(B)}$$

[1] Zeit. phys. Chem., 41, 483 (1902).

[2] Senter and Porter: Jour. Chem. Soc., 99, 1049 (1910).

where the brackets indicate concentrations and K the mass action constant. If the rate of reaction be proportional to (A), it will also be proportional to $K\frac{(AB)}{(B)}$ and, therefore, inversely as (B) so long as (A) is small compared with (B) or, alternatively, if the undissociated portion AB is very considerable, for then (AB) can be regarded as constant.

The inhibitory power of water in the esterification of acids in alcoholic solutions[1] and in the decomposition of diazo esters in alcoholic solutions[2] represents a complex case of the Titoff type of inhibition. In these reactions, the hydrogen ion either nonhydrated (Lapworth) or alcoholated (Goldschmidt) is a positive catalyst for the reaction. The changes in ionisation and in the extent either of hydration or solvation due to addition of water complicate the case, as a perusal of the above literature or a résumé of the same[3] will reveal.

There are, however, a number of cases of negative catalysis for which, hitherto, no adequate explanation has been forthcoming; they do not appear to be the result of the suppression of a positive catalyst as in the cases studied by Titoff nor do they find a ready explanation on the assumption of simultaneous reaction of two forms of the reacting molecules as in the case of the halogen-substituted acids studied by Senter. It seems necessary to find some other explanation for the remarkable inhibitory powers of a wide variety of substances, organic and inorganic, in the autoxidation of various organic compounds such as benzaldehyde, styrolene, oils, fats, rubber, resins and animal tissues,[4] possibly also in some cases of autoxidation of sodium sulphite solutions.

The inhibitory power of ether on the slow oxidation of various magnesium alkyl halides of the Grignard type, which

[1] Goldschmidt: Ber. deutsch. chem. Ges., **28**, 3218 (1895); **39**, 711 (1906); Zeit. Elektrochemie, **12**, 432 (1906); Lapworth: Jour. Chem. Soc., **93**, 2167, 2187 (1908).

[2] Bredig and Fraenkel: Zeit. phys. Chem., **60**, 202 (1907).

[3] Rideal and Taylor: "Catalysis in Theory and Practice," pp. 280 ff., 292 ff.

[4] *Moureu and Dufraisse: Comptes rendus,* **174**, 258; **175**, 127 (1922); Seyewetz and Sisley: Bull. Soc. chim. France, **31**, 672 (1922).

oxidation is revealed by luminescence on exposure of the free agent to air,[1] also requires explanation. The same is true of the suppression by inhibitors of the luminescence due to the oxidation of organic sulphur compounds as discussed recently by Delépine.[2] Finally, there are a number of inhibitions by water, of reactions in a variety of solvents, for which no completely satisfactory explanation has hitherto been offered. The inhibitory rôle of water in the decomposition of oxalic acid in sulphuric acid solutions was intensively studied by Bredig and Lichty.[3] Water has a similar inhibitory action on the velocity of conversion of acetophenoxime to acetanilide in concentrated sulphuric acid solutions,[4] and on the velocity of decomposition of triethyl sulphine bromide in acetone and to a less degree in acetic acid solutions.[5] An attempt will be made in the following paragraphs to show that these cases of inhibition are all due to the same type of negative catalysis, the simultaneous interaction of the inhibitor with one of the reacting materials to form a molecular compound which subsequently decomposes, regenerating inhibitor and reactant, without change of the latter. For marked inhibition to occur, it must follow that the rate of reaction between inhibitor and reactant shall be rapid as compared with the rate of the inhibited reaction. The rate of molecular compound formation is known to be exceedingly rapid. The rôle of the inhibitor in all these cases would therefore be that of a competitor for one of the molecular species undergoing change.

Bredig and Lichty are very reticent as to the mechanism of the action of water. "Upon what chemical equilibrium in the concentrated sulphuric acid the influence of water makes itself felt cannot now be determined . . . the action of the water depends on a constituent of the concentrated sul-

[1] Lifschitz and Kalberer: Zeit. phys. Chem., **102**, 393 (1922).

[2] Delépine: Bull. Soc. chim. France, **31**, 762 (1922).

[3] Bredig and Lichty: Zeit. Elektrochemie, **12**, 450 (1906); Jour. Phys. Chem., **11**, 255 (1907).

[4] Lobry de Bruyn and Sluiter: Proc. Akad. Wetenschap. Amst., **6**, 773 (1904).

[5] H. von Halban: Zeit. phys. Chem., **67**, 129 (1909).

phuric acid (e. g. $SO_3$, $H_2S_2O_7$ or the like) or on an intermediate product of the reaction whose active mass is strongly suppressed by addition of water." It will be shown that the last phrase contains the germ of the whole explanation now to be advanced. Lamble and Lewis[1] attempting to correlate all the above cited inhibitions by water with their own radiation theory of catalysis offer the following conclusion:—"On the radiation view this [inhibitory power] is to be explained by the hypothesis that the water molecules absorb some of the radiation emitted by the acetone and sulphuric acid molecules which would otherwise have been effective in catalysing the reaction. That is to say, the critically active state is effectively removed to a greater distance from the mean value when water is present than is the case in acetone or sulphuric acid alone; and hence, a fewer number of molecules reach the reactive state per second, thus decreasing the velocity." An explanation which would translate such terminology into the simpler and well understood concepts of rate of reaction and chemical equilibrium would be welcome. It would seem that such is possible.

The relatively small amounts of inhibitors which modify profoundly the rate of these reactions excite attention. According to Moureu and Dufraisse[2] a trace of hydroquinone can suppress the autoxidation of benzaldehyde. The time required to decompose a given quantity of oxalic acid, at 25° C, rose from fifteen minutes in 100 percent sulphuric acid to two hundred and eighty-five minutes when 0.1 percent of water was present. It is at first difficult to realise how one molecule of an inhibitor in, for example, 10,000 molecules of the reacting substance can so profoundly modify the rate of reaction of all the ten thousand molecules. The human impossibility of being in two places at the same time suggests at once the difficulty of a molecule being in ten thousand places at the same time. Nevertheless one can satisfy oneself that this ratio of inhibitor to reactant is not absurd by a simple experiment and calculation. Under a given set of conditions it was found that redistilled

[1] Lamble and Lewis: Jour. Chem. Soc., **107**, 245 (1915).
[2] Moureu and Dufraisse: Comptes rendus, **174**, 258; **175**, 127 (1922).

benzaldehyde absorbed 2 cc of oxygen per minute. The same amount of benzaldehyde containing 0.005 grams of hydroquinone, equivalent to M/1000 concentration of inhibitor, absorbed less than 0.005 cc per minute under the same conditions.

Now 2 cc of oxygen represents

$$\frac{2}{22400} \times \frac{6.06 \times 10^{23}}{1}$$

molecules of oxygen or the equivalent number of benzaldehyde molecules reacting per minute, i. e., approximately $5 \times 10^{19}$ molecules per minute. Similarly 0.005 grams of hydroquinone represents

$$\frac{0.005}{110} \times \frac{6.06 \times 10^{23}}{1}$$

molecules hydroquinone or approximately $3 \times 10^{19}$ molecules of hydroquinone. There are therefore present a sufficient number of hydroquinone molecules to form an equimolecular compound with all of the benzaldehyde molecules normally proceeding to reaction in approximately one-half minute. As the rate of molecular compound formation is known to be so rapid as to be beyond our present methods of measurement,[1] it is apparent that even in such low concentrations as above indicated there are an adequate number of molecules of inhibitor present to interact in stoicheiometrically simple ratios with the molecules which would have reacted normally in the same time interval.[2]

It is therefore apparent that the Titoff concept of the presence of a positive catalyst, of high activity, present in minute amount, and which the negative catalyst suppresses by combination therewith, is not essential to all of these cases of retardation by minute amounts of negative catalyst. Further-

[1] Kendall and Booge: Jour. Am. Chem. Soc., **38**, 1719 (1916).

[2] In discussing this matter with my friends I have used, by way of analogy, the case of a warden caring for 100 lunatics. The warden would be powerless were all the lunatics simultaneously violent. Only at intervals does an occasional lunatic become a candidate for a padded cell. The warden cares for him, the gentler 99 do not require attention.

more, I have shown by experiment in several cases that, in certain oxidations, concentrations of positive catalysts, probable as impurities in the substance undergoing oxidation, produce accelerations of a lower order of magnitude than the retardations produced by the same concentration of inhibitor. Thus, M/1000 copper benzoate, partly in solution, partly suspended in benzaldehyde has a measurable accelerative effect on the autoxidation of benzaldehyde, an acceleration however which is but a minute fraction of the retarding effect of M/1000 hydroquinone. Compound formation in simple stoicheiometric ratios between positive catalyst and inhibitor is therefore excluded as the mechanism of retardation in all such cases. Similar observations hold with reference to iron and manganese oxides as catalytic accelerants.

A word of warning is apposite at this stage as to possible misconceptions which may result from such a statement as that of Moureu and Dufraisse[1] that an inhibitor will prevent the autoxidation of a given substance. Let us assume that under a given set of conditions redistilled benzaldehyde absorbs 1 cc of oxygen per minute. If to this benzaldehyde a concentration of inhibitor be added such that the rate of oxidation is cut down to 0.0001 cc per minute, the velocity of reaction will have passed beyond the limits of our experimental technique. Measurements over 1000 minutes would only show a volume absorption of 0.1 cc. *Nevertheless, there will still be* $2.70 \times 10^{15}$ *molecules of oxygen reacting per minute*, a not inconsiderable number to have eluded the activity of the added inhibitor.

The present hypothesis of molecular compound formation between inhibitor and one of the reactants as an explanation of the inhibitory power, will be discussed in detail first with reference to the influence of water on the rate of decomposition of oxalic acid in sulphuric acid solutions. This case is simplest since it occurs in homogeneous medium between reactants for which, being all acids varying in strength from sulphuric acid to water, predictions as to compound formation can be trust-

[1] Moureu and Dufraisse: Comptes rendus, **174**, 258; **175**, 127 (1922).

worthily made as a result of the investigations of Kendall and his students[1] in the last years. The reaction moreover was studied very comprehensively by Lichty with a wide variation of added water and over a considerable temperature range.

The decomposition of oxalic acid in sulphuric acid solution most probably proceeds via the intermediate oxalic-sulphuric acid molecular compound

$$(COOH)_2 + H_2SO_4 \rightleftarrows (COOH)_2 \cdot H_2SO_4 \longrightarrow CO_2 + CO + H_2O + H_2SO_4.$$

The researches of Kendall have established the existence of such compounds. When water is present, however, compound formation may occur between sulphuric acid and water on the one hand and between oxalic acid and water on the other.

$$H_2SO_4 + H_2O \rightleftarrows H_2SO_4 \cdot H_2O$$
$$(COOH)_2 + H_2O \rightleftarrows (COOH)_2 \cdot H_2O$$

Such compounds are also known and the above equilibria are also known to exist. The occurrence of compound formation between water and sulphuric acid will result in a diminution of the compound formation between oxalic and sulphuric acids and will reduce therefore, the amount of decomposition. The extent of inhibition will depend in part on the relative rates of compound formation in the three cases.

The influence of successive additions of water on the velocity of the reaction is in agreement with the hypothesis of simultaneous reactions and of equilibria as set forth. The fraction of each addition of water which will remain as free water and not be converted to molecular compound will increase with increase of water concentration. Thus, there will be more than ten times the concentration of free water molecules in a solution containing 0.1 percent added water than in one containing 0.01 percent added water. This explains what Lichty describes as the very striking differences in times required to secure the decomposition of equal quantities of oxalic acid. "It will be seen, for example, that when 0.05 percent of water is added at 25° C, the time increases to over six-fold

[1] Kendall, et al.: Jour. Am. Chem. Soc., 1915, et seq.

of that required when no water has been added and that when the amount reaches 0.1 percent the time required is increased 19-fold." This exponential increase with water addition is characteristic of this and other reactions subsequently to be considered.

The hypothesis enables one to predict also the influence of temperature on the inhibitory power of the added water. Increase in temperature will tend to increase the dissociation of the molecular compound in all three cases. Now the rate of change of the equilibrium constant K with temperature is given by the equation of the reaction isochore

$$\frac{d \log K}{dt} = \frac{Q}{RT^2}$$

where K is defined as

$$\frac{(H_2SO_4)\ (H_2O)}{(H_2SO_4\ .\ H_2O)} = K$$

in the one case and similarly in the other two, Q being the heat of formation of the molecular compound. Now since the heat of formation of the sulphuric acid-water complex is undoubtedly much greater than either that of the sulphuric acid-oxalic acid or that of the oxalic acid-water complex[1] it follows that the influence of temperature on the sulphuric acid-water equilibrium will be pronouncedly greater than that on the other two. Raising the temperature should therefore lead to a reduction in the inhibitory power of the water. This was actually found in the experimental work. With concentrations of water greater than 0.1 percent, Bredig and Lichty found that the rate of reaction at 25° C was impractically slow. At 45° C, the concentration interval 0.1–0.6 percent water could readily be investigated. Higher concentrations of water could only be studied at 75° C.

In respect to the magnitude of the temperature coefficient of the reaction velocity, the hypothesis of simultaneous reaction of the sulphuric acid with water to yield molecular compounds is instructive. An abnormally high temperature coeffi-

[1] 1 mol. $H_2SO_4$ + 1 mol. $H_2O$ = $H_2SO_4$ aq. + 6.4 Kg. cal.
$(COOH)_2 + 2H_2O = (COOH)_2\ .\ 2H_2O$ + 6.26 Kg. cal.

cient of reaction would be anticipated upon the basis of the hypothesis. For, temperature influences the sulphuric acid-water equilibrium and the oxalic acid-water equilibrium in favour of the dissociated molecules water, oxalic and sulphuric acids. In addition, however, to this increase in the concentration of acid molecules as a result of the dissociation of the acid-water complexes there will be the normal increase with temperature of the reaction velocity between oxalic acid and sulphuric acid, leading to the decomposition products. Hence a temperature coefficient of the whole reaction greater than normal would be anticipated. Bredig and Lichty's values range between 4.42 and 3.35., an abnormally high coefficient which has not hitherto received any adequate explanation.

Furthermore, since the heat evolution per mol on the addition of water to sulphuric acid diminishes rapidly with each successive addition of water and since the same doubtless holds true with oxalic acid it follows that the influence of temperature on the dissociation of the acid-water molecular compounds will be less pronounced the more water there is present in the reaction mixture. Therefore, the temperature coefficient of the whole decomposition process should diminish with increase in water content of the solution. This is actually the case. The higher value, 4.42, in the preceding paragraph is for a dilution of 0.1 percent water in the interval 25–35° C. At 70–80° C, for a 3 percent water concentration, the lower coefficient of 3.35 is obtained. Lichty appears to attribute the decrease in coefficient to temperature increase. It is much more probably the change in coefficient due to the dilution of the acid.

Kendall and Landon[1] have demonstrated the presence of compounds in mixtures of sulphuric acid and alkali sulphates, which may be regarded as the bases corresponding to sulphuric acid as solvent. Compound formation should therefore be somewhat more marked than between sulphuric acid and water, which latter are less divergent in acidic properties. What the

[1] Kendall and Landon: Jour. Am. Chem. Soc., 42, 2131 (1920).

speed of interaction between sulphuric acid and alkali sulphates is as compared with that of water and acid cannot be predicted. Nevertheless using compound formation as a criterion it would be anticipated that the alkali sulphates would show inhibitory powers similar to water. Such is indeed the case. The influence of equivalent quantities of sodium and potassium sulphates is nearly the same and they decrease the speed of reaction to about the same extent as does an equivalent quantity of water.

Making use of compound formation as a criterion of inhibitory power, forecast can be made of other substances which should show more or less inhibition of the oxalic acid decomposition. Acetic acid is a weaker acid than oxalic acid but stronger than water. Sulphuric acid should show compound formation with acetic acid to a less extent than with water but to a greater extent than with oxalic acid. It should therefore show a definite inhibitory power on the decomposition process, the actual magnitude of which will depend on the velocity of its compound formation with sulphuric acid as compared with that of oxalic acid. Similarly Kendall[1] showed that dimethyl pyrone is very similar to water in its behaviour with respect to compound formation with sulphuric acid. It also should show inhibitory power on the reaction under consideration. Both these forecasts will receive experimental tests in the laboratory. The success which has attended similar forecasts in the case of other reactions subsequently to be considered warrants optimism in regard to these cases.

With respect to the inhibitory power of water on the conversion of acetophenoxime to acetanilide in sulphuric acid solutions[2] and on the decomposition of triethyl sulphine bromide in acetone and acetic acid solutions,[3] it is not possible so definitely to illustrate the applicability of the theory, since the relative capacities of compound formation of the several con-

[1] Kendall: Jour. Am. Chem. Soc., 1915.

[2] Bredig and Lichty: Zeit. Elektrochemie, **12**, 450 (1906); Jour. Phys. Chem., **11**, 256 (1907).

[3] H. von Halban: Zeit. phys. Chem., **67**, 129 (1909).

stituents of the reaction mixture cannot be so definitely stated as in the sulphuric acid-oxalic acid-water case just considered. Nevertheless, each of these reactions has the very definite characteristics of the reaction just considered. Thus, the acetophenoxime conversion is characterised by the high temperature coefficient of 3 per 10° rise with a water concentration as high as 6–7 percent. The reaction of triethylsulphine bromide shows the same exponential function of the concentration of water on the reaction velocity in acetone. An extended investigation of these reactions would be well worth while.

The existence of molecular compound formation as a criterion of inhibitory power has been applied with conspicuous success in the case of inhibition of autoxidation processes. Moureu and Dufraisse[1] have shown that phenols as a class exhibit marked inhibitory power in a variety of such autoxidations. Search of the literature for substances showing compound formation with benzaldehyde has revealed several other classes of substances showing compound formation with this substance. Thus, Kendall and Gibbons[2] have shown that trichloracetic acid forms a well-defined equimolecular compound with benzaldehyde. I have been able to show that this acid is a moderate inhibitor of autoxidation of benzaldehyde when present in 1000th molar concentration. This compound was hitherto unknown in the rôle of inhibitor. Similarly, as typical of yet another class of compounds, stannic chloride has been shown to form a benzaldehyde addition compound. As an inhibitor it proved to be of moderate activity. Other types are now being studied in detail.

An alternative test for the hypothesis consists in the examination of the extent of compound formation between inhibitor and autoxidant. This is at present being carried out; the earliest efforts, however, show promise of good results. β-Naphthol was chosen as a typical inhibitor of the autoxidation of benzaldehyde. Freezing point measurements of various

[1] Comptes rendus, **174**, 258; **175**, 127 (1922).
[2] Kendall and Gibbons: Jour. Am. Chem. Soc., **37**, 152 (1916).

mixtures of the two, demonstrated the existence of a well-defined molecular compound, $2C_{10}H_7OH.C_6H_5CHO$, the freezing point curves revealing marked compound formation when compared with the curves of naphthol-benzene taken as an ideal physical mixture. That the study of compound formation between inhibitor and autoxidant will multiply such cases is evident from the following table compiled by Mr. F. D. Abbott who is engaged on this work. The first column gives the inhibitors listed by Moureu and Dufraisse in their recent publication. In the second column are listed the substances noted in Chemical Abstracts as giving condensations with benzaldehyde. Assuming with Kendall[1] and with Schmidlin and Lang[2] that such condensations are preceded by addition-compound formation, the parallelism between inhibitory power and tendency to compound formation is manifest.

TABLE I

| Inhibitors | Condensation products with benzaldehyde |
|---|---|
| Phenol | Phenol |
| Salicylic aldehyde and acid | Salicylic acid |
| Resorcinol | Resorcinol |
| Hydroquinone | Hydroquinone |
| Guaiacol | Guaiacol |
| $\alpha$ and $\beta$ Naphthol | 2-7 Naphthalene diol |
| *o* -amino phenol | Ethyl 1-3 dihydroxy 2 naphthoate |
| *o* -nitro phenol | $\alpha$ Nitrotoluene |
| Trihydroxy benzenes | Isoamylamine |
| Gallic acid | Glycerol |
| Tannic acid | *p* -amino oxanilic acid |
| | Cyclic ketone bases |
| | Cyclopentanone |
| | Acetonaphthone |

It is interesting to record that the inhibitory power of the phenols upon certain autoxidation processes increases very definitely with increase in the number of hydroxyl groups

[1] Kendall: Loc. cit.; Kendall and Booge: Jour. Am. Chem. Soc., **38**, 1733 (1916).

[2] Schmidlin and Lang: Ber. deutsch. chem. Ges., **43**, 2806 (1910).

present in the ring structure. This is paralleled by the capacity of these phenols to form polymolecular compounds. Thus acetone forms addition compounds with phenol, resorcin and pyrogallol containing, respectively, 1, 2 and 3 molecules of ketone to a single molecule of the phenol.[1] Benzaldehyde,

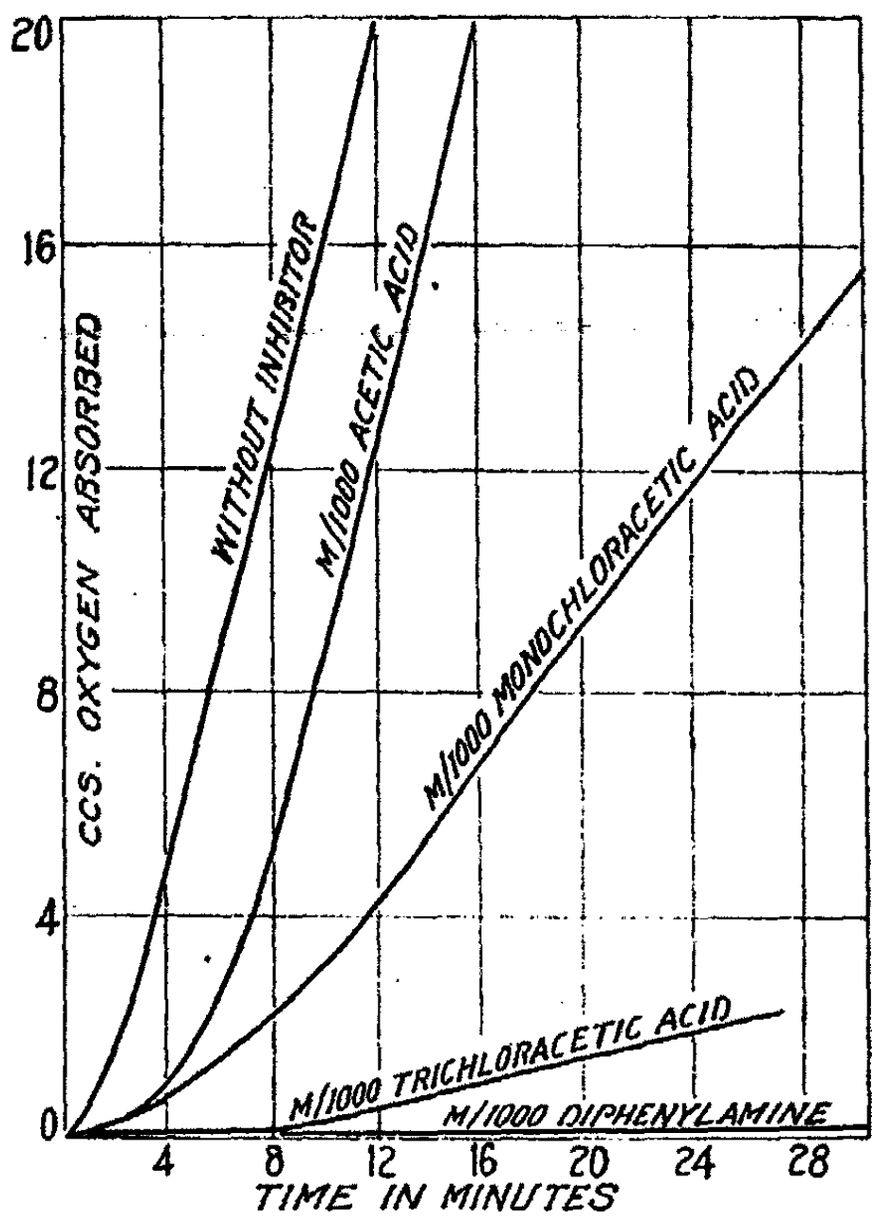



Fig. 1

which also contains a $-CO$ grouping, doubtless parallels this behaviour. Pyrogallol therefore is able to form molecular compounds with three times as many molecules of reactant as can phenol in equal concentration. A higher activity of pyrogallol would therefore be anticipated.

[1] Schmidlin and Lang: Ber. deutsch. chem. Ges., **43**, 2806 (1920).

Kendall and Gibbons[1] have established that the extent of compound formation between a given aldehyde and various acids is determined in part by the strength of the acid, the stronger the acid, the greater the compound formation manifested. This, therefore, suggests another test of the relationship between inhibitory power and compound formation. In the acid series trichloracetic, monochloracetic and acetic acid the tendency to compound formation with benzaldehyde is greatest with trichloracetic and least with acetic acid. Investigation of these three acids with benzaldehyde in concentrations equal to M/1000 showed the same order as regards inhibitory power, as the accompanying diagram, showing oxygen absorption plotted against time, reveals.

The same diagram shows that diphenylamine in M/1000 concentration reduces the rate of oxygen absorption from 1.5 cc per minute to less than 0.001 cc per minute, thus ranking equal with good phenolic inhibitors of the type of hydroquinone and considerably more efficient than, for example, trichloracetic acid. Examination of the freezing point diagram, diphenylamine-benzaldehyde showed no separation of solid molecular compounds between 100 and 50 molecular percentages of diphenylamine. Comparison of the freezing point curve for this system with that of diphenylamine-benzene,[2] which may be taken as that of an ideal physical mixture, showed that 35 molecular percentages of benzaldehyde effected the same depression of the freezing point as 40 molecular percentages of benzene, thus showing some compound formation between solute and solvent. At other molecular concentrations similar conditions hold. Examination of the corresponding curves for benzene-trichloracetic acid[3] and benzaldehyde-trichloracetic acid[4] show that 27 molecular percentages of benzaldehyde produce the same lowering of the freezing point of trichloracetic acid as do 40 molecular percentages of benzene; that,

[1] Kendall and Gibbons: Jour. Am. Chem. Soc., **37**, 152 (1916).
[2] Dahms: Wied. Ann., **54**, 486 (1895).
[3] Kendall and Booge: Jour. Am. Chem. Soc., **38**, 1732 (1916).
[4] Kendall and Gibbons: Jour. Am. Chem. Soc., **37**, 152 (1916).

furthermore, trichloracetic acid and benzaldehyde form an isolable equi-molecular solid compound. It therefore follows that the substance showing greater extent of compound formation (trichloracetic acid) is less efficient as an inhibitor than one showing less compound formation (diphenylamine). Evidently therefore *extent of compound formation alone* is no criterion of inhibitory power. That this must be so is evident from the consideration of a hypothetical case. Suppose a potential inhibitor B form with a reactant A, an extremely stable molecular compound AB, which is practically completely undissociated in the solvent A. Under these circumstances the concentration of inhibitor B will be negligibly small and hence will have an entirely negligible effect on the velocity of the reaction studied.

The necessary conditions for successful inhibitory power may now be laid down for the general case in which B is an inhibitor for a reaction between A and C giving AC, by reason of the capacity of A to form the molecular compound AB. The reactive molecules of A have the two alternatives of reaction

(1) $A + C \longrightarrow AC$

(2) $A + B \longrightarrow AB$

The extent to which reaction (1) will proceed will be determined among other factors by (*a*) the concentration of B, the inhibitor, and therefore by the value of K in the equilibrium

$$K = \frac{(A)\ (B)}{(AB)}$$

and (*b*) by the rate of the reaction (2). The rate of this reaction is expressed by the equation

$$\text{rate } (A + B) = k(A)\ (B).$$

Hence it is that the inhibitory power of a substance depends, according to this viewpoint, on the *actual* concentration of the inhibitor and on its speed of reaction with the principal reacting substance to form the molecular compound.

Little is known as to the velocities of molecular compound formation beyond that they are extremely rapid. Certain of the present results suggest, however, that the several individual

velocities may be widely different. Thus, in the series trichloracetic, monochloracetic, and acetic acids with benzaldehyde, since acetic acid is the weakest acid it follows that its actual concentration in benzaldehyde solution will be greater than that of either monochloracetic or trichloracetic acids in solutions to which equimolar additions of the several acids have been made. Similarly the actual concentration of monochloracetic acid will be greater than that of the trichloracetic acid in such solutions because of the increasing extent of compound formation with increase in acid strength. The order of inhibitory power is exactly the reverse of this order of concentration of uncombined molecules. This suggests therefore that the reaction velocity constant $k$ for the rate of formation of molecular compound must be greatest in the case of trichloracetic acid and least with acetic acid. It would be interesting to ascertain by some other means whether this viewpoint is correct.

The differences obtained in luminescence phenomena with the magnesium aryl and alkyl halides of the Grignard type, as recently investigated by Lifschitz and Kalberer,[1] are further illustrations of the same kind of divergence. Both aryl and alkyl halides in the free state show luminescence when exposed to air. Ether which, as is well known,[2] forms double compounds with the alkyl halides inhibits the oxidation and consequent luminescence of these reagents. This is not so in the case of the magnesium aryl halides. From the standpoint of the present theory it would be interesting to ascertain whether the tertiary amines, which also form molecular compounds with the alkyl halides, show similar inhibitory power.

Finally, in reference to the oxidation of sodium sulphite solutions it may be pointed out that it is very probable that the manifold inhibitors known for this reaction do not all act by suppressing an active positive catalyst. A number of the negative catalysts listed by Bigelow[3] and Young[4] are such as

[1] Zeit. phys. Chem., **102**, 393 (1922).
[2] Tschelinzeff: Ber. deutsch. Chem. Ges., **38**, 3664 (1904).
[3] Bigelow: Zeit. phys. Chem., **26**, 493 (1898).
[4] Young: Jour. Am. Chem. Soc., **23**, 119, 450 (1901); **24**, 237 (1902).

are known to exhibit compound formation with sodium sulphite. The mechanism of inhibition here proposed is equally as probable as the mechanism proposed by Titoff, though there seems little doubt that the latter is responsible for the observed retardation in several cases.

The mechanism of negative catalysis here proposed represents the direct opposite of the mechanism of intermediate compound formation whereby positive catalysis in homogeneous media finds its most reasonable explanation. In positive catalysis the reactants proceed via the intermediate compound to the final state more rapidly than is possible in the absence of the positive catalyst. In the negative catalysis of this paper the formation of the intermediate compound slows down the rate of reaction because one (or more) of the reactants is thereby sidetracked from the main reaction under observation, its energy being dissipated in the process of compound formation. The theory emphasizes anew the fact that the concentration of a substance is not the active mass of the substance, but a very much greater quantity. The negative catalyst indicates more nearly the true active mass of the reacting substance; and, in the interaction of these active molecules either with the second reactant or with the negative catalyst the history of these active molecules is written in such wise that the student of the reaction velocity may read.

## Summary

1. A new theory of negative catalysis has been proposed to supplement the theories hitherto held to explain special cases.

2. It has been shown that the inhibitory power of water and alkali sulphates in the decomposition of oxalic acid in sulphuric acid solutions, of water in various reactions in sulphuric acid and acetone solutions and of a large variety of compounds, organic and inorganic, in the inhibition of autoxidation processes can be explained according to the theory.

3. The experimental evidence accumulated in these cases is explained by the theory and various predictions have been made and already verified in part.

4. The theory accounts for inhibitory power by assuming interaction between one of the reactants and inhibitor to form a molecular compound, as an alternative to reaction between the two (or more) reactants. The extent of the inhibition is determined by the degree and velocity of compound formation.

*Princeton, N. J.*

# REFRACTIVE INDICES OF SOLUTIONS OF HYDROCHLORIC ACID, ACETIC ACID AND ETHANOL IN WATER AT 25° AND 30°

BY HOWARD M. ELSEY AND GEORGE L. LYNN*

The convenience of the dipping refractometer as a quick means of determining the concentration of solutions of pure substances in water is well known. However, its ready use in our laboratory for the analysis of solutions of hydrochloric acid,[1] acetic acid,[2] and ethanol[3] in water was hampered by the lack of sufficient data at the usual laboratory temperatures, the data of previous observers usually being taken at temperatures not conveniently maintained in many American laboratories, or else not covering the range of concentrations desired.

The hydrochloric acid and acetic acid solutions used in the following measurements were prepared from C. P. chemicals which were diluted with distilled water and the solutions aerated with clean air to remove carbon dioxide. The strength of these acid solutions was then determined by titrating a weighed amount of a solution with standard barium hydroxide. The strength of the barium hydroxide was determined by titrating

* Contribution from the Chemical Laboratory of the University of Kansas.

[1] Willigen: Arch. Mus. Teyler, **2**, 209 (1869); Schivers: Jour. Chim. phys., **8**, 530 (1910); Schivers: Bull. Acad. roy. belg. (1910); Le Blanc: Zeit. phys. Chem., **4**, 553 (1889); Wagner: Zeit. öffentl. Chem., **11**, 404 (1905); Wagner: Tabellen zum Eintauchrefraktometer, Sondershausen (1903); Hallwachs: Wied. Ann., **53**, 1 (1894).

[2] Rimbach and Wintgen: Zeit. phys. Chem., **74**, 233 (1910); Buchkreimer: Diss. Bonn (1890); Halwachs: Wied. Ann., **53**, 1 (1894); Wagner: Tabellen zum Eintauchrefraktometer, Sondershausen (1903); Zeit. öffentl. Chem. **11**, 404 (1905); LeBlanc: Zeit. phys. Chem., **4**, 553 (1889) (R); Landolt: Pogg. Ann., **117**, 353 (1862).

[3] Andrews: Jour. Amer. Chem. Soc., **30**, 363 (1908); Schivers: Zeit. phys. Chem., **75**, 357 (1911); Leech and Lythgoe: Jour. Am. Chem. Soc., **37**, 954 (1905); Wagner: Tabellen zum Eintauchrefractometer. Sondershausen (1903); Zeit. öffentl. Chem., **11**, 404 (1905); Hess: Wien. Ber., **114**, 1231 (1905); Sidersky: Bull. assoc. chim. sucr. dist., **27**, 1169 (1910).

it against a hydrochloric acid solution which has been standardized by precipitation as silver chloride.

TABLE I

Refractive Indices of Water Solutions at 25°

| Hydrochloric Acid | | | Hydrochloric Acid | | |
|---|---|---|---|---|---|
| C | S | $N_D$ | C | S | $N_D$ |
| 160.3 | 98.06 | 1.36395 | 54.79 | 44.20 | 1.34433 |
| 148.6 | 92.17 | 1.36187 | 46.07 | 39.46 | 1.34255 |
| 114.6 | 75.56 | 1.35590 | 36.92 | 34.32 | 1.34060 |
| 103.3 | 69.62 | 1.35374 | 26.81 | 28.72 | 1.33847 |
| 93.49 | 64.59 | 1.35190 | 17.72 | 23.57 | 1.33651 |
| 84.67 | 60.10 | 1.35025 | 8.02 | 17.90 | 1.33432 |
| 73.81 | 54.46 | 1.34816 | 0.00 | 13.20 | 1.33251 |
| 65.90 | 50.32 | 1.34662 | —— | —— | —— |
| **Acetic Acid** | | | **Acetic Acid** | | |
| C | S | $N_D$ | C | S | $N_D$ |
| 405.32 | 64.52 | 1.35187 | 179.87 | 40.86 | 1.34308 |
| 407.12 | 65.56 | 1.35226 | 152.45 | 37.25 | 1.34172 |
| 367.90 | 61.28 | 1.35068 | 120.41 | 32.76 | 1.34001 |
| 333.44 | 58.06 | 1.34949 | 92.93 | 28.76 | 1.33848 |
| 303.94 | 55.05 | 1.34838 | 71.75 | 25.40 | 1.33720 |
| 266.89 | 51.17 | 1.34694 | 47.42 | 21.46 | 1.33569 |
| 239.65 | 48.11 | 1.34579 | 25.37 | 17.76 | 1.33427 |
| 220.39 | 45.82 | 1.34493 | —— | —— | —— |
| **Ethanol** | | | **Ethanol** | | |
| C | S | $N_D$ | C | S | $N_D$ |
| 397.12 | 62.75 | 1.35123 | 161.94 | 37.51 | 1.34181 |
| 283.73 | 61.77 | 1.35086 | 129.24 | 32.76 | 1.34001 |
| 341.34 | 58.37 | 1.34961 | 104.72 | 29.17 | 1.33864 |
| 301.30 | 54.52 | 1.34818 | 82.92 | 25.87 | 1.33739 |
| 274.87 | 51.56 | 1.34709 | 59.46 | 22.35 | 1.33604 |
| 241.17 | 47.75 | 1.34566 | 41.23 | 19.60 | 1.33498 |
| 211.10 | 44.06 | 1.34428 | 24.93 | 17.11 | 1.33402 |
| 181.05 | 40.07 | 1.34278 | —— | —— | —— |

The ninety-five percent grain alcohol used in preparing the ethanol solutions was diluted with water, filtered through magnesium carbonate, and then twice distilled, the final dis-

tillate[1] being diluted with distilled water to prepare the samples.

TABLE II
Refractive Indices of Water Solutions at 30°

| Hydrochloric Acid | | | Hydrochloric Acid | | |
|---|---|---|---|---|---|
| C | S | $N_D$ | C | S | $N_D$ |
| 160.3 | 96.37 | 1.36336 | 54.79 | 43.12 | 1.34393 |
| 148.6 | 90.58 | 1.36130 | 46.07 | 38.25 | 1.34210 |
| 114.6 | 74.00 | 1.35534 | 36.92 | 33.24 | 1.34019 |
| 103.3 | 68.26 | 1.35325 | 26.81 | 27.52 | 1.33802 |
| 93.49 | 63.33 | 1.35144 | 17.72 | 22.45 | 1.33608 |
| 84.67 | 58.80 | 1.34977 | 8.02 | 16.76 | 1.33389 |
| 73.81 | 53.20 | 1.34769 | 0.00 | 12.00 | 1.33204 |
| 65.90 | 49.00 | 1.34613 | — | — | — |
| **Acetic Acid** | | | **Acetic Acid** | | |
| C | S | $N_D$ | C | S | $N_D$ |
| 405.32 | 61.52 | 1.35077 | 179.87 | 38.63 | 1.34223 |
| 407.12 | 62.53 | 1.35115 | 152.45 | 35.17 | 1.34092 |
| 367.90 | 58.47 | 1.34964 | 120.41 | 30.80 | 1.33926 |
| 333.44 | 55.31 | 1.34847 | 92.93 | 26.92 | 1.33779 |
| 303.94 | 52.41 | 1.34740 | 71.75 | 23.73 | 1.33657 |
| 266.89 | 48.62 | 1.34598 | 47.42 | 19.86 | 1.33509 |
| 239.65 | 45.73 | 1.34490 | 25.37 | 16.18 | 1.33366 |
| 220.39 | 43.44 | 1.34405 | — | — | — |
| **Ethanol** | | | **Ethanol** | | |
| C | S | $N_D$ | C | S | $N_D$ |
| 397.12 | 59.43 | 1.35000 | 161.94 | 35.65 | 1.34111 |
| 283.73 | 58.72 | 1.34974 | 129.24 | 31.00 | 1.33934 |
| 341.34 | 55.30 | 1.34847 | 104.72 | 27.65 | 1.33807 |
| 301.30 | 51.82 | 1.34718 | 82.92 | 24.31 | 1.33679 |
| 274.87 | 48.90 | 1.34609 | 59.46 | 20.94 | 1.33550 |
| 241.17 | 45.35 | 1.34476 | 41.23 | 18.20 | 1.33444 |
| 211.10 | 41.79 | 1.34342 | 24.93 | 15.76 | 1.33351 |
| 181.05 | 38.10 | 1.34204 | — | — | — |

The concentrations of these ethanol solutions were then calculated from the densities.[2] The accurate work on the

[1] The ethanol thus obtained may have contained a trace of aldehydes and ketones.

[2] Bureau of Standards Circular, No. 19.

refractive indices of potassium chloride solutions at 25° by Baxter and his students[1] was utilized in checking the scale of the refractometer used and it was found to be correct.

The temperature of the solutions was kept constant to ±.05° during the measurements by an automatically controlled thermostat.

The results obtained are given in Tables (I) and II) where C is the concentration of solute in grams per 1000 grams of water, S is the scale reading of the refractometer and $N_D$ is refractive index for sodium light.

By plotting the above data, curves may be drawn from which a set of tables can be prepared. By reference to these tables, the concentration of a solution of any one of the three substances can be found by taking a single reading with the dipping refractometer at room temperature.

**Summary**

The refractive indices at 25° and 30° are given for a number of solutions of hydrochloric acid, acetic acid and ethanol in water.

*Lawrence, Kansas*

[1] Jour. Am. Chem. Soc., **33**, 922 (1911).

# THE ANOMALOUS OSMOSE OF SOLUTIONS OF ELECTROLYTES WITH COLLODION MEMBRANES. III. THE EFFECT OF STIRRING SOLUTIONS

BY F. E. BARTELL AND D. C. CARPENTER

The experimental work described in this paper was undertaken to test further the hypothesis of the authors that passage of solute through the membrane was largely responsible for the N shaped curves observed with collodion membranes. If this hypothesis is correct, we shall expect that even with the least permeable collodion membrane (pore diameter = 0.7 micron) the N shaped curve will be initially apparent in the case of potassium salts when the solutions are stirred. In addition, we should expect a much greater positive osmose in the shaken cell with potassium salts giving the correct electrical orientation for abnormally positive osmose, for the reason that in the shaken cell, diffused solute should be rapidly removed from the face of the membrane on the water side, thereby maintaining a greater potential and concentration gradient across the membrane. In the cases of $CaCl_2$ and $AlCl_3$, salts giving an electrical orientation favorable to negative osmose, we shall expect a greater negative effect in the shaken than in the stationary cell. Diffusion of solute in the shaken cell may be so augmented by the effect of the continuous stirring that an N shaped osmose curve may also be observable with $AlCl_3$, which hitherto has shown no such tendency in our experiments with menbranes of different pore size.

It has been shown by Kahlenberg[1] that the osmose rate is materially changed by stirring the solution in the cell. Cohen and Commelin[2] also report osmose experiments in which the solutions were stirred, but they could not duplicate their results. A decided change in osmose values has often been

[1] Kahlenberg: Jour. Phys. Chem., **10**, 141 (1906).

[2] Cohen and Commelin: Zeit. phys. Chem., **64**, 1 (1908).

observed in this laboratory when the stationary osmose cells have been accidentally disturbed.

The contents of the osmose cell of the T-type was found to be stirred to uniform composition very quickly by placing a metal ball in each compartment, then rocking the entire cell slowly back and forth. This method of stirring possessed none of the mechanical difficulties such as are encountered when externally driven rotary stirrers are used. Changes in concentration in each compartment of the cell were noted by measuring the conductivity of the solutions.

### Construction and Assembly of Rocking Cell

The construction of the cell, shown in Figure 1, was the same as used in our previous work with the exception of the

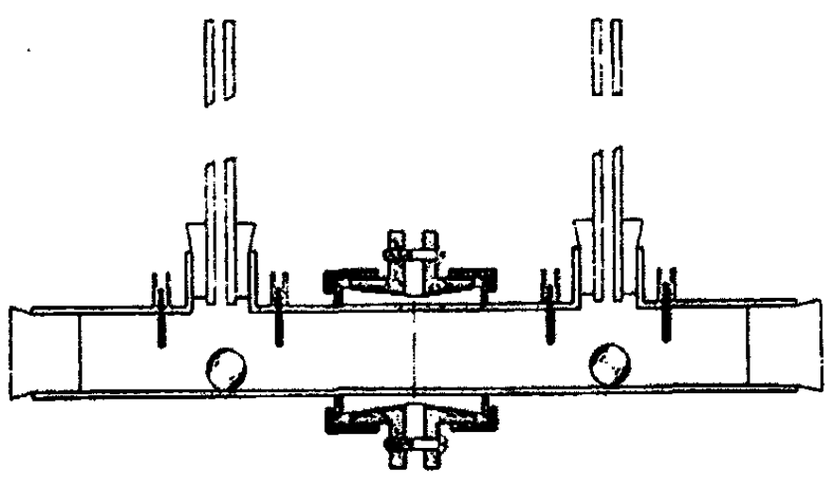


Fig. 1

Osmose Cell, Rocking Type with Electrodes

introduction of two circular platinum electrodes, connections to which were made through glass inseals in each compartment. The inseal glass tubing was cut off at an appropriate length so as to serve as a mercury cup through which electrical contact with the outside of the cell could be established.

The cell was assembled in the usual manner. The platinizing of the electrodes and the washing was done in the usual way and before the membrane was put in place. The assembled cell was rinsed with several changes of water and then placed under an hydrostatic pressure to clean the membrane capillaries.

The conductivity constant for each chamber of the cell

was determined before each pair of osmotic experiments (M/50 KCl solution being used for this purpose). It was found that the specific conductance of the M/50 KCl at first changed gradually at constant temperature. This was traced to adsorption of KCl from the solution by the membrane. It was found necessary to allow the membrane to come to equilibrium with the KCl solution after which this solution was replaced with fresh KCl solution before the cell constant could be determined. This manipulation was found to yield reproduceable results. After the cell constant had been determined, the cell was rinsed with water several times, and then the hydrostatic pressure applied; finally the cell was again rinsed with conductivity water.

### The Thermostat and Rocking Machine

The thermostat was a large air bath, approximately 2 x 4 x 6 feet high, electrically heated, and cooled by a large metal cold water coil. Rapid circulation of air was maintained by an electric fan. The temperature was $25° \pm 0.02°$ C. During operation the current in the heater was thrown off and on by a sensitive toluene regulator approximately every five seconds. Within the thermostat was an electric motor which through reducing gears drove the rocking platform, which carried the osmotic cell, at a slow and even rate. Uprights were attached to the platform, and carried between them a cross piece with narrow slots cut at the proper distance to support the osmometer tubes. Two coiled wire springs of equal tension were attached from the base of the apparatus to each side of the upright. This avoided any jerking motion of the rocking platform during operation.

The front and one side of the thermostat were of glass. The front was in two sections, the upper and lower halves of which could be raised or lowered as occasion required.

### Method of Setting up Cell for Experiment

Previous to setting up the cell, the solutions and conductivity water to be used were allowed to come to the tempera-

ture of the thermostat. The long osmometer tubes were then half filled with solution or water, depending on the chambers with which they were to be used. Each compartment of the osmose cell was then rinsed twice with the solution it was to contain, filled with solution, air bubbles removed and a monel metal ball lowered into each compartment. The osmometer tubes were next inserted and adjusted to the same level. The apparatus was then fastened onto the rocking platform and the stoppers of the osmometer tubes waxed into place.

At the close of an experiment, the rocking machine was stopped, the cells taken out and the solutions and metal balls removed by taking out the stoppers in the two ends of the cell. The osmometer tubes were then removed and the cell washed in the usual manner.

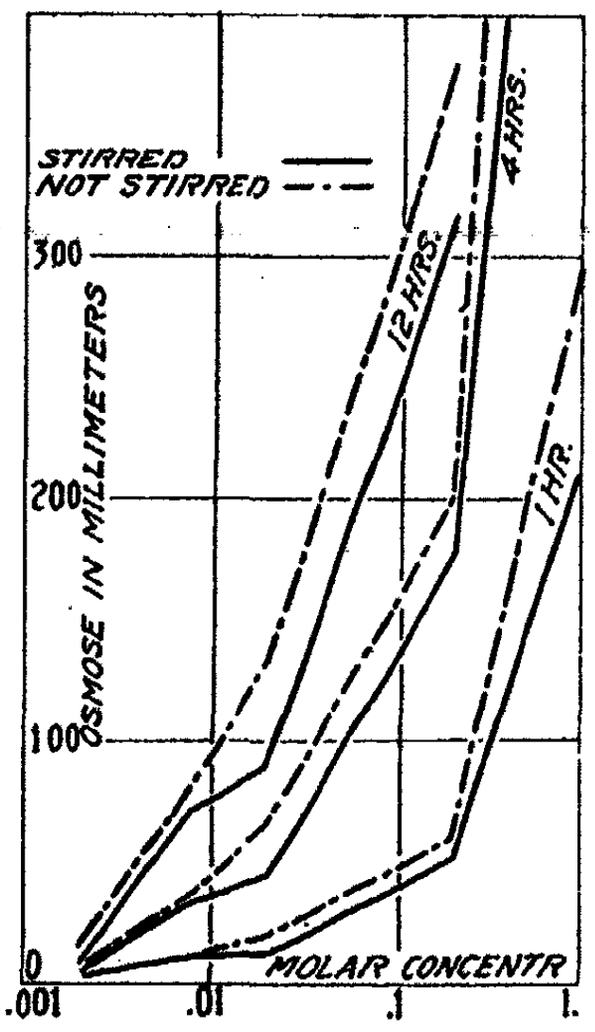



Fig. 2
Osmose Rate of $AlCl_3$ comparing Effect of Stirring vs. not Stirring Solutions

### Results

Readings were taken every half hour for the first two hours and then every two hours thereafter, until maximum osmose values were reached. The results at the end of the two hour period, twelve hour period and maximum osmose are given in Tables I and II. Comparisons of the effect of stirring and not stirring on the osmose of $K_3FeC_6N_6$ and $AlCl_3$ are shown in Figures 2 and 3, respectively.

The following generalizations concerning the effects of stirring on osmose were disclosed by the foregoing data.

1. The shape of the "initial osmose—concentration curves" (2 hour readings) and the "maximum osmose—concentration curves" for the potassium salts, were of the N type throughout and were more strongly accentuated than when the solutions were not stirred.

2. With dilute solutions stirring increased both the initial and maximum osmotic effects in the case of KCl, $CaCl_2$, and $K_2SO_4$, but decreased the effect with $AlCl_3$ and the maximum effect with $K_3FeC_6N_6$.

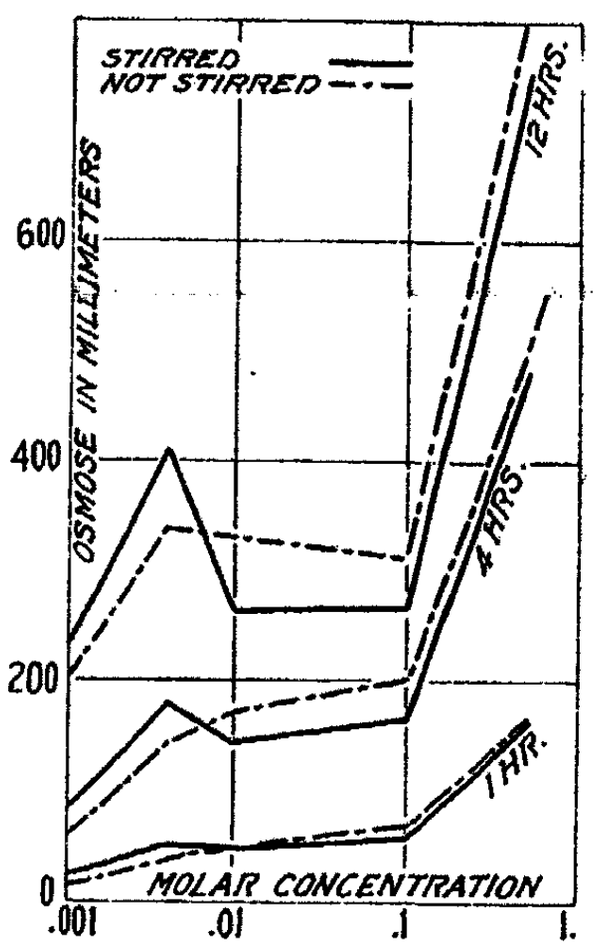



Fig. 3
Osmose Rate of $K_3Fe(CN)_6$ comparing Effect of Stirring vs. not Stirring Solutions

3. With concentrated solutions of electrolytes, greater than 0.1 M, stirring had but little influence on either the initial rate or maximum osmose.

4. Stirring produced a tendency toward the N shaped curve even in the case of $AlCl_3$ which tendency hitherto had not been observed.

5. With sucrose solutions, stirring increased the initial osmose rate, but decreased the maximum osmose.

6. The above results are in harmony with the hypothesis that passage of solute through the membrane is largely responsible for the appearance of the N shaped curve in osmosis through collodion membranes.

## Passage of Salt through the Membrane during Osmose in the Rocking Cell

For the purpose of measurement of the concentration of solute in each compartment during the osmotic process, the specific conductance of the respective solutions was deter-

TABLE I

Osmose Values in Millimeters at the End of 2 Hr. and 12 Hr. Periods with a Rocking Cell

| Salt | 2 Hr. period | | | | | 12 Hr. period | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Concentration | 0.001 M | 0.004 M | 0.01 M | 0.1 M | 0.5 M | 0.001 M | 0.004 M | 0.01 M | 0.1 M | 0.5 M |
| $K_3Fe(CN)_6$ | 49 | 101 | 85 | 98 | 290 | 232 | 408 | 263 | 264 | 755 |
| $K_2SO_4$ | 29 | 60 | 53 | 45 | 146 | 170 | 283 | 187 | 143 | 470 |
| KCl | 14 | 33 | 35 | 23 | 52.5 | 48 | 91 | 83 | 48 | 113 |
| $CaCl_2$ | 5 | 3 | −7 | 17 | 98 | 13 | 3 | −18 | 33 | 275 |
| $AlCl_3$ | 3 | 15 | 22 | 99 | 412 | 9 | 72 | 89 | 316 | 1300 |
| Sucrose | — | — | — | 22 | 143 | — | — | — | 79 | 512 |

TABLE II

Maximum Osmose Values obtained with Salt Solutions of Different Concentrations with Rocking Cell

| Salt | *0.001 M* | | *0.004 M* | | *0.01 M* | | *0.1 M* | | *0.5 M* | |
|---|---|---|---|---|---|---|---|---|---|---|
| Concentration | Time in hrs. | Osmose | Time in hrs. | Osmose | Time in hrs. | Osmose | Time in hrs. | Osmose | Time in hrs. | Osmose |
| $K_3Fe(CN)_6$ | 48 | 425 | 24 | 480 | 14 | 265 | 14 | 267 | 14 | 760 |
| $K_2SO_4$ | 30 | 245 | 18 | 315 | 14 | 192 | 10 | 143 | 14 | 475 |
| KCl | 24 | 50 | 14 | 93 | 10 | 83 | 10 | 48 | 14 | 113.5 |
| $CaCl_2$ | 10 | 13 | 8 | 3 | 12 | −18 | 12 | 33 | 14 | 277 |
| $AlCl_3$ | 16 | 14 | 18 | 77 | 14 | 93 | 18 | 356 | 20 | 1374 |
| Sucrose | — | — | — | — | — | — | 20 | 95 | 24 | 615 |

mined. The specific conductance of the various electrolytes was calculated at all known dilutions from molar and equivalent conductivity data already published by Kohlrausch[1] and Jones.[2]

TABLE III

Molar Concentrations of Solutions Two Hours after starting Osmose Experiment

Rocking Cell

| Salt solution | Initial molar conc. of salt | Molar conc. of salt. Compartment $C_1$ | Molar conc. of salt. Compartment $C_2$ | Ratio $C_1/C_2$ |
|---|---|---|---|---|
| $K_3FeC_6N_6$ | 0.001 | 0.000981 | 0.0000212 | 46.3 |
| | 0.004 | 0.003795 | 0.000218 | 17.4 |
| | 0.01 | 0.00919 | 0.000862 | 10.65 |
| | 0.1 | 0.0907 | 0.01036 | 8.76 |
| | 0.5 | 0.422 | 0.0597 | 7.29 |
| $K_2SO_4$ | 0.001 | 0.000956 | 0.0000405 | 23.6 |
| | 0.004 | 0.003806 | 0.000248 | 15.3 |
| | 0.01 | 0.00907 | 0.000947 | 9.58 |
| | 0.1 | 0.0879 | 0.01201 | 7.31 |
| | 0.5 | 0.4151 | 0.0760 | 5.47 |
| KCl | 0.001 | 0.000977 | 0.0000768 | 12.7 |
| | 0.004 | 0.00347 | 0.000613 | 5.65 |
| | 0.01 | 0.00872 | 0.00152 | 5.75 |
| | 0.1 | 0.0784 | 0.0138 | 5.68 |
| | 0.5 | 0.423 | 0.1195 | 3.54 |
| $CaCl_2$ | 0.001 | 0.000971 | 0.0000684 | 14.0 |
| | 0.004 | 0.00373 | 0.000443 | 8.42 |
| | 0.01 | 0.00899 | 0.00124 | 7.25 |
| | 0.1 | 0.0899 | 0.0124 | 7.25 |
| | 0.5 | 0.456 | 0.0661 | 6.89 |
| $AlCl_3$ | 0.002 | 0.00178 | 0.000198 | 9.0 |
| | 0.008 | 0.00674 | 0.000671 | 10.03 |
| | 0.02 | 0.01601 | 0.00165 | 9.71 |
| | 0.2 | 0.1628 | 0.0219 | 7.43 |

It was originally planned to determine the hydrogen ion concentration of each compartment as osmose developed. It was believed that this might throw some light on the problem. This would be of particular interest in cases of highly

[1] Kohlrausch and Holborn: "Leitvermögen der Elektrolyte" (1898).

[2] Jones: Carnegie Institute of Washington, Publ. 170 (1912).

hydrolyzable salts, such as $AlCl_3$, where the HCl undoubtedly passes into the water compartment more rapidly than $Al(OH)_3$. These data could not be obtained in the time available for this research, but a correction can be applied to the conductivity measurements hereinafter given, from data which may be presented at some future time.

TABLE IV

Molar Concentrations of Solutions when Maximum was registered Rocking Cell

| Salt solution | Initial molar conc. of salt | Molar conc. of salt. Compartment $C_1$ | Molar conc. of salt. Compartment $C_2$ | Ratio $C_1/C_2$ |
|---|---|---|---|---|
| $K_3FeC_6N_6$ | 0.001 | 0.000761 | 0.000183 | 4.16 |
| | 0.004 | 0.002378 | 0.001384 | 1.72 |
| | 0.01 | 0.00595 | 0.003876 | 1.53 |
| | 0.1 | 0.0635 | 0.0438 | 1.45 |
| | 0.5 | 0.2973 | 0.2128 | 1.40 |
| $K_2SO_4$ | 0.001 | 0.00746 | 0.000276 | 2.70 |
| | 0.004 | 0.002526 | 0.001662 | 1.52 |
| | 0.01 | 0.005895 | 0.00424 | 1.39 |
| | 0.1 | 0.0676 | 0.03868 | 1.75 |
| | 0.5 | 0.2966 | 0.2190 | 1.35 |
| KCl | 0.001 | 0.000640 | 0.000471 | 1.356 |
| | 0.004 | 0.002315 | 0.001755 | 1.320 |
| | 0.01 | 0.00612 | 0.00410 | 1.493 |
| | 0.1 | 0.0546 | 0.0426 | 1.281 |
| | 0.5 | 0.2765 | 0.2338 | 1.182 |
| $CaCl_2$ | 0.001 | 0.000792 | 0.000237 | 3.34 |
| | 0.004 | 0.003024 | 0.001237 | 2.45 |
| | 0.01 | 0.00618 | 0.00420 | 1.47 |
| | 0.1 | 0.0656 | 0.0432 | 1.52 |
| | 0.5 | 0.3182 | 0.2300 | 1.38 |
| $AlCl_3$ | 0.002 | 0.00121 | 0.000714 | 1.70 |
| | 0.008 | 0.00445 | 0.003017 | 1.47 |
| | 0.02 | 0.0088 | 0.00658 | 1.65 |
| | 0.2 | 0.1154 | 0.0803 | 1.44 |

The ratio of salt concentrations on the two sides of the membrane was calculated from conductivity measurements for the two hour period and also for the maximum osmose period. Several experiments continued beyond the maximum

osmose period showed that eventually identical concentration in both chambers was reached and at this point the osmose value had diminished to zero. The "least permeable" membranes were used throughout this part of the work.

TABLE V

Millimols of Salt passing through Least Permeable Membrane into Water Compartment during Two Hour Osmose Period

| Salt | Initial molar conc. in salt compartment | Stationary cell A | Rocking cell B | $\frac{B}{A}$ |
|---|---|---|---|---|
| $K_3FeC_6N_6$ | 0.001 | ——— | 0.00036 | ——— |
| | 0.004 | 0.0015 | 0.00371 | 2.46 |
| | 0.01 | 0.0090 | 0.01465 | 1.62 |
| | 0.1 | 0.164 | 0.1760 | 1.07 |
| | 0.5 | ——— | 0.9840 | ——— |
| $K_2SO_4$ | 0.001 | ——— | 0.00069 | ——— |
| | 0.004 | 0.0034 | 0.00421 | 1.23 |
| | 0.01 | 0.0144 | 0.0163 | 1.13 |
| | 0.1 | 0.1803 | 0.2040 | 1.15 |
| | 0.5 | ——— | 1.291 | ——— |
| KCl | 0.001 | ——— | 0.00130 | ——— |
| | 0.004 | 0.0020 | 0.0104 | 5.20 |
| | 0.01 | 0.0107 | 0.0258 | 2.41 |
| | 0.1 | 0.217 | 0.2346 | 1.13 |
| | 0.5 | ——— | 2.032 | ——— |
| $CaCl_2$ | 0.001 | ——— | 0.00118 | ——— |
| | 0.004 | 0.00275 | 0.00755 | 2.76 |
| | 0.01 | 0.01225 | 0.02105 | 1.73 |
| | 0.1 | 0.199 | 0.2105 | 1.05 |
| | 0.5 | ——— | 1.125 | ——— |
| $AlCl_3$ | 0.002 | ——— | 0.00336 | ——— |
| | 0.008 | 0.00587 | 0.01141 | 1.94 |
| | 0.02 | 0.0234 | 0.02801 | 1.21 |
| | 0.2 | 0.282 | 0.3722 | 1.32 |

## Summary

The foregoing data warrant the following conclusions:

1. Stirring increased the rate of passage of all electrolytes through the membrane at all concentrations. The relative increase in diffusion rate due to stirring was greatest in dilute solutions.

2. The rate of passage of solutes into the water compartment was greater for concentrated solutions than dilute, but in no case proportional to concentration, except in two cases with $CaCl_2$.

3. In the region of 0.01 M concentration, the percent increase in mols of salt passing through the membrane in two hours, due to stirring, was as follows: KCl 140, $K_2SO_4$ 13, $K_3FeC_6N_6$ 63, $CaCl_2$ 72, $AlCl_3$ 95.

4. The ratio of concentrations of solute in the two compartments decreased in magnitude as osmose progressed. In concentrated solutions this ratio approached 1:1 (approximately 1:1.4) at the maximum osmose period. For more dilute solutions, this ratio remained much greater.

5. With potassium salts, the relation of anion valence to rate of passage of electrolyte through the membrane showed the following order i neach case: $Cl' > SO_4'' > FeC_6N_6''$. This order was the same at all concentrations and was the inverse of the order of magnitude of maximum osmose. With chlorides, the cation order was $K > Ca > Al$ at all concentrations. This cation order was the inverse of the order of magnitude of maximum osmose in concentrated solutions. The above *orders* were the same as those obtained when the solutions were not stirred.

6. Stirring does accentuate the N shaped osmose curve.

# THE ADSORPTION OF CARBON MONOXIDE AND HYDROGEN BY PLATINIZED ASBESTOS

BY FRANK HOWELL POLLARD

The adsorption by colloidal platinum of substances which poison the hydrogen peroxide reaction has never been worked out even by qualitative experiments. That the determination of adsorption isotherms of gases in the presence of so-called catalytic poisons is necessary, to establish the generally accepted theory that this poisoning is due to the preferential adsorption of the poisons, has been pointed out by Bancroft.[1]

Berliner[2] was one of the first to take up quantitatively the adsorption of gases by platinum, using platinum foil. He concluded that the catalytic action of the metal on oxyhydrogen gas is due invariably to the occlusion of hydrogen, which when occluded always seems to act like nascent hydrogen, as Graham[3] had previously shown to be the case with hydrogen and palladium. Berliner pointed out that, when the metallic surface is not clean, catalysis still takes place at high temperatures, a fact which he attributed to the partial removal of the film of impurity by the action of heat.

In 1895, Mond, Ramsay and Shields[4] studied the adsorption of gases by platinum black, using air, carbon dioxide, oxygen, and hydrogen. They called attention to precautions which are necessary to prevent the poisoning of the platinum black by contamination from greased stop-cocks and rubber connections. They found that platinum black may adsorb from two to fourteen volumes of carbon dioxide. They wrote as follows: "Platinum black dried at 100° C contains rather less than 100 volumes, or about 0.66 percent by weight, of oxygen. . . . . The amount of hydrogen occluded by platinum black independent of that required to form water

[1] Jour. Ind. Eng. Chem., 13, 83 (1921).
[2] Wied. Ann., 35, 791 (1888).
[3] Phil. Mag., 32, 503 (1866).
[4] Phil. Trans., 186, 657 (1895).

with the oxygen already contained in it, is about 100 volumes for the best samples of black, the total amount of hydrogen adsorbed being about 310 volumes. This amount, however, is influenced very largely by the presence of accidental impurities, probably grease, etc. . . . . A portion of the hydrogen occluded by platinum black can be removed at the ordinary temperature by means of the pump alone, but not until the pressure has been reduced to about 300 millimetres. The bulk of the hydrogen can be extracted in vacuo at about 300° C, but a red heat is necessary for its complete removal. On heating platinum black charged with hydrogen in an atomosphere of hydrogen, a portion of the gas is immediately liberated, and in this respect it differs entirely from platinum black charged with oxygen." The hydrogen isotherms obtained by Ramsay and Shields are shown in Figure 1. The break in Curve II corresponds to a leakage into the pump.

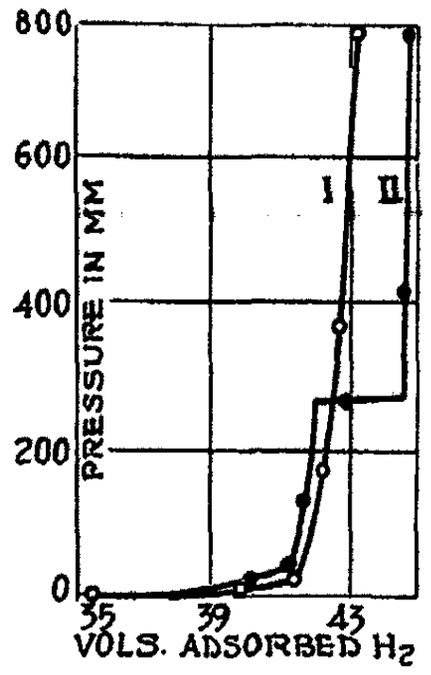



Fig. 1
Isotherms by Ramsay and Shields

Harbeck and Lunge[1] found that platinum black adsorbs about sixty times its volume of carbon monoxide and they concluded that a true chemical compound is formed, since the carbon monoxide is not eliminated by the subsequent action of other gases such as hydrogen and since it is very stable but suddenly decomposes at 250° C into its constituents. They were unable, however, to isolate such a compound.

De Hemptinne[2] studied the catalytic action of platinum black and palladium at very low temperatures in the hope of settling the question of the formation of compounds, assuming that if the occlusion is due to the formation of a compound, it

[1] Zeit. anorg. Chem., 16, 15 (1898).
[2] Zeit. phys. Chem., 27, 429 (1898).

would be diminished greatly at low temperatures. His results are rather bewildering. He claims that in all cases the adsorption of hydrogen is greater at 15° C than at —78° C, while if the tube is allowed to regain slowly the higher temperature, a marked adsorption of the gas occurs at about —40° C. Results with carbon monoxide were completely analogous. These results raise the question as to whether the platinum had been previously reduced to eliminate the combined oxygen. For palladium and hydrogen, on the other hand, the adsorption was greater at low temperatures, but with palladium and carbon monoxide the results were similar to those with platinum.

Taylor and Burns[1] have determined the adsorption of gases by various metallic catalysts. They used the metals copper, cobalt, iron, palladium, platinum sponge, and platinum black, and the gases nitrogen, hydrogen, carbon dioxide carbon monoxide, ethylene, and oxygen. Their apparatus consisted of an adsorption bulb connected to a measuring burette on one side for the introduction of known quantities of gas and to a Toepler vacuum pump on the other side for evacuating the cell and for measuring the gas withdrawn. An interesting detail of their work is the method of determining the free space of the adsorption bulb and the subsequent determination of isotherms at reduced pressures.

"The free space of the adsorption bulb was readily obtained from the nitrogen value since all available data confirmed the assumption that this gas is not measurably adsorbed, at least at these temperatures, by any of the six metals investigated. Calculations of this free space, made by weighing the amount of water required to fill the bulb after it had been evacuated, gave results which agreed with the nitrogen value. In the case of copper, the helium value obtained with a specially purified sample of the gas, obtained through the courtesy of Dr. R. B. Moore of the United States Bureau of Mines, served as additional evidence that the nitrogen value represents zero adsorption."

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[1] Jour. Am. Chem. Soc., **43**, 1273 (1921).

The low adsorption values obtained by Taylor and Burns for platinum black with hydrogen seem to indicate that the metal contained impurities, possibly grease carried over from the stop-cocks, although no mention is made of the nature of the lubricant used.

## EXPERIMENTAL PART

### I. Platinum Black

At first, experiments were attempted using platinum black as the adsorbent in an apparatus shown later in Figure 2. This apparatus had no rubber connections and all stop-cocks were lubricated with phosphorus pentoxide in order to prevent the poisoning of the platinum by grease carried over from the stop-cocks by the gas.

The platinum black was prepared by the method used by Ramsay and Shields. A solution of chlorplatinic acid was evaporated to small volume and neutralized with sodium carbonate. The boiling solution was then poured into a five percent solution of sodium formate and allowed to stand over night. The platinum black was then filtered off and boiled eight or ten times with fairly large volumes of distilled water, and finally dried in a vacuum desiccator over sulphuric acid. In these preliminary experiments, six to seven grams of the platinum black was used.

The hydrogen was prepared electrolytically and purified by passing it through an alkaline pyrogallol solution and then over phosphorus pentoxide.

In two experiments, hydrogen was passed into the cell containing platinum black which had not been previously reduced with hydrogen. The cell was kept at 0° C by immersion in an ice bath. In one case a total "adsorption" of 291.8 volumes of hydrogen was obtained, and in the other, 369.9 volumes. The method and apparatus used, however, did not permit the determination of the amount of water formed, so that the amount of gas actually adsorbed was not determined.

In one experiment using platinum black which had previously been treated with hydrogen and evacuated at 250° C,

an adsorption of 84.8 volumes of hydrogen was obtained. This was probably considerably less than the amount of gas adsorbed in the previous experiments. It was found that the reduced platinum black could not be heated above 100° C without a marked decrease in the amount of hydrogen adsorbed. Apparently even moderate heating causes a very appreciable coalesence of the finely divided platinum when it is not more or less covered by an oxide film. In other words, the heating converted the platinum black to a certain extent into the form of platinum sponge which is known to have a lower adsorptive for gases. As all the work of the earlier investigators indicated that considerable heating was required to displace the adsorbed gas, it seemed probable that the duplication of results by successive runs with a given sample of platinum black would be impossible.

### II. Platinized Asbestos

In the hope of securing platinum in a very active form and at the same time in a form which could be heated to a high enough temperature to remove the adsorbed gases without changing the physical nature of the platinum, platinized asbestos was substituted for platinum black. This form of the metal proved to have a higher adsorptive power than platinum black. In all of the experiments performed with platinized asbestos, the cell containing it has been evacuated at 400° C without any apparent reduction in the adsorptive power. Experiments with pure asbestos fibre alone showed no measurable adsorption of hydrogen.

### Apparatus and Manipulation

The apparatus used was a modified form of the apparatus designed by Browne[1] and his co-workers in the study of pressure-concentration isotherms of certain ammonia systems. A diagram of the apparatus is shown in Figure 2. It consisted of a gas burette *A*, for measuring gas samples added or withdrawn and also serving as a pump for evacuating the cell,

[1] Jour. Am. Chem. Soc., 35, 649 (1913).

connected with the cell $C$ and a mercury manometer $M$. The cell $C$ was a bulb of 150 to 200 cc capacity and was connected to the burette and the manometer through the small bulb $B$ which was filled with phosphorus pentoxide to adsorb moisture resulting from the reduction of the platinized asbestos in the cell. The cell $C$ was so placed that it could be immersed in an ice bath or could be surrounded by an electrically heated air oven.

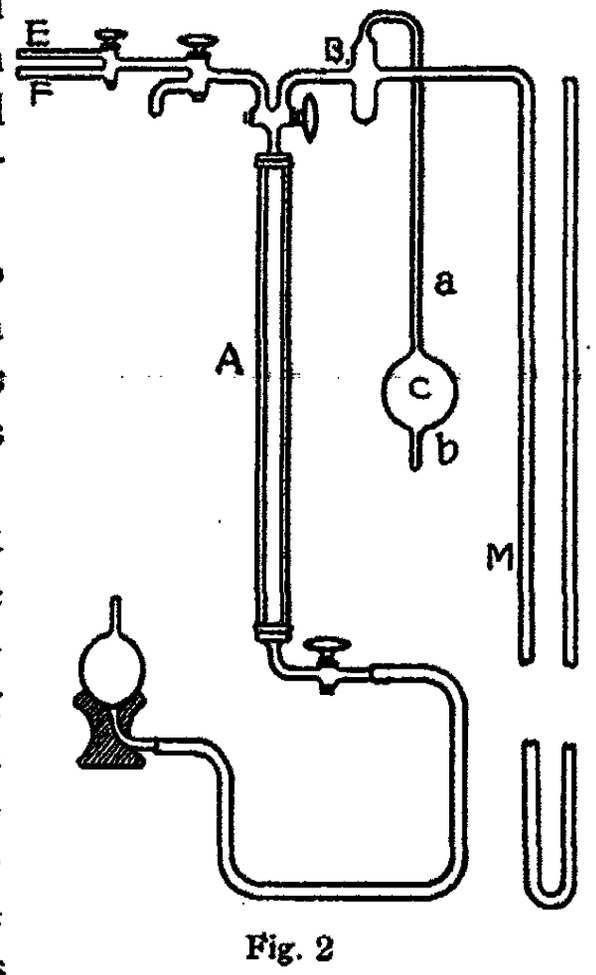



Fig. 2

Hydrogen was admitted to the apparatus at $E$, and carbon monoxide at $F$. All stop-cocks were lubricated with phosphorus pentoxide.

The empty cell was first sealed to the apparatus and the volume of the adsorption chamber determined by withdrawing measured volumes of air from the cell and observing the manometer readings. The total volume of the cell and tubes to the manometer and burette was thus obtained either by plotting the pressure volume curve or by determining the total volume of air removed. During this calibration, the cell was immersed in an ice and water bath, as all of the experiments were performed with the cell at 0° C.

The cell was then broken off at ($a$), filled with platinized asbestos by blowing out the end of the tube ($b$), and resealed after the introduction of the material. The volume occupied by the platinized asbestos, computed from its density, subtracted from the previously determined volume of the cell gave the net volume or free space of the adsorption chamber. In some of the later runs, this net volume was determined by the method of Taylor and Burns already described, using the inert gas nitrogen.

The gas to be investigated was drawn into the burette from the generator, measured, and passed into the cell. As soon as equilibrium had been reached, the manometer pressure was observed. From this pressure the volume of the gaseous phase (volume of gas occupying the free space in the cell) could be computed. The difference between this and the total volume of gas added represented the volume of adsorbed gas. This volume of gas in cubic centimeters could then be converted into volumes of platinum.

In the evacuation process, the cell was in every case heated to 400° C in an electric air oven. It was assumed that the adsorbed gases would be completely removed by evacuation at that temperature. Ramsay and Shields, however, found that about five volumes of hydrogen were retained by platinum black even at this temperature.

## Materials

The platinized asbestos used was furnished by the General Chemical Company through the kindness of the late Mr. T. L. Briggs. It was prepared with especial care to give a catalyst of the maximum efficiency. It was reported to contain 15 percent platinum by weight. Its density was determined with a pyknometer to be 2.866.

The hydrogen, prepared electrolytically, was purified by bubbling it through alkaline pyrogallol and dried by passage through a tube of phosphorus pentoxide.

Carbon monoxide was prepared by heating potassium ferrocyanide with concentrated sulphuric acid to 160° C. The generation of gas in this way could not be controlled very readily so the method was later abandoned. Formic acid was used in place of potassium ferrocyanide. By means of a dropping funnel the formic acid could be added to the hot sulphuric acid to give carbon monoxide at the desired rate. This gas was passed through 1 : 1 potassium hydroxide solution and then through concentrated sulphuric acid and finally over phosphorus pentoxide.

## Experiments

With the apparatus described a number of attempts were made, twelve or fourteen in all, to determine the adsorption isotherms for hydrogen and for carbon monoxide with platinized asbestos. Much trouble was encountered however with the stop-cocks lubricated with phosphorus pentoxide. After each addition of gas to the cell, it required from eight to twelve hours for the system to reach equilibrium. When exposed to a vacuum, or very low pressure, on one side, even the best stop-cock that could be obtained either leaked or set fast. No stop-cock was found that would function under these conditions long enough to permit the determination of a complete isotherm.

One carbon moxoxide isotherm was determined from 0 to 400 mm pressure. The data are given in Table I. Curve 1 in Figure 4 shows these results.

The best results obtained with hydrogen are given in Table II and are plotted in Curve 1 in Figure 3.

TABLES I–II

Cell Data

| | | |
|---|---|---|
| Volume of Cell | 226.6 | cc |
| Weight of Platinized Asbestos | 11.3145 | gm |
| Volume of Platinized Asbestos | 3.95 | cc |
| Net Volume of Cell | 222.65 | cc |
| Weight of Platinum | 1.6972 | gm |
| Volume of Platinum | 0.08 | cc |

TABLE I

Carbon Monoxide at 0° C

| Equilibrium pressure (mm Hg) | Reduced volume of CO added (cc) | Reduced volume of CO remaining (cc) | Volume of adsorbed CO | |
|---|---|---|---|---|
| | | | Cc | Vol.CO/vol.Pt |
| 5.5 | 4.50 | 1.80 | 2.70 | 33.1 |
| 20.0 | 9.00 | 5.90 | 3.20 | 40.0 |
| 36.0 | 14.20 | 10.55 | 3.65 | 45.8 |
| 51.0 | 19.20 | 14.90 | 4.30 | 53.8 |
| 68.5 | 24.10 | 20.10 | 4.00 | 50.0 |
| 85.1 | 29.65 | 24.90 | 4.75 | 59.0 |
| 116.6 | 38.95 | 34.20 | 4.75 | 59.0 |
| 160.7 | 52.85 | 47.10 | 4.75 | 59.0 |
| 274.2 | 86.90 | 80.90 | 6.00 | 75.0 |
| 402.8 | 125.80 | 118.00 | 7.70 | 96.3 |

TABLE II
Hydrogen at 0° C.

| Equilibrium pressure (mm Hg) | Reduced volume of $H_2$ added (cc) | Reduced volume of $H_2$ remaining (cc) | Volume of adsorbed $H_2$ | |
|---|---|---|---|---|
| | | | Cc | Vol.$H_2$/vol. Pt |
| 9.0 | 4.60 | 2.60 | 2.00 | 25.0 |
| 19.7 | 9.20 | 5.80 | 3.40 | 42.6 |
| 32.3 | 13.90 | 9.50 | 4.40 | 55.0 |
| 46.7 | 20.50 | 13.70 | 6.80 | 85.0 |
| 57.0 | 25.10 | 16.70 | 8.40 | 104.2 |
| 71.0 | 29.90 | 20.90 | 9.00 | 112.5 |
| 83.9 | 34.65 | 24.60 | 10.05 | 125.6 |
| 99.0 | 39.55 | 29.00 | 10.55 | 132.0 |
| 114.2 | 44.75 | 33.45 | 11.30 | 141.0 |
| 130.0 | 50.30 | 38.10 | 12.20 | 152.5 |

The use of a good rubber-vaseline lubricant was then attempted. The results showed very conclusively the "poisoning" effect of such a lubricant. The results of two successive experiments are shown in Curves 2 and 3 of Figure 3.

A modification was next made in the apparatus by the insertion of a trap between the burette and the phosphorus pentoxide tube above the cell to remove as completely as possible the volatilized impurities carried over in the gas from the greased stop-cock. This trap consisted of a deep U shaped tube of ordinary sized glass tubing, packed with fine glass wool and so arranged that it could be surrounded by a Dewar flask containing liquid air.

A series of hydrogen isotherms was run, the data for which are given in Table III, and curves 4 and 5 in Figure 3. By keeping liquid air around the trap the poisoning effect of greasy impurities was reduced materially. It is very evident however on comparing Tables II and III that while the liquid air eliminates part of the grease, it does not by any means remove it completely.

Similarly, a series of carbon monoxide isotherms were determined, the data for which are given in Table IV and curves 2 and 3 in Figure 4.

In connection with these experiments, an attempt was made to show definitely whether or not hydrogen and carbon monoxide formed compounds with the platinum and whether or not the process of adsorption in these cases is to some extent irreversible as the results of certain earlier workers seem to

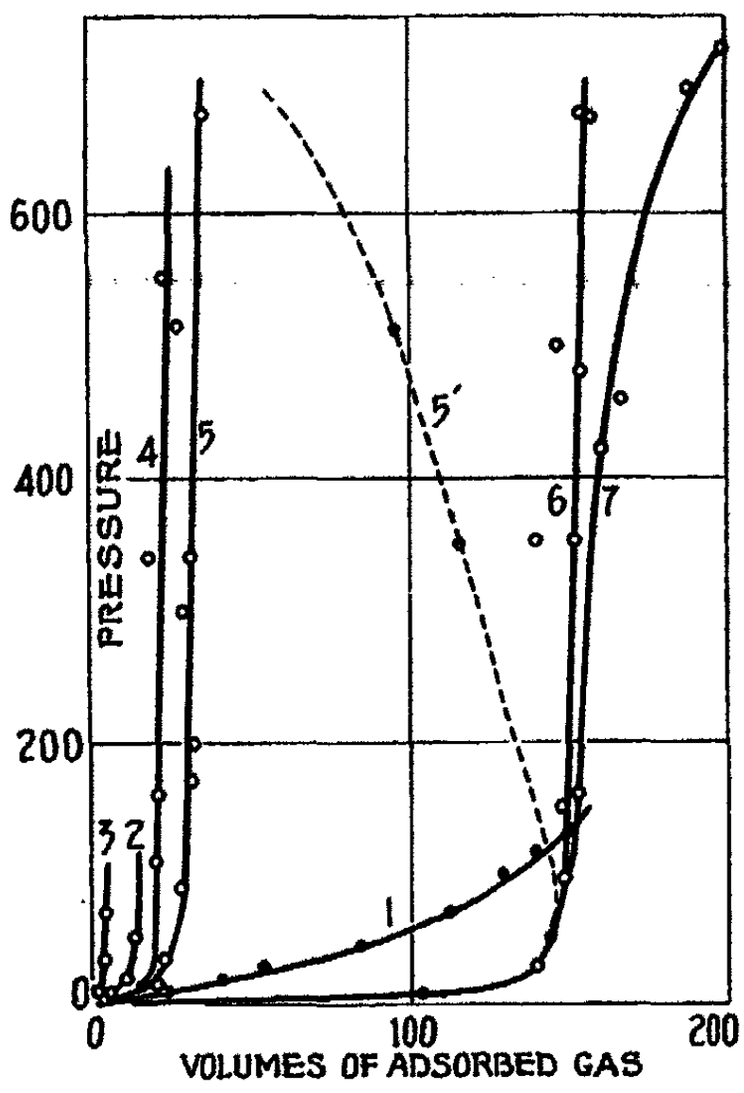



Fig. 3
Adsorption of Hydrogen by Platinized Asbestos

indicate. Ramsay and Shields, as has been pointed out, state that only a portion of the adsorbed hydrogen can be removed by evacuation. Their adsorption isotherms, shown in Figure 1, represent an adsorption of about 35 volumes of hydrogen at zero pressure. With carbon monoxide, the statement of Harbeck and Lunge, that a compound with platinum is

formed which decomposes suddenly when heated to 250° C, has never been clearly disproved.

TABLES III–IV

Cell Data

| | | |
|---|---|---|
| Volume of Cell | 229.22 | cc |
| Weight of Platinized Asbestos | 15.5583 | gm |
| Volume of Platinized Asbestos | 5.43 | cc |
| Net Volume of Cell | 223.8 | gm |
| Weight of Platinum | 2.3337 | gm |
| Volume of Platinum | 0.11 | cc |

TABLE III

Hydrogen at 0° C

| Equilibrium pressure (mm Hg) | Reduced volume of $H_2$ added (cc) | Reduced volume of $H_2$ remaining (cc) | Volume of adsorbed $H_2$ | |
|---|---|---|---|---|
| | | | Cc | Vol.$H_2$/vol. Pt |
| | | Run 1 | | |
| 14.5 | 7.0 | 4.5 | 2.5 | 22.8 |
| 36.4 | 13.9 | 11.3 | 2.6 | 23.4 |
| 61.5 | 21.7 | 19.1 | 2.6 | 23.4 |
| 89.6 | 30.0 | 27.3 | 2.7 | 24.1 |
| 139.0 | 46.9 | 43.1 | 3.7 | 33.5 |
| 170.3 | 56.5 | 52.9 | 3.6 | 32.5 |
| 203.0 | 66.6 | 63.0 | 3.6 | 32.5 |
| 239.8 | 77.6 | 74.4 | 3.2 | 28.6 |
| 207.2 | 86.9 | 83.9 | 3.0 | 27.2 |
| 299.6 | 96.3 | 93.0 | 3.3 | 30.0 |
| 342.8 | 110.0 | 106.4 | 3.6 | 32.0 |
| 654.7 | 212.6 | 203.2 | 9.4 | 84.5 |
| 718.2 | 246.2 | 222.9 | 23.3 | 209.3 |
| | | Run 2 | | |
| 157.5 | 49.9 | 47.5 | 2.4 | 21.4 |
| 338.7 | 104.3 | 102.1 | 2.2 | 20.0 |
| 515.6 | 158.6 | 155.5 | 3.1 | 27.7 |
| 672.3 | 207.1 | 202.8 | 4.3 | 38.5 |
| 750.7 | 231.5 | 226.4 | 5.1 | 46.4 |
| 731.3[1] | 231.5 | 220.6 | 10.9 | 99.0 |
| 510.3 | 164.6 | 153.9 | 10.7 | 96.4 |
| 347.5 | 117.7 | 104.8 | 12.9 | 115.9 |
| 51.7 | 31.1 | 16.2 | 14.9 | 135.5 |
| 1.4 | 13.0 | 0.4 | 12.6 | 112.8 |

| | | | | |
|---|---|---|---|---|
| | | Run 3 | | |
| 55.4 | 18.3 | 16.7 | 1.5 | 13.9 |
| 108.3 | 34.8 | 32.6 | 2.2 | 20.0 |
| 520.7 | 159.2 | 157.0 | 2.2 | 20.0 |
| 655.0 | 200.7 | 197.5 | 3.2 | 28.7 |
| 762.2 | 234.7 | 229.2 | 5.5 | 50.0 |
| 759.9[1] | 234.7 | 229.2 | 5.5 | 50.0 |
| 550.8 | 168.7 | 166.2 | 2.5 | 22.9 |
| 384.0 | 118.0 | 115.8 | 2.2 | 20.0 |

TABLE IV

Carbon Monoxide at 0° C

| Equilibrium pressure (mm Hg) | Reduced volume of CO added | Reduced volume of CO remaining | Volume of adsorbed CO | |
|---|---|---|---|---|
| | | | Cc | Vol.CO/vol.Pt |
| | | Run 1 | | |
| 31.8 | 14.5 | 9.6 | 4.9 | 44.5 |
| 90.7 | 32.3 | 27.4 | 4.9 | 44.5 |
| 155.8 | 54.5 | 47.0 | 7.5 | 68.2 |
| 229.6 | 77.1 | 69.3 | 7.8 | 70.1 |
| 289.4 | 95.9 | 87.3 | 8.6 | 77.3 |
| 342.4 | 114.5 | 103.3 | 11.2 | 101.0 |
| 546.5 | 182.0 | 164.8 | 17.2 | 154.5 |
| 751.0 | 246.1 | 226.5 | 19.6 | 176.4 |
| 745.8[2] | 246.1 | 224.9 | 21.2 | 190.3 |
| 529.9 | 178.6 | 159.9 | 28.7 | 261.0 |
| 382.2 | 130.4 | 115.3 | 15.1 | 128.6 |
| 272.6 | 95.1 | 82.0 | 13.1 | 117.5 |
| 193.1 | 70.1 | 58.2 | 11.9 | 108.2 |
| 139.5 | 52.4 | 42.1 | 10.3 | 92.7 |
| 99.0 | 39.8 | 29.8 | 10.0 | 90.1 |
| 82.8 | 29.7 | 25.0 | 4.7 | 42.7 |
| | | Run 2 | | |
| 49.2 | 19.1 | 14.9 | 4.2 | 37.6 |
| 260.6 | 88.0 | 78.6 | 9.4 | 84.5 |
| 404.6 | 135.4 | 122.0 | 13.4 | 120.0 |
| 544.1 | 179.5 | 164.1 | 15.4 | 138.2 |
| 39.4[2] | 17.9 | 11.9 | 6.0 | 54.5 |
| 35.4 | 15.5 | 10.6 | 4.9 | 44.5 |
| 16.0 | 8.3 | 4.8 | 3.5 | 31.9 |

[1] The system was allowed to stand several days and then the gas was withdrawn in stages.

[2] The system was allowed to stand several days and then the gas was withdrawn in stages.

In order to obtain evidence for or against these ideas, after determining the adsorption isotherm up to about one atmosphere by gradual addition of gas, the isotherm was redetermined by the gradual removal of gas. With both hydrogen and carbon monoxide, it was found that the two curves so obtained did not coincide. In the case of hydrogen the digression was very marked in some experiments, as is shown by

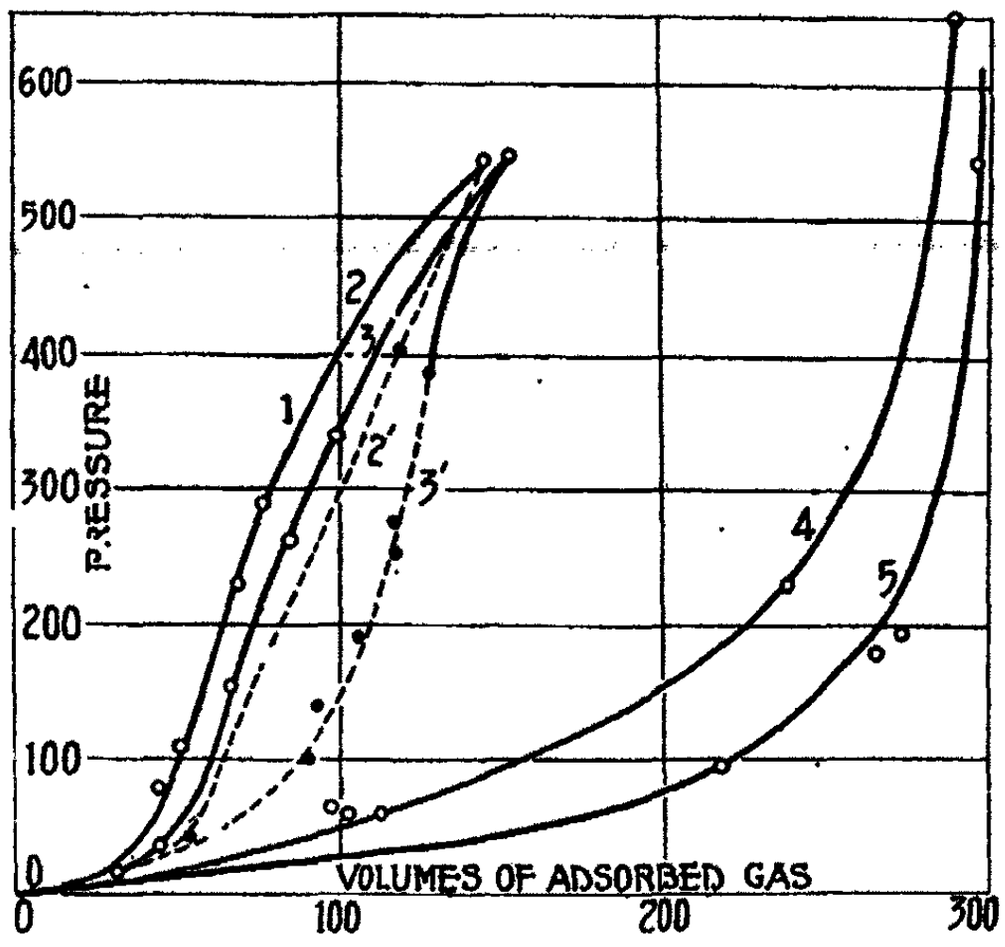



Fig. 4
Adsorption of Carbon Monoxide by Platinized Asbestos

the dotted curve 5′ in Figure 3. The adsorbed gas was apparently not liberated until the greater part of the gas phase had been removed. The amount of adsorbed gas seemed to increase to a higher value, and then, when the pressure was decreased below 50 mm, to decrease rapidly. It was found that by allowing sufficient time to elapse, the adsorbed gas can be removed completely.

With carbon monoxide, although the difference between the two curves was less marked, nevertheless, no mater how

long a time was allowed for equilibrium to be reached after adding the gas, the isotherm plotted upon the removal of gas always gave higher adsorption values. In Figure 4, curves 2 and 2′, 3 and 3′ show this relation. As in the case of hydrogen, however, it was found that the adsorbed gas was completely removable if sufficient time was allowed, two or three days being required to give true equilibrium.

These results seem to establish two things. First, the difference in adsorption upon the addition and removal of gas indicate that for some reason (other than the time factor) the full adsorption capacity of the platinum was not being reached in these experiments. The conclusion reached was that, while the cooling of the incoming gases with liquid air froze out part of the impurities carried over from the stop-cocks, these were not completely removed. Although such an impurity inhibits the adsorption, it does not influence strongly the liberation of the gas once it has been adsorbed

Secondly, the results show conclusively that the combination of these gases with finely divided platinum is an adsorption phenomenon, and is not due in any way to the formation of definite homogeneous compounds with the platinum.

Although the use of a trap surrounded with liquid air seemed to cut down the poisoning effect of the grease from stop-cocks, it was evident from the data that this arrangement only eliminated the trouble partially. Another set of experiments was therefore attempted to determine the adsorption of hydrogen and of carbon monoxide from mixtures of each of these gases with nitrogen. Preliminary tests were made with pure nitrogen to check up the results of Taylor and Burns which showed that nitrogen was not adsorbed. These results were confirmed.

Nitrogen was prepared by adding a saturated solution of sodium nitrite from a dropping funnel to a flask containing a hot solution of ammonium chloride. The gas was dried by bubbling it through wash bottles containing concentrated sulphuric acid. It was then passed through a tube containing finely divided copper heated to about 300° C to insure the

removal of any possible traces of oxides of nitrogen. Finally it was passed through a tube of phosphorus pentoxide.

Hydrogen and nitrogen were added in varying proportions to the freshly evacuated cell of a second apparatus until approximately an atmosphere of gas was present. By working at ordinary pressures in this way it was possible to use phosphorus pentoxide on the stop-cocks without danger of leakage. The data for the adsorption of hydrogen from hydrogen-nitrogen mixtures are given in Table V. These results did not give as smooth adsorption isotherms as the previous experiments had, but this was not to be expected since each point had to be determined by a separate experiment, heating the cell to 400° C and evacuating it at that temperature before each mixture was added to the cell. Fairly consistent checks were obtained, however. The results are given in Table V and the mean values are shown in curves 6 and 7 in Figure 3. The corresponding data and curves for carbon monoxide are given in Table VI and Figure 4.

TABLE V

Mixtures of Hydrogen and Nitrogen at 0° C

| Hydrogen partial pressure | Volume of adsorbed gas | |
|---|---|---|
| | Cc | Vol. $H_2$/vol. Pt |
| 44.6 | 10.6 | 133 |
| 75.0 | 11.5 | 144 |
| 148.3 | 11.9 | 149 |
| 160.0 | 12.3 | 154 |
| 279.0 | 11.8 | 148 |
| 350.5 | 12.2 | 152 |
| 416.0 | 12.9 | 161 |
| 462.1 | 13.4 | 167 |
| 463.6 | 11.6 | 145 |
| 470.0 | 13.2 | 165 |
| 481.1 | 12.3 | 154 |
| 502.4 | 11.8 | 148 |
| 632.1 | 12.2 | 152 |
| 671.1 | 18.7 | 159 |
| 672.7 | 12.3 | 154 |
| 696.5 | 15.1 | 188 |

TABLE VI

**Mixtures of Carbon Monoxide and Nitrogen at 0° C**

| Carbon monoxide partial pressure | Volume of adsorbed gas | |
|---|---|---|
| | Cc | Vol. CO/vol. Pt |
| 59.5 | 9.0 | 113 |
| 63.6 | 7.8 | 98 |
| 95.7 | 17.5 | 219 |
| 180.6 | 21.3 | 266 |
| 195.1 | 21.9 | 274 |
| 231.7 | 19.2 | 240 |
| 544.6 | 23.8 | 297 |
| 648.7 | 23.2 | 290 |
| 681.0 | 23.9 | 298 |

The adsorption values obtained by this last method are consistently higher for both hydrogen and carbon monoxide than are the values obtained in any of the earlier methods used and the indications are that they represent more nearly the true adsorption of these gases by the form of platinum used. These determinations were made with a sample of platinized asbestos that had not been used previously. They were carried out in an entirely new apparatus to eliminate as far as possible the presence of any impurities which might contaminate the gases or the platinum.

Finally, having determined satisfactorily the adsorption isotherms for carbon monoxide and for hydrogen, the adsorption of gas from mixtures of the two was investigated as follows.

The cell was filled with hydrogen and allowed to come to equilibrium so that the hydrogen adsorption was known. Then a certain volume of hydrogen was withdrawn and an approximately equal volume of carbon monoxide was added. When the system had come again to equilibrium, the volume of adsorbed gas was computed in the usual way. In order to determine the composition of this adsorbed gas, a sample of the gas phase was withdrawn and analyzed. About 70 cc of gas was withdrawn quickly from the cell and divided into two portions for analysis. The composition was determined by burning

the sample with oxygen in a Hempel combustion pipette and subsequently determining the carbon dioxide by adsorption over caustic alkali solution. As the volume of the free space of the cell at the equilibrium pressure was known, it was possible from this analysis to calculate the amount of each gas present in the gaseous phase. The difference between this amount and the amount of that gas introduced into the apparatus gave the volume of the gas adsorbed. The results of a number of such experiments are given in Table VII. Although the cell had been evacuated after the experiments of Table VI the trace of carbon monoxide left in the platinum cut down the hydrogen adsorption from over 150 volumes to about 50 volumes.

TABLE VII

Adsorption of Mixtures of Hydrogen and Carbon Monoxide by Platinized Asbestos

| Run 1 | |
|---|---|
| Initial volume of hydrogen | 212.24 cc |
| Equilibrium pressure | 767.20 mm |
| Volume of cell | 208.64 cc |
| Volume of adsorbed hydrogen | 3.60 cc<br>45.00 vol. Pt |
| Volume of hydrogen removed | 46.84 cc |
| Volume of carbon monoxide added | 46.18 cc |
| Final volume of hydrogen | 165.40 cc |
| Final volume of carbon monoxide | 46.18 cc |
| Total volume of gas present | 211.58 cc |
| | |
| Equilibrium pressure | 718.06 mm |
| Volume of cell corresponding | 195.27 cc |
| Volume of adsorbed gas | 16.31 cc |
| Analysis of gas phase | 204.00 vol. Pt |
| Hydrogen 80.4% | |
| Carbon monoxide 20.0% | |
| Volume of hydrogen in gas phase | 166.22 cc |
| Volume of carbon monoxide in gas shape | 29.05 cc |
| Volume of adsorbed hydrogen | −0.78 cc<br>−9.70 vol. Pt |
| Volume of adsorbed carbon monoxide | 17.13 cc<br>214.10 vol. Pt |

| | |
|---|---|
| **Run 2** | |
| Volume of hydrogen | 150.83 cc |
| Volume of carbon monoxide | 62.29 cc |
| Total volume of gas present | 220.12 cc |
| Equilibrium pressure | 777.70 mm |
| Corresponding volume of cell | 211.49 cc |
| Volume of adsorbed gas | 8.63 cc |
| Analysis of gas phase | 108.00 vol. Pt |
| Hydrogen 71% | |
| Carbon monoxide 29% | |
| Volume of hydrogen in gas phase | 150.16 cc |
| Volume of carbon monoxide in gas phase | 61.33 cc |
| Volume of adsorbed hydrogen | 0.67 cc |
| | 8.40 vol. Pt |
| Volume of adsorbed carbon monoxide | 7.96 cc |
| | 99.50 vol. Pt |
| **Run 3** | |
| Initial volume of hydrogen | 209.83 cc |
| Equilibrium pressure | 761.22 mm |
| Corresponding volume of cell | 206.57 cc |
| Volume of adsorbed hydrogen | 3.26 cc |
| | 40.70 vol. Pt |
| Volume of hydrogen removed | 49.02 cc |
| Volume of carbon monoxide added | 50.03 cc |
| Final volume of hydrogen | 160.81 cc |
| Final volume of carbon monoxide | 50.03 cc |
| Total volume of gas present | 210.84 cc |
| Equilibrium pressure | 749.96 mm |
| Volume of cell corresponding | 203.52 cc |
| Volume of adsorbed gas | 7.32 cc |
| Analysis of gas phase | 91.50 vol. Pt |
| Hydrogen 78.3% | |
| Carbon monoxide 21.7% | |
| Volume of hydrogen in gas phase | 159.36 cc |
| Volume of carbon monoxide in gas phase | 44.16 cc |
| Volume of adsorbed hydrogen | 0.45 cc |
| | 5.60 vol. Pt |
| Volume of adsorbed carbon monoxide | 6.87 cc |
| | 86.00 vol. Pt |

These experiments show conclusively that carbon monoxide will displace adsorbed hydrogen practically completely from the platinized asbestos. Taking into consideration the volume of the cell (about 200 cc), and the volume of gas taken for an individual analysis (30 to 40 cc), it will be seen that an error

in reading of 0.1 cc during the analysis would amount to more than the final volume of adsorbed hydrogen obtained in any of these experiments. Therefore, it may be said that, within the limits of experimental error, the carbon monoxide displaces the adsorbed hydrogen completely.

This displacement of hydrogen by carbon monoxide bears out the principle that adsorption is purely a selective phenomenon. It furnishes, likewise, much needed experimental evidence concerning the problem of catalytic poisons and supports strongly the hypothesis advanced by Bancroft[1] "that all substances which poison catalytic agents do cut down the adsorption of the essential reacting substances. . . . . ." Since it has now been shown that carbon monoxide does actually displace adsorbed hydrogen from platinum, it is possible to account for the fact that carbon monoxide is a catalytic poison in many hydrogenation processes carried out with platinum.

The results of this investigation may be summarized as follows:

1. The adsorption of hydrogen, carbon monoxide, and mixtures of these gases by platinized asbestos has been determined at 0° Centigrade and for pressures up to one atmosphere.

2. The determination of the actual adsorption isotherms is made difficult by the fact that minute quantities of impurities such as may be entrained by passing the gases through stopcocks lubricated by grease, decrease greatly the adsorptive power of the platinum. The observations of Berliner in this regard have been amply confirmed. It seems probable that all determinations of the adsorption of gases by platinum are untrustworthy and the results are too low unless scrupulous care be taken to eliminate all possible contamination of the adsorbent.

3. The adsorption process is a reversible one providing sufficient time is allowed to elapse so that equilibrium may be

[1] Jour. Phys. Chem., **21**, 571 (1917).

established. The adsorbed gas may be removed completely from the platinum merely by long continued pumping-out at 0° Centigrade.

4. No evidence has been found to support the contention that the gases mentioned above form definite solid compounds with platinum at this temperature.

5. When contamination of the adsorbent is most effectively prevented platinized asbestos as used in this work is able to adsorb 200 volumes of hydrogen or 300 volumes of carbon monoxide at 0° C and atmospheric pressure, the volumes of gas being expressed in terms of the volume of platinum actually present.

6. Carbon monoxide, added in relatively small amounts to the system hydrogen and platinized asbestos in equilibrium, is able completely to displace the adsorbed hydrogen from the platinum. This evidence supports directly Bancroft's theory of catalytic poisoning and accounts for the fact that carbon monoxide is known to be a poison toward platinum in certain catalytic hydrogenations.

7. The adsorption coefficient of 200 volumes of hydrogen is greater than that obtained by previous investigators, who used platinum black instead of platinized asbestos. The greater value of the coefficient now reported is without doubt the result, at least partly, of the greater precautions taken in this investigation to prevent contamination of the catalyst, but it may also indicate that platinum in the form of platinized asbestos has a greater specific surface than platinum as platinum black.

**Acknowledgment**

To Dr. W. D. Bancroft and to Dr. T. R. Briggs, under whose joint direction this work was carried on, the author desires to express his sincere gratitude for their suggestions and advice. He also wishes to express to them his appreciation for their never failing patience and encouragement during the experimental difficulties which were encountered.

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# STUDIES IN ADSORPTION. IV.
# CHARGE REVERSAL OF SOME COLLOIDS

BY N. R. DHAR AND K. C. SEN

It is well known that ferric hydroxide sol, as ordinarily prepared, is positively charged. In the foregoing paper of this series, however, it has been shown that freshly precipitated ferric hydroxide when shaken with a solution of arsenious acid, passes into a negatively charged colloid. Cataphoretic experiments prove that this negatively charged colloid moves towards the anode with a velocity of about $23 \times 10^{-4}$ cm per sec. per volt gradient, corresponding to a potential difference approximately $-0.036$ volt.

In the same paper it has also been observed that in presence of protecting substances like glycerol, cane sugar, grape sugar, etc., the hydroxides of iron, copper, cobalt, nickel, etc. can be peptised and can be made to take up negative charge. By the gradual addition of alkali to a mixture of ferric chloride and glycerol or sugar, there are three definite stages through which the colloid passes—first it becomes positively charged then coagulation occurs on neutralisation of charge and finally it passes into a negatively charged colloid.

In the present paper several other cases of charge reversal have been investigated and the question of the reversal of charge on colloids has been considered from general principles.

### (a) Ferric Hydroxide and Acids

When freshly precipitated ferric hydroxide is shaken with boric, meconic, malic, tartaric, or molybdic acid, the hydroxide passes into a negatively charged colloid. Cataphoretic experiments show that they move towards the anode. In the case of molybdic acid in water, it is itself a negatively charged colloid. The negatively charged sol of ferric hydroxide is obtained by the adsorption of the negative ion from the acids.

### (b) Hydroxide of Metals and Caustic Soda

When hydroxides of copper, chromium, aluminium, zinc, cobalt, etc., are dissolved in the least quantity of alkali, the hydroxides are mainly in the peptised condition. When clear solutions of these hydroxides in the alkali are subjected to cataphoretic experiments, they all move towards the anode. In the case of chromium and aluminium, immediate deposition of the hydroxides takes place at the anode when the electric current is passed through the solutions. In the case of zinc, copper, etc., the hydroxides are precipitated at the anode less readily. From these cataphoretic experiments it appears therefore that the hydroxides become negatively charged colloids when peptised by caustic alkali due to the preferential adsorption of the negative hydroxide ions from the alkali.[1]

### (c) Hydroxides of Metals and Ammonia

When hydroxides of copper, nickel, zinc, cadmium, etc., are treated with ammonia and filtered, clear solutions are obtained. These solutions were subjected to cataphoretic experiments. It was observed that the respective metals were deposited at the cathode whilst the precipitates of the hydroxides could be obtained at the anode. It follows, therefore, that in all these ammoniacal complex solutions, a part of the metallic hydroxide remains peptised and is a negatively charged colloid. Grimaux[2] long ago suggested that in ammoniacal copper salt solutions a part of the copper is complex, and a part is suspended. From our observations it seems probable that the hydroxides of copper, nickel, zinc, and cadmium remain partly in the complex condition and partly as negatively charged colloids; this negative charge is due to the adsorption of the hydroxide ion from ammonium hydroxide.

### (d) Sulphides of Arsenic and Antimony

It is well known that the sulphides of arsenic and antimony can be obtained very easily as negatively charged colloids. We

[1] Compare Chatterji and Dhar: Trans. Faraday Soc., 16, 122 (1921).
[2] Comptes rendus, 89, 1434 (1884).

have succeeded in obtaining these sulphides as positively charged colloids in the following way.

A dilute solution of arsenious oxide in water is taken in a burette, and this solution is added drop by drop to a large volume of water containing a small quantity of thorium nitrate, through which sulphuretted hydrogen is made to bubble. Only a small part of the sulphide settles at the bottom of the flask, leaving a clear supernatant sol, which is found to be positively charged. The sol is quite stable.

In the case of antimony sulphide, a positively charged sol is obtained when sulphuretted hydrogen is passed through a dilute solution of tartar emetic containing thorium nitrate or uranium nitrate; but sols prepared in this way are unstable, and therefore these sols are stabilised by means of the protective substance, gelatine.

A few bubbles of sulphuretted hydrogen are passed through a dilute solution of tartar emetic containing a little gelatine and various electrolytes, such as thorium nitrate, uranium nitrate, potash alum, ferric chloride, barium chloride, hydrochloric acid etc., and quite stable positively charged sols are obtained. When these sols are subjected to the action of an electric current very small particles of antimony sulphide appear at the cathode where gaseous hydrogen is also set free. The separation of antimony sulphide is much more readily observed in the cases of sols containing thorium nitrate, ferric chloride or potash alum than in the case of sols containing barium chloride or hydrochloric acid as electrolytes.

A positively charged sol of antimony sulphide is also obtained in the following manner. At first a negatively charged stable sol of antimony sulphide is prepared in the ordinary way. This negative sol is taken in a beaker and diluted with water containing a little gelatine. To this mixture, drop by drop, solutions of electrolytes, such as thorium nitrate, uranium nitrate, ferric chloride, hydrochloric acid, etc., are added, and the mixture vigorously stirred. In this way a stable positively charged sol of antimony sulphide is obtained.

It has thus been observed that the charge on colloids can

be readily reversed by the addition of suitable electrolytes, and this appears to be a general phenomenon. It will also be noticed that by the mere presence of an electrolyte, such as thorium nitrate, in the solution before the colloid is actually formed, the arsenic sulphide sol takes up a positive charge. These phenomena immediately point out the influence of the medium on the nature of the electrical charge carried by the colloidal particles.[1] The presence or absence of certain kinds of ions in the medium accounts for the nature of the electric charge on the colloid particles. In order to explain the action of electrolytes in reversing the charge of colloids, it is generally assumed that one ion of the electrolyte is preferentially adsorbed by the suspensoid and that this adsorbed ion confers the charge found on the colloid. Taking the case of a colloid with a particular kind of charge, in order to reverse this, the colloid must pass through the coagulation point. This occurs through adsorption of one ion and consequent neutralisation of the charge on the colloid, and on further adsorption the colloid is stabilised with an opposite kind of charge. In dealing with the reversal of charge of colloids, the amount of preferential adsorption of one ion will therefore determine the nature of the resulting product, whether the colloid is coagulated, or becomes stable on charge reversal. In considering, therefore, the actions of various ions on the charge reversal of a particular colloid, two facts are of great importance, namely, the amount of adsorption of the ions, and their valency. Since adsorption must precede either coagulation or charge reversal, it is of fundamental importance, though nothing very definite about its nature is known. But as coagulation or charge reversal is mainly electrical in nature, the valency of the ions is an important factor in these cases, for a divalent or trivalent ion can either coagulate or reverse the charge more easily than a monovalent ion simply because the total charge on it is greater than that on the monovalent ion. Valency is, therefore, only an important factor in so far as it denotes the quantity of charge on an ion. If the amount of

[1] Compare Hardy: Jour. Physiol., 33, 254 (1905); Powis: Jour. Chem. Soc., 107, 818 (1915).

adsorption for two ions, differing in valency, by a particular colloid be the same, then the minimal concentrations of these ions required to coagulate the same amount of the sol, will be proportional to the electrochemical equivalents of these ions. In other words, if the same amounts of sol are coagulated by different electrolytes, the amounts of the coagulated ion absorbed by the coagulum will be proportional to the electrochemical equivalents of these ions. This has been experimentally confirmed by Whitney and Ober[1] who showed that the amounts of the metals calcium, barium, strontium, and potassium entrained by the coagulum from the same amount of a given colloid were exactly proportional to the electrochemical equivalents of the metals. Freundlich[1] has also shown that for a given colloid, ions of differing valency are adsorbed equally strongly in equimolecular concentrations of the ions in solution. The variations in some cases, which have been observed in connection with this generalisation, are probably due to different adsorbability of the ions in question. It is, therefore, clear that valency is only important when it implies amount of charge on an ion, because in order to have reversal of charge, the colloid need adsorb only a small amount of ions of higher valency in comparison with ions of lower valency. Hence if the amount of adsorption is great, a monovalent ion can easily reverse the charge on a colloid. This has been experimentally observed in the case of antimony sulphide containing gelatine and hydrochloric acid, where charge reversal has been effected by monovalent hydrogen ions, and in the case of ferric hydroxide containing glycerol or sugars and alkali, the hydroxyl ions being effective in the reversal of charge.[2]

It is generally believed that alkaline solutions of tartrate dissolve cupric hydroxide forming a complex negative ion, and the colour of these solutions is blue.[3] The same sort of blue colour is obtained when cupric hydroxide is dissolved in ammo-

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[1] Jour. Am. Chem. Soc., 23, 842 (1901).

[2] For a different view compare Mukheigi: Trans. Faraday Soc., 16, 103 (1921); Phil. Mag., August, p. 321 (1922).

[3] Masson and Steele: Jour. Chem. Soc., 75, 725 (1897).

nia, or caustic soda, as also in the case of peptisation of cupric hydroxide by means of alkali in presence of glycerol or sugars. It is very difficult to explain the production of the same colour in all these cases on the view of complex formation as the same colour is developed by so many different reagents. We have to assume that the positive ion $[Cu(NH_3)_4]^{\cdot\cdot}$ in ammoniacal copper solutions, the negative ion $[Cu(OH)_4]''$ in alkaline copper hydroxide solutions, the negative ion $[C_{12}H_7CU_4O_{18}]'''$ in tartrate solutions, and the complex copper salt solutions containing alkali and glycerol or sugars, having such different compositions, all have the same blue colour. The real explanation of the existence of the same blue colour in all these different substances seems to lie in the fact that we are probably considering the same substance in all cases, namely, negatively charged colloidal cupric hydroxide due to the adsorption of hydroxyl ions which are present in all cases, and this negatively charged colloidal cupric hydroxide has the blue colour. In all these cases cataphoretic experiments show that a part of the copper exists as negatively charged colloidal cupric hydroxide which goes to the anode.

Cataphoretic experiments with peptised solutions of zinc, cobalt, aluminium, and chromium hydroxides show that the hydroxides precipitate on the anode. It might be thought that a complex negative ion is really formed which breaks down at the anode, but our qualitative experiments show, that with these hydroxides, especially with aluminium and chromium hydroxides, large quantities of the substances separate at the anode immediately when the current is started. If, however, it is the complex ion which breaks up, then a greater quantity of the current would have been required in order to neutralise the greater charge on each of the complex ions. But since the colloidal particles carry very small charges, it is quite possible to neutralise them with a small amount of the current. From our experiments we are led to the view that in all these solutions, at least a part of the hydroxide remains as peptised. Quantitative experiments in this line are in progress.

An investigating fact in connection with ferric hydroxide

as an adsorbent is that it can adsorb ferric salts to a marked extent. But if there is much free acid in the solution, then the hydroxide becomes peptised. Thus when freshly precipitated and washed ferric hydroxide is shaken with solutions of ferric acetate, salicylate, meconate or thiocyanate, the salts as a whole are adsorbed, and if dilute solutions are used and shaken with ferric hydroxide, the filtrates become perfectly colourless and are not acidic. These are cases of adsorption of the whole molecule. Similar is the behavior of charcoal in its adsorption of electrolytes.

In a foregoing communication it has been shown that freshly precipitated hydrated manganese dioxide can adsorb the basic portions from salt solutions, leaving the filtrates acid. It has also been observed in that paper that from substances like silver nitrate, copper sulphate, ferric chloride etc., the basic portion is adsorbed and the less the valency of the metal, the greater is the adsorption. Monovalent silver is adsorbed most by hydrated manganese dixoide and it seems probable that the negatively charged manganese dioxide will become positive by the adsorption of the basic portions from electrolytes.

The views that ions of higher valency are adsorbed more strongly by adsorbents has not been supported from our experiments on the adsorption by hydrated manganese dioxide. We have observed that ferric hydroxide or aluminium hydroxide adsorbed by manganese dioxide can be completely replaced by the hydroxides of potassium or sodium when the manganese dioxide containing ferric or aluminium hydroxide is shaken with an excess of potassium and sodium salt solutions. Our experiments on the adsorption of the basic portion from electrolytes, leaving the filtrate acid; are helpful in explaining the cause of soil acidity. It seems probable that just like hydrated manganese dioxide, humus acid of the soil can adsorb the basic portions of the salts contained in the soil. The familiar case of the adsorption of bases by fuller's earth from salt solutions is well known.[1]

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[1] Bancroft: Applied Colloid Chemistry, p. 121 (1921).

**Summary**

1. Freshly precipitated ferric hydroxide when shaken with solutions of arsenious acid, boric acid, meconic acid, tartaric acid and molybdic acid passes into a negatively charged colloid.

2. Cataphoretic experiments show that the hydroxides of copper, aluminium, chromium, zinc and cobalt peptised by caustic alkalis are negatively charged due to the adsorption of $OH'$ ions.

3. The ammoniacal solutions of the hydroxides of copper, cadmium, zinc and nickel contain negatively charged hydroxides of the respective metals, owing to the adsorption of $OH'$ ions from ammonium hydroxide.

4. Positively charged arsenious sulphide sol is obtained by the adsorption of thorium ions.

5. In presence of gelatine as a protective colloid, positively charged antimony sulphide sol is obtained, due to the adsorption of thorium, uranyl, aluminium, barium and hydrogen ions.

6. Charge reversal of antimony sulphide has been effected in presence of gelatine by the addition of electrolytes like thorium nitrate, uranium nitrate, potash alum, barium chloride, hydrochloric acid, and ferric chloride.

7. Charge reversal is primarily due to the amount of adsorption of ions. An univalent ion, if it is highly adsorbed, may reverse the charge on a colloid.

8. The blue colour in ammoniacal cupric salt solutions, in Fehling's solution, in the solution of copper hydroxide in caustic alkali, in the mixture containing alkali, cupric salts and glycerol or sugars, is most likely due to peptised negatively charged cupric hydroxide.

9. Ferric hydroxide has been found to be a good absorbent of ferric salts.

10. The adsorption of the basic portion from salt solutions by hydrated manganese dioxide can throw light on the phenomenon of soil acidity.

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# BASIC CHROMIC SULPHATE

BY F. S. WILLIAMSON

Liechti and Hummel[1] placed ten grams of wool in 600 cc tap water along with ten percent chrome alum (referred to wool) and heated the bath. At about 80°–82° the bath began to become turbid, the turbidity increasing rapidly so that the bath became quite opaque. The precipitate was excessively fine and had by no means the ordinary flocculent character of chromic hydrate. Analyses of the precipitate gave ratios of 0.836 0.819, 0.538, and 0.360 $SO_3$ to one of $Cr_2O_3$. This proves that the precipitate is either a phase of widely varying concentration or a mixture of two phases in varying relative amount, presumably the latter. The absolute figures mean nothing because Liechti and Hummel were not familiar with the phenomena of adsorption and consequently could not have washed the precipitate adequately. They say: "The varying composition here shown is not surprising, and it is no doubt caused by the different lengths of time taken to heat the bath up to the point of initial turbidity. Moreover, the last portion of chrome alum may also become insoluble by long-continued heating at the boiling point." Having a profound confidence in the elimination of errors by arithmetical operations, Liechti and Hummel average these data and conclude that the precipitate is a definite compound having the formula $(Cr_2O_3)_3.(SO_3)_2$. Since the wool contained 1.9, 2.3, and 1.7 $SO_3$ to one $Cr_2O_3$, Liechti and Hummel decide that the wool takes up the basic sulphate and free sulphuric acid simultaneously.

In order to check the results obtained "an experiment was made in which chrome alum was titrated with normal sodium hydroxide, and it was observed that a first change of colour

[1] Jour. Soc. Chem. Ind., **13**, 223, 225 (1894).

really occurred when one-sixth of the $SO_3$ was neutralized, and a second change to a decided yellowish green color was noticed, when one-third of the $SO_3$ was saturated. These observations correspond exactly with the appearance noticed during the mordanting process, so that the decomposition of the wool can scarcely be explained in any other manner than by considering that the wool gradually absorbs the sulphuric acid from the dissociated green solution with the formation of a more and more basic salt; and that this process continues until the wool becomes saturated under the existing conditions."

Instead of postulating the formation of a more and more basic salt, it might well be that a definite basic salt was formed up to a certain point, after which there was present a mixture of that basic salt and hydrous chromic oxide. It seemed desirable therefore to find out what basic salt, if any, is formed on adding varying amounts of caustic soda to a chrome alum solution.

Four hundred eighty grams of potassium chrome alum, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$, were dissolved in distilled water and diluted to make six liters. This was divided into six portions, one liter being placed in each of six two-liter beakers. To these beakers were added definite amounts of standard sodium hydroxide solution, equivalent to 1, 2, 3, 4, 5, 6 mols per mol of chrome alum. The sodium hydroxide was added slowly, at ordinary temperature, with constant stirring. The washing and drying of the precipitates was carried on in precisely the same way as in the work on basic aluminum sulphate.[1] The methods of analyses were the same.

The addition of one mol of sodium hydroxide to the chrom-alum solution did not give enough precipitate to provide a sample for analysis. The results of the analyses of the other five samples are given in Table I.

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[1] Williamson: Jour. Phys. Chem., 27, 280 (1923).

TABLE I

| Mols NaOH | Average % $Cr_2O_3$ | Average % $SO_3$ | % $H_2O$ by difference |
|---|---|---|---|
| 2 | 55.4 | 19.5 | 25.1 |
| 3 | 55.3 | 21.0 | 23.7 |
| 4 | 55.6 | 21.0 | 23.4 |
| 5 | 55.5 | 20.2 | 24.3 |
| 6 | 65.6 | 9.7 | 24.7 |

It is evident from these results that the precipitate obtained by adding 2–5 mols NaOH is practically constant in composition and differs radically from the precipitate obtained on adding six mols. The results can be expressed by the formula $7Cr_2O_3.5SO_3.25H_2O$, as shown in Table II.

TABLE II

| | $Cr_2O_3$ | $SO_3$ | $H_2O$ |
|---|---|---|---|
| Calculated for $(Cr_2O_3)_7.(SO_3)_5.25H_2O$ | 55.5 | 20.8 | 23.7 |
| Found by analysis (2–5) | 55.5 | 20.4 | 24.1 |
| Found by analysis (3–5) | 55.5 | 20.7 | 23.8 |

As in the case of the corresponding basic aluminum sulphate, it was impossible to remove all the water by standing the precipitate in a desiccator over concentrated sulphuric acid. On heating at 150° to constant weight the precipitate lost about 8.7%, equivalent to about 36% of the total water content. At 200° the loss rose to about 15.4% or about 64% of the total moisture. At 250° the total loss was about 22.9% equivalent to 95% of the original water content. It was not deemed advisable to heat the product higher because $SO_3$ begins to come off at about 300°. The chromic compound holds on to the water more firmly than does the corresponding aluminum salt and does not lose the whole of it under atmospheric pressure at any given temperature.

When the dried product was moistened with water and dried at 100°–110° several times, the amount of water taken up was less than two milligrams whereas the loss in water had

been just over twenty-three milligrams. We are, therefore, not dealing with a reversible hydrate. The basic salt obtained in this way does not differ very much from the one postulated by Liechti and Hummel. The ratio of $Cr_2O_3$ to $SO_3$ is 1.4 in these experiments and 1.5 in those of Liechti and Hummel, which is quite within the limit of their experimental error, since their single observations varied from about 1.2 to about 3.0. This agreement does not prove that this basic salt is actually adsorbed by wool; but it is certainly necessary to consider seriously the possibility that this happens.

Schrötter[1] claims to have obtained a basic salt in which the molecular ratio of $Cr_2O_3:SO_3$ was 1.5 by heating a solution prepared by treating an excess of hydrous chromic oxide with dilute sulphuric acid. He assigns to the product the formula[2] $(Cr_2O_3)_3.(SO_3)_2.14H_2O$; but Schiff[3] states that almost all the sulphate can be washed out of it and that it is, therefore, not a definite compound. Schiff himself prepared a salt having the composition $Cr_2O_3.SO_3.6H_2O$ by adding an insufficient amount of ammonia; but there is of course no evidence that it is really a compound. The other alleged basic sulphates are obtained by analyzing so-called solutions[4] of basic salts; but these are nothing more than colloidal solutions of chromic oxide peptized by chromic sulphate. On that basis the precipitates from such solutions must be chromic oxide or a basic sulphate with an undetermined amount of adsorbed chromic sulphate. The true basic salt may, therefore, have a composition differing quite a little from the product analyzed. This will have to be cleared up at some future time.

This work has been carried on under the direction of Professor Bancroft and was made possible by a grant from the Chemical Foundation.

The general results of this paper are:

1. The precipitate obtained by adding 2–5 mols NaOH

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[1] Pogg. Ann., **53**, 516 (1841).

[2] Dammer's Handbuch der anorganischen Chemie, **3**, 548 (1893).

[3] Liebig's Ann., **124**, 167 (1862).

[4] Siewert: Liebig's Ann., **126**, 97 (1863).

to one mol of potassium chrome alum has a practically constant composition and must, therefore, be considered for the present as a definite basic salt. The composition can be represented by the formula $(Cr_2O_3)_7.(SO_3)_5.25H_2O$.

2. At ordinary temperature the salt is practically stable when standing over concentrated sulphuric acid.

3. A portion of the water is lost at 150°, more at 200°, and nearly all at 250°. The salt does not, therefore, lose all its water at any constant pressure, which makes it unlikely that we are dealing with water of crystallization.

4. The salt which has been dehydrated at 250° takes up only a slight portion of the water at a lower temperature. It is, therefore, not a reversible hydrate.

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# NEW BOOKS

**Rays of Positive Electricity and Their Application to Chemical Analysis.** *By Sir J. J. Thomson. Second edition. 23 × 15 cm; pp. x + 237. New York and London: Longmans, Green and Co., 1921. Price: $5.25.*—The first edition was reviewed nine years ago (**18**, 699). In the preface to the second edition the author says that "the hope expressed in the first edition that the method of Positive Rays would be of service in connection with important chemical problems has been fulfilled to a remarkable extent by the researches of Mr. Aston and others on the determination of atomic weights and the detection of isotopes."

On p. 8 we read that "the positive rays passing through a hole in a plane cathode are not by any means identical with those which would have struck the site occupied by the hole had the cathode been continuous. . . . . There are many points of interest in the behaviour of perforated cathodes which are, I think, probably connected with the question of the transmission of the electric charge from a positively charged atom or molecule to a metallic electrode. . . . . .

"When a positive atom gives up its charge to a metal, it must, when close to the metal, regain an electron and become neutral. If it comes close to a piece of metal at a place where there is no electric force, then an electron in the neighbourhood would run into the atom and might become attached to it. If, however, there is an intense electric field close to the metal the electron will acquire a high velocity and instead of combining with the positive atom may shoot past it. We see from this that the discharge of positive electricity to the electrode may be hampered by a strong electric field, such as might be produced by a double layer of electricity, close to the electrode. Now, when the electrode is emitting cathode rays there is at the seat of emission such a double layer, which not only gives rise to an intense electric field close to the cathode but also diminishes the electric field in the gas beyond the double layer. The layer does two things: (*a*) it makes it more difficult for the positive ions to lose their charges; (*b*) it concentrates the electric field close to the cathode. When this concentration is great the positive ions will acquire by far the larger part of their energy close to the surface of the cathode, and thus ions originating in different parts of the dark space in front of the cathode would reach the surface of the cathode with practically the same energy. Again, the cathode rays which originated in the dark space would only possess a very small fraction of the energy of those which started from the cathode itself. The cathode rays would thus consist of two groups—the energy in one group being constant while that in the other would be variable but small compared with the energy of those in the first group. This is consistent with the behaviour of the cathode rays coming from a continuous cathode. The positive rays coming through a perforated cathode show a wider variation in energy than is indicated by these considerations," p. 10.

"The places from which the positive rays originate can be traced in a very simple way by means of a screen covered with a layer of fused lithium chloride. This substance when struck by rapidly-moving positively-electrified particles phosphoresces with a deep red light; the red lithium line being very

prominent when the light is examined with the spectroscope. When lithium chloride is struck by cathode rays the phosphorescence is steely blue and the spectrum is continuous. To explore the tube for positive rays a thin rectangular strip of mica or metal covered with the fused chloride is attached to a closed glass tube which contains a piece of iron and can slide along the bottom of the discharge tube. The strip can be moved to or from the cathode by moving the piece of iron along the tube by a magnet. If we start with the mica strip near to the cathode we find that the anode side of the screen is a brilliant red, proving that in this region there are plenty of positive rays moving up to the cathode. When the strip is pulled further away from the cathode the red light on the anode light persists and is quite bright until the screen almost reaches the limit of the dark space close to the negative glow, when it gets into the negative glow the phosphorescence on the anode side disappears. This shows that many of the positive rays start from close to the junction of the dark space and the negative glow. It is surprising to find how short is the distance which the screen has to travel from the boundary of the negative glow for the red phosphorescence to be quite marked. As at this end of the dark space the electric force is very feeble, the charged particles cannot have fallen through more than a small fraction of the potential difference between the anode and the cathode," p. 14.

"On many theories of the origin of spectra the emission of series lines is connected with the return of an electron to a positively charged atom, so that the series lines of the gas through which the positive rays are passing would not be excited unless these rays produced some positively charged atoms in this gas. We see from the preceding considerations that, when a positively electrified particle loses its charge, positively charged atoms are produced in the gas; when however, it regains its charge no such atoms need be produced. Thus, on the theories of the origin of spectra referred to, the positive rays would excite the line spectra of the gas through which they pass when they lose their charge but not when they regain it. This might be tested in the following way: If a pencil of positive rays were sent between two parallel plates, with a large potential difference between them all the positively electrified particles would be driven against one of the plates, and the beam when it first emerged from the plates would contain nothing but uncharged particles; these would gradually acquire a positive charge, but this process does not excite the series lines of the gas through which they are passing, hence the region traversed by the rays just after they leave the plates ought not to give out the series lines of the gas," p. 55.

"We may point out in passing that the ionizing effect of radiation would be to make a self-sustained electric discharge possible even in an absolute vacuum. For, suppose we have two electrodes in such a vacuum and that an electron is in the field, under the electric force it will be driven against the anode and will give rise to radiation; this radiation falling upon the cathode will cause it to give out electrons; these will in turn be driven against the anode and will give rise to radiation which will again eject electrons from the cathode. Thus the discharge will be maintained when the potential difference between the electrodes is great enough to give so much energy to an electron that the radiation it produces when it strikes against the anode is sufficiently intense to liberate one electron from the cathode. Thus a body charged up to more than a certain potential would lose its charge even if placed in an absolute vacuum. It is interesting to

notice that in a case like this the speed of the electrons might exceed that due to a fall through the potential difference between the anode and cathode," p. 114.

"A comparison of this [electroscopic] curve [for carbon monoxide] with a photograph of the discharge through the same gas shows many interesting features. On the photograph the strongest lines are those corresponding to the atom and molecules of hydrogen. The curve on the other hand shows that the number of hydrogen particles is only a small fraction of the number of CO particles. The extraordinary sensitiveness of the photographic plate for the hydrogen atom in comparison with that for atoms and molecules of other gases is shown in all the curves taken by this method. But great as is the discrepancy in the case of the photographic plate between the effects produced by hydrogen atoms and an equal *number of heavier* atoms, it is not nearly so great as it is for a willemite screen; such a screen may show the hydrogen lines very brightly while the CO line is hardly visible, when measurements made with the electroscope in the way just described show that the number of particles of hydrogen is only a few percent of the number of the CO particles.....

"The negatively charged hydrogen atoms seem to have the same preponderance in their effect on the photographic plate over other negative atoms as positive hydrogen atoms have over other positive atoms. Thus on all the plates the line corresponding to the negatively electrified hydrogen atoms is well marked, often being comparable with the negatively electrified oxygen atom. With the electroscopic method the negative hydrogen atom can only just be detected, while the negatively electrified oxygen atoms produce a large negative deflection," p. 124.

"The production of spectra by bombardment with cathode rays has been investigated by Gyllensköld and by Stark and Wendt, who have shown that the colourless salts of the alkalies and alkaline earths and also of thallium, zinc, and aluminum give out the series lines of the metals when struck by the positive rays, and that the lines given out do not depend upon the character of the salts. According to Stark and Wendt the seat of the emission is not the surface of the salt itself but a layer of gas, less than 1 mm thick, close to the surface. This is what might have been expected, for to get a line spectrum we must have the substance in the gaseous state. This layer is analogous to the velvety glow which covers the surface of the cathode where an electric discharge passes through a gas at a low pressure," p. 170.

"To answer the question how many atoms are detached from the cathode when one positive ray strikes against it, we should require to know the proportion of current carried by the positive rays and the cathode rays respectively. We do not know this, but we have every reason to believe that the greater part of the current is carried by the cathode rays; if this is so, the table shows that every positive ray which strikes the cathode must on the average detach a large number of silver atoms from the cathode. Whatever the proportion between the currents carried by the positive and negative carriers may be, the table shows that, at any rate in oxygen and argon, each positive ray detaches more than one atom of silver. It may be that the mechanism by which the metal is torn from the cathode is such that the atoms of the metal are not liberated separately, but in groups. Thus, to take a purely mechanical view of the process we may suppose that the atom struck by a positive ray is driven further into the metal, that its

displacement forces outwards the atoms in a ring surrounding it, and that these atoms acquire a considerable part of the energy in the positive ray. On this view the process would be analogous to that which occurs when a marble falls upon the surface of water, a crater is formed under the marble but the rim of the crater moves upwards and escapes, if the marble has fallen from a considerable height, from the surface of the liquid in drops. So in the case of the cathode it may be that it is not the atom struck by the positive ray which is torn from the metal, but a ring of atoms in its neighbourhood," p. 175.

"When salts and minerals are bombarded we find when we analyse by the positive rays the gases given off, a line corresponding to a substance with atomic weight 3 as well as the helium line. In face the '3' line occurs even more frequently in such cases than the helium line, for it is rare to find it absent after any solid has been bombarded by the cathode rays, and it not infrequently occurs when no trace of the helium line can be detected.....

"Summing up the results, we see that $X_3$ can be obtained by passing the discharge through gases such as phosphonium iodide, through hydrogen under special conditions of discharge, through hydrogen acted on by $\alpha$ particles; that when it is obtained by bombarding a salt a continuous supply can be obtained when the salt contains hydrogen, while from salts which do not contain hydrogen the supply is soon exhausted. And again, that under certain conditions, such as exposure to bright light or by vigorous sparking, $X_3$ combines with oxygen, and that it is removed by copper oxide at a red heat. All these results seem to point to the conclusion that $X_3$ is $H_3$ triatomic hydrogen. At the same time I do not feel certain that in some cases the '3' line may not arise from another source. My grounds for this view are: (1) the yield of $X_3$ is exceptionally large from certain minerals; this is what would happen if $X_3$ were a permanent gas absorbed by the mineral; (2) when these minerals are bombarded the '3' line shows some characteristics which are not generally present, e. g., the parabolas are very long, sharp and of very uniform intensity. In the majority of cases the '3' line is rather shorter than, say, the other hydrogen lines, and the intensity is apt to vary along the parabola.

"It is interesting to find that Fabry, from the measurements of the broadening of the 'nebulium' line due to thermal agitation, came to the conclusion that the source of this line is an element with atomic weight 3," p. 202.

"The gases liberated when the surfaces of solids are bombarded by cathode rays furnish a very direct proof that the surfaces of these solids and the walls of the tube itself are liable to be coated with layers of gas. These layers play an important part in positive ray work at very low pressures, both in the methods which have to be adopted to succeed in obtaining these pressures and in the interpretation of the results when the positive ray method is used to analyse a gas. The amount of gas which adheres to solid surfaces or is diffused throughout their volumes is exceedingly large, and its removal is a matter of great difficulty. This is not surprising, for to separate a molecule from the surface of a solid or liquid requires the expenditure of a considerable amount of energy which we can estimate without difficulty if we know the latent heat of evaporation of the substance. Thus from the latent heat of steam we find that the work required to separate a molecule of water from a water surface is that corresponding to the fall of the atomic charge of electricity through about half a volt. The tendency

to evaporate diminishes very rapidly as this work increases. Thus if it took twice as much energy to remove a water molecule from a glass surface as it does from a water one, the vapour pressure of water vapour over a film of water one molecule thick on glass at 273°C would be about that over a free water surface at 0°C. So that if the glass were heated to 273°C the water films would only evaporate at about the rate ice at 0°C would evaporate in a vacuum at that temperature. If the removal of a molecule required 1.5 volts we should have to heat the surface to 546°C to attain this rate of evaporation. So that we see that for quite moderate amounts of adhesion the film may be so firmly held that it would be practically impossible to liberate it by heating the glass to any temperature below its melting point [p. 207].....

"The existence of a highly compressed layer of hydrogen atoms over the surface of solids would explain the very interesting fact that $H_3$ is produced so much more readily by bombarding solids than in any other way, for on the surface of these solids we have the atoms in an ideal condition for combination, packed so close together that they are almost in contact, and at the same time ionized and liberated by the action of cathode rays," p. 209.

On p. 230 the author says that "we might expect that the inert gases might be able to form compounds if they were positively electrified.....The compounds formed by electrified atoms of the inert gases would, I think, be an interesting subject for investigation. In this connection it may be remarked that the helium parabola in the positive ray photographs sometimes shows an abrupt increase in intensity at a place twice as far from the vertical as the head of the parabola, showing that two helium atoms have combined to form a molecule which broke up after passing through the cathode."

Aston's mass-spectrograph is described on p. 36 under the name of Aston's focus-method, and a few of the general results are taken up on pp. 213–221.

*Wilder D. Bancroft*

**An Introduction to the Chemistry of Plant Products.** *By Paul Haas and T. G. Hill. Vol. II. 22 × 15 cm; pp. viii + 140. New York and London: Longmans, Green and Co., 1922. Price: $2.50.*—This volume deals with the metabolic processes of the plants under the headings: the living plant; the synthesis of fats; the synthesis of carbohydrates; the synthesis of proteins; respiration; growth.

"Growth is to a certain degree an understandable problem which, on the present elementary occasion, can be sufficiently indicated in a few words. Of necessity must a cell be nourished through its surface and growth will take place if assimilation be greater than waste by oxidative and kindred processes. But growth means increase, and as this increase in bulk takes place the surface area of the cell is proportionally lessened. A stage ultimately will be reached when the area of the surface is so limited in proportion to the volume of the cell as to permit the entry of only sufficient food to make good the losses; thus the surface area is a limiting factor. One of three things now is possible: the cell may remain as it is, a permanent tissue element; it may develop further, using up its own contents either entirely or in part in fitting itself for another function, water transport for instance; or it may divide and by so doing increase its surface area in relation to its volume, in which case the cycle may restart. Growth thus can

be interpreted in terms of physical chemistry: the first possibility mentioned hardly requires contemplation, since nothing is easier to do than nothing. The third proposition is less easy to understand; the second is a mystery. For instance, why should the daughter of a merismatic cell develop into a phloem element if it be cut off on the one side of its parent and into a xylem element if it be born on the other? Is it due to some subtle influence or stimulus which has its origin in the adjacent structural elements; or is it due to some quality in the cell itself, an heredital predetermination; or is it due to some obscure colloidal property comparable to the Liesegang phenomenon?" p. 2.

"The term carbon assimilation, although unfortunate from some points of view, is employed to designate all those activities, in part physical, in part chemical, which play a rôle in the anabolism of carbon dioxide by green tissues. The conspicuous facts of the process are that active chlorenchyma on exposure to light forms, by means of its chlorophyll, carbohydrate from the initial substances carbon dioxide and water; oxygen, in volume roughly equivalent to the volume of carbon dioxide consumed, is evolved during the process. Carbohydrate is the obvious and chief end-product, but protein also may be so formed, and such diverse materials as fat, tannin and various organic acids have been considered, probably on insufficient evidence, to be of direct photosynthetic origin. The earlier phases in these synthetic processes are photochemical, a mutation of radiant into chemical energy, and it is during this phase that the oxygen, a waste product, is evolved. The presence of oxygen in the air-space system of the active chlorenchyma may thus be considerably greater than in normal air, and since this gas is continually excreted during the process, it is not surprising to find that the quantity of oxygen in the surrounding atmosphere is immaterial to the process and that it may be decreased to 2 percent or increased to 50 percent without adverse effect: but since the formation of chlorophyll is dependent upon the presence of oxygen, the prolonged maintenance of a low oxygen pressure will inhibit the development of more chlorophyll and this will in turn react on carbon assimilation," p. 14.

"Plant physiologists for long have recognized that the intensity of carbon assimilation must be dependent on the chlorophyll and its amount; it is, however, but recently that the problems involved have been critically examined. Irving, who used the leaf's carbon dioxide of respiration in her experiments, found by gasometric methods that etiolated leaves, either when they are orange-yellow or when they have attained a considerable degree of greenness, do not possess any appreciable power of synthesizing carbon dioxide. If there be any photosynthetic activity, it cannot be greater than one-tenth part of respiration nor come within 1 percent of the activity subsequently developed. Carbon assimilation begins when the leaves are fully green and develops very quickly; wherefore it follows that the first origin of this function is not correlative to the amount of chlorophyll produced, or, in other words, that the amount of chlorophyll is not a conditioning factor in the early stages of carbon assimilation," p. 32.

"Mention has just been made of the importance of soil substances other than nitrates in the protein synthesis of plants: potassium may be taken in illustration. Species of bacteria grown in the dark in culture media containing the requisite organic food materials and salts but lacking potassium show but poor development and no protein synthesis. Under similar cultural conditions

seedlings of the beet showed seven times less protein and eighteen times less sugar, when grown without potassium, as compared with the controls; when grown under sterile conditions in a culture medium containing a sugar and supplied with known amounts of carbon dioxide, it was found that those grown in the light were independent of potassium as regards the synthesis of protein, and that the addition of sugar to the culture medium resulted in an increase of protein. In darkness, on the other hand, a less vigorous development obtained and only those plants supplied with potassium salts showed protein formation.

"It would therefore appear that the action of potassium is partly indirect, and only in darkness does it play an important rôle in the production of proteins. Since potassium is mildly radioactive, it may possibly serve as a source of energy in promoting the analysis of carbohydrate.

"These observations introduce the problems connected with the light factor. Earlier opinions were that light was an important and a direct factor in the synthesis of proteins: radiant energy is certainly of great importance in that it is a necessity for the green plant in the making of carbohydrate, which is in turn a requisite in the formation of proteins," p. 51.

"There is considerable ground for regarding the biological oxidations as being primarily due to enzymes such as dehydrase which activate hydrogen in the oxidizable substances so that it may be removed by a suitable hydrogen acceptor, which may be atmospheric oxygen. Wherefore the oxidizable substance is to be regarded as a potential hydrogen donator, and, in fact, Thunberg goes so far as to regard hydrogen as the essential fuel of the living cell and regards only those substances as possible intermediate metabolites which when left in contact with methylene blue in the absence of oxygen decolorize this substance and therefore act as hydrogen donators. His technique consists in placing the material under examination in a test tube with freshly washed frog's muscle, to supply the dehydrase, and methylene blue, filling the tube with boiled water, and leaving the whole in a thermostat and examining at intervals. If the methylene blue is decolorized, the substance in question is a hydrogen donator and consequently a possible intermediate metabolite," p. 67.

"The study of regeneration, correlation, polarity, and cognate subjects leads to conclusions in some respects indefinite in that no tangible factor is discoverable that will account for the beginning or for the control of certain phenomena. A cambium cell divides; the daughter cell destined to become a permanent tissue element will develop into a phloem element if cut off on one side and into a xylem element if cut off on the opposite side; what is it that determines the fate of the cell? The leader of a spruce is negatively geotropic, the lateral branches are diageotropic; if the leader be removed, a lateral branch from the topmost whorl will change its habit, become negatively geotropic and carry on the functions of the leader. Why must the leader be removed before a change in tone of a plagiotropic shoot can be effected? The primordium of a lateral bud is laid down and, apparently, all conditions are favourable for development, yet the bud remains dormant until, say, the apex of the main shoot is removed, then the bud will immediately start its development. It is true that in many cases the diversion of food will account for the subsequent phenomena but in other instances such an explanation is inadequate and in such examples the question is: What is it that presses the trigger?

"The subject properly is beyond the scope of an introduction to the physiology of metabolism of plants but the introduction is desirable even though the acquaintance be not cultivated until some future occasion.

"For long it has been known that very small quantities of various materials act as powerful stimulants; the extraordinary effect of minute traces of zinc on the growth of moulds may be instanced. Animal physiologists recognize the effect of traces of substances in stimulating various activities, especially those associated with secretion. These substances are produced in one organ and stimulate another organ to which they are conveyed by the blood. Hence the idea of a chemical messenger, or, to use the current term, hormone.

"Errera was amongst the first of botanists to suggest that hormones play a part in the economy of the plant; his explanation of the changes in the spruce instanced above is that the apical shoot continually is secreting an inhibiting substance which is distributed to other parts of the plant, keeping them in their normal tone. The removal of the leader of the spruce removes the source of the inhibiting hormone, wherefore a near lateral shoot assumes the qualities and functions of the lost leader.

"This idea has been adopted by Loeb who concludes from many observations on the development of buds and roots on the leaves of *Bryophyllum calycinum* that the apical bud secretes a hormone which inhibits the development of buds more basal in position. It is not until the apex is removed that the buds below will develop.

"The degree of inhibition depends on the amount of hormone and the mass of the lateral bud; it is presumably for this reason that the inhibition may only extend to these primordia situated more immediately below the apex," p. 132.

*Wilder D. Bancroft*

**The Nature and Properties of Soils.** *By T. Lyttleton Lyon and H. O. Buckman. 21 × 14 cm: pp, v + 588. New York: The Macmillan Co., 1922. Price: $3.25.* The authors dispense with a preface and start right in with a table of contents: some conception of the soil and its relation to plants; soil-forming processes; the geological classification of soils; the soil particle and certain important relations; the organic matter of the soil; the colloidal matter of the soil; soil structure and its modification; the forms of soil water and their characteristics; the water of the soil in its relation to plants; the control of soil moisture; soil heat; soil air; the absorptive properties of soils; the soil solution; the removal of nutrients from the soil by cropping and leaching; chemical analysis of soils; alkali soils; soil acidity; liming the soils; soil organisms, carbon, sulphur and mineral cycles; soil organisms—the nitrogen cycle; commercial fertilizer materials; the principles of fertilizer practice; farm manure; green manure; the maintenance of soil fertility.

On p. 21 is the statement that in desert storms 200 tons of materials have been known to float over every acre of land and Southern Italy has received as much as one inch of dust from Africa during a single storm. Arid soils, p. 31, are poorer in silica than humid soils but richer in iron and aluminia, indicating a less weathered condition of the feldspars. Due to a greater amount of leaching, the humid soils are much lower in phosphoric acid, lime, magnesia and potash.

On p. 61 there is a discussion of loess. "During glaciation much fine mate-

rial was carried miles below the front of the ice sheets by streams that found their source within the glaciers. This fine sediment was deposited over wide areas by the over-loaded rivers. The accumulations occurred below the ice front at all points, but seem to have reached their greatest development in what is now the Missouri Valley and the Great Plains. Much of the sediment in the latter area probably came from local glaciers, which debouched from the Rockies.

"It is generally agreed by glacialists, that a period of aridity, at least as far as this particular region is concerned, immediately followed the retreat of the ice. The low rainfall of this period was accompanied by strong westerly winds. These winds, active perhaps through centuries, were instrumental in picking-up and distributing of this fine material over wide areas of the Mississippi, Ohio, and Missouri valleys. One strong argument for this aeolian origin is that the soil has its deepest and most characteristic development along the eastern banks of the large streams. Especially noticeable is the extension down the eastern side of the Mississippi River almost to the Gulf of Mexico. This wind-blown material, called loess, is found over wide areas in the United States, in most cases covering the original till mantle. It covers eastern Nebraska and Kansas, southern and central Iowa and Illinois, northern Missouri and parts of Ohio and Indiana, besides a wide band, as already noted, extending southward along the eastern border of the Mississippi River. Due to its mode of origin, its depth is always greatest near the streams and gradually becomes less farther inland. In places, notably along the Missouri and Mississippi rivers, its accumulation has given rise to great bluffs, which bestow a characteristic topography to the region. . . .

"Loess is usually a fine calcareous silt or clay loam, of a yellowish or yellowishy buff color. While it may be readily pulverized when subjected to cultivation, it possesses remarkable tenacity in resisting ordinary weathering. The vertical walls and escarpments formed by this soil show one of its striking physical characteristics. In China caves that house thousands of persons are dug in the defiles and canyons existing in this deposit. Another feature of loess is the presence, especially in the subsoil, of minute vertical canals lined with a deposit of calcium carbonate. These canals are supposed to give the soil its vertical cleavage and its tenacity. The particles of loess are usually unweathered and angular. Quartz seems to predominate, but large quantities of feldspare, mica, hornblends, augite, calcite, and other minerals are found."

"The term 'adobe' is applied to a fine calcareous clay or silt formed in a manner somewhat like loess. It is supposed that, while part of the deposit came from the waste of talus slopes as mountains were weathered under conditions of aridity, the remainder had aeolian origin. Certain characteristics also seem to indicate that the valley adobe might have been deposited almost entirely by water. It appears, therefore, that, while the physical characteristics of all adobe are somewhat similar, its mode of origin and chemical composition may be variable.

"Like the loess, the adobe is an exceedingly rich soil, but it occurs in an arid or a semi-arid region. When irrigated, its fertility seems inexhaustible. It is found in Colorado, Utah, Southern California, Arizona, New Mexico, and Texas. It has an especially wide distribution in New Mexico. Like loess, its elevation is variable, ranging from sea level in California and Arizona to 6000 feet along the eastern border of the Rocky Mountains. Its maximum thickness cannot be esti-

mated, as it is very little eroded and is supposed to be still accumulating. Some valleys are known to be filled to a depth of 3000 feet with this material. Its characteristics are its fine texture, its great depth, its wide distribution, and its great fertility when moisture conditions are suitable for crop growth."

"The burning of straw and cornstalks, especially in the Middle West, entails an enormous waste of carbon as well as of nitrogen. The value of crop residues has been demonstrated very conclusively by the Illinois Experiment Station on their outlying experimental farms. At Bloomington, for instance, the turning under of crop residues for five years increased the wheat yields 4.4, 7.9 and 5.9 bushels in 1911, 1912 and 1913, respectively," p. 124.

The authors are quite definite as to the importance of colloid chemistry, p. 138. "The attempt to explain natural phenomena from the standpoint of crystalloidal chemistry alone is a failure. Nature has chosen to reveal herself, largely in colloidal form. Such a condition of matter is the rule and not the exception. Whether the sky, the ocean, or the land is dealt with, the larger part of the natural phenomena are explained plausibly only through knowledge of colloidal chemistry.

"The modification of the structural condition of a heavy soil is not such a simple problem as in the case of a sandy one. In the latter the plasticity and cohesion is never high even after the addition of large amounts of organic materials that rapidly develop into a colloidal state. In clays and similar soils the potential plasticity and cohesion are always high, due to the presence of large amounts of complex hydrated aluminum silicates in a colloidal condition. The more plastic a soil becomes, the more likely it is to puddle, especially if worked when wet. Moreover, a soil of high plasticity is prone to become hard and cloddy when dry, due to the cohesive tendencies of the small particles. Heavy soils must therefore, be treated very carefully, especially in tillage operations. If plowed too wet, puddling occurs, the aggregation of particles is broken down, and an unfavorable structure is sure to result. If plowed too dry, great lumps are turned up which are difficult to work down into a good seed-bed. In a sandy soil, no such difficulties are encountered," p. 140.

"One of the effects of lime in soil, especially of the oxide and hydroxide forms is a flocculating action. This agglomeration, as already explained, is the drawing together of the finer particles of a soil mass into granules. When calcium hydroxide is mixed with water containing fine particles in suspension there is almost immediately a change in the arrangement of the particles. They first draw together in light, fluffy groups, or floccules, which then rapidly settle so that the supernatant liquid is left clear or nearly so. This phenomenon is termed flocculation, because of the peculiar appearance of the aggregates. This flocculating tendency when lime is added goes on in the soil as well as with suspensions, although more slowly. In general, the lime tends to satisfy the absorptive capacity of the colloidal material and by throwing down these colloids develops lines of weakness. The cohesive power of the soil is thus localized and agglomeration must necessarily occur. The various forms of lime differ in their flocculating capacities, calcium oxide and hydroxide being very active, while calcium carbonate is relatively inactive in this regard.

"It must not be inferred that lime is generally added for its flocculating influence. It is used primarily for other reasons, the amounts applied being in general too small to have very much influence on the structural condition of the

soil. Warington, however, reports a statement of an English farmer to the effect that by the use of large quantities of lime on heavy clay soil, he was enabled to plow with two horses instead of three. It is generally true that oils rich in lime are well granulated, and maintain a much better physical condition than soils of the same texture that are low in lime," p. 143.

"The evaporation from the bare soil in the Rothamsted lysimeters averaged about seventeen inches a year, with a rainfall ranging from twenty-two to forty-two inches. This means that from one-third to one-half of the effective rainfall was lost entirely as thermal water. The necessity of checking such a loss becomes apparent, especially in regions where rainfall is slight or drought periods are likely to occur," p. 182. "Any material applied to the surface of a soil primarily to prevent loss by evaporation or to keep down weeds may be designated as a mulch. Mulches are of two general sorts, artificial and natural. In the former case, foreign material is merely spread over the soil surface. Manure, straw, leaves, and the like may be used successfully. Such mulches while effective, especially in preventing weed growth, are not generally applicable to field crops where inter-tillage is practiced, since they would make cultivation impossible. Their use is, therefore, limited to such crops as strawberries, blackberries, and the like.

"The second type of mulch is called a soil-mulch since it is formed from the soil itself. With proper tillage, a loose dry layer of soil may be formed on the surface. Such a layer is designed to obstruct capillary movement to such an extent as to reduce evaporation loss to a minimum. In theory a soil-mulch should be formed as quickly as possible so that the only moisture sacrificed will be that which is present in the soil forming the mulch. Moreover, the mulch should be renewed after every rain and should, except in special cases, be not more than three inches deep. Late in the season, especially for corn, the cultivation should be shallow to prevent root-pruning.

"For many years cultivation for a soil-mulch has been advocated for two reasons: (1) checking of evaporation, and (2) the killing of weeds. Either procedure if successful, will allow the crop a larger proportion of the rainfall. Recent experimental results, however, seem to indicate that a soil-mulch with an intertilled crop does not check evaporation compared with a soil uncultivated and kept free from weeds. This is probably due to the fact, that even with moisture a limiting factor, the water sacrificed in renewing the mulch is not offset by that conserved. The tendency of soils, especially those of a sandy character to self-mulch as well as the action of the roots of the crop in intercepting the water, may also be factors. Under greenhouse conditions and in regions of very little rainfall, the soil-mulch probably does not conserve moisture," p. 218.

"The soil is a porous mass of material of which only about one-half is solid matter. The pore space that results is occupied by water and by air in a constantly varying proportion. When a soil is in good condition for crop growth, the air space rarely makes up more than from 20 to 25 percent of its volume. The texture of the soil and the amount of moisture are obviously the main controls. The individual air spaces of the soil are more or less continuous and seem to maintain a fairly complete communication between the various horizons. The better the granulation of the soil and the greater the number of cracks and burrows the easier and quicker is this communication. The air of the soil is either in

contact with the roots and soil the bacteria or separated from them by only a thin layer of moisture or colloidal material," p. 247.

"A very peculiar type of alkali spot occurs in the Grand Valley of Colorado and elsewhere, the predominant salt being the nitrate, which does not usually occur in large amounts as alkali. Two theories have been advanced to account for the presence of the nitrate salts. One hypothesis is that the surrounding shales are comparatively rich in nitrates and that the alkali accumulation if a leaching and seepage process. The other theory is biological in nature. Such soils are capable of rapid nitrogen fixation by means of their bacterial flora. The idea is advanced that the nitrogen is fixed from the air very rapidly in these spots and later oxidized to the nitrate form. Whatever the origin of the soluble salts the fact remains that such spots are quite destructive, spreading very rapidly until whole orchards are wiped out," p. 332.

"In irrigated regions the injurious effect of alkali are in many cases developed only after irrigation has been practiced for a few years. This is due to what is known as a 'rise of alkali,' and comes about through the accumulation, near the surface of the soil, of salts that were formerly distributed throughout a depth of perhaps many feet. Before the land was irrigated the rainfall penetrated only a slight depth into the soil, and when evaporation took place salts were drawn to the surface from only a small volume of soil. When, however, irrigation water is turned on the land, the soil becomes wet to a depth of perhaps fifteen or twenty feet. During the portion of the year in which the soil is allowed to dry large quantities of salts are carried toward the surface by the upward-moving capillary water. . . .There are large areas of land in Egypt, in India, and even in France and Italy, as well as in this country, that have suffered in this way, and not infrequently they have reverted to a desert state," p. 339.

*Wilder D. Bancroft*

**L'Azote.** *By Louis Hackspill. 20 × 14 cm; pp. xii + 271. Paris: Masson and Cie, 1922. Price: 14 francs.*—This is one of the volumes in the *Encyclopédie Léauté*, the object of which is to present clearly but briefly the scientific development of a topic with the idea that this will furnish the basis for understanding the industrial side. The subject is presented under the following general headings: the nitrogen cycle; nitrogen and the nitrates; fixation of nitrogen as cyanide; calcium cyanamide; synthesis of ammonia; the plants at Oppau and Merseburg; developments by the Allies during the war; the Claude process; ammoniacal salts and urea; synthesis of nitric oxide; technical preparation of nitric oxide; oxidation of ammonia; comparison of different processes for the fixation of nitrogen; methods of using nitrogeneous fertilizers; total production of fixed nitrogen.

The author draws the conclusion that with the present rate of exchange it will be quite a while before France can compete economically with Germany in the fixation of nitrogen and that it is absolutely essential to have a French plant both for the needs of agriculture and the needs of war. This means that the factory must be subsidized by the French Government directly or indirectly.

*Wilder D. Bancroft*

# STRUCTURAL COLORS IN FEATHERS. II

BY CLYDE W. MASON[1]

## Iridescent Feathers

In addition to white and blue, the structural basis of which has been recognized for some time, another type of color claims our attention. Iridescent or "metallic" colors occur in feathers of peacocks, humming birds, trogons, pheasants, pigeons, ducks, chickens, grackles, etc., and are characterized by their brilliancy and lustre, and by the marked change in color which they show with changing positions, as well as by their occurrence in the barbules alone. The uniformly opaque brownish appearance of these feathers when held against the light shows that more than ordinary pigmentation is present. The variety of causes to which these colors have been ascribed is sufficient justification for the present study, which is an attempt to evaluate the numerous theories which have been advanced. Structures similar to prisms, to diffraction gratings, or to thin plates, have all been suggested as causing the iridescent colors, while selective reflection (surface color) has been considered by some investigators to account for these colors. Of so many possibilities, including all the ordinary types of structural color, one ought to fit the facts, without the need of postulating a type of structural color not yet discovered. For this reason, these various causes suggested will be examined in some detail, as a basis for comparison with the properties of iridescent feathers. Although there are other types of structural colors, such as resonance, Christiansen effect, etc., these show their colors only by transmitted light, whereas we are concerned with colors which are observed only

[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.

by reflected light, since it is only thus that the iridescent colors of feathers are seen.

Prismatic structure is assumed by Gadow[1] to be the cause of the iridescence of feathers. He observes that the colors which a feather shows by reflected light change "from the violet toward the red end of the spectrum" as the angle of incidence of the reflected light is increased from normal toward grazing, and gives a diagrammatic drawing of the cross-section of a barbule having a prismatic ridge along the outer surface. This drawing which shows the paths of the rays of light of different color seems to have clinched his argument, from the extent to which it has been copied in dictionaries of birds and similar works, though how a prism, in the position shown, could refract any light from a beam falling on the outer surface of the barbule at any angle, to the eye of the observer on the same side of the barbule, requires more than the known laws of refraction for its explanation; as Strong[2] points out, the light refracted by the prism to the eye would always have to make an angle of more than 180° with the incident ray—a physical impossibility, as far as the structure shown by Gadow is concerned, and absolutely at variance with the behavior of feathers. Incidentally, none of the iridescent feathers studied in the present work show such prismatic structure. Walter[3] also points out that a prism, to produce color, requires a narrow illuminating beam of light, and gives no color whatever with diffuse light. He emphasizes the fact that with the most highly dispersive transparent substances known, the whole spectrum only occupies a few degrees, "so that if we are to account for the gradual and continuous change of the tints of the surface colors when the angle of incidence varies between 0° and 90°, we must postulate an almost infinitely large number of prisms arranged in a very peculiar way, with the refracting edges all parallel. Even then one would have accounted for the play of colors only in one plane, for light falling perpendic-

[1] Proc. Zoöl. Soc. London, 1882, 409.
[2] "Mark Anniversary Volume," 263.
[3] "Die Oberflächen- oder Schillerfarben," (1895).

ular to the refracting edges. In order to have the same effect in all other directions there must be an infinite number more of these prisms, or twice infinity all told."

Gadow explains the fact that every feather does not show the whole spectrum, by the barbules acting as screens to cut out all but a part of the spectrum, or by the spectra from two neighboring prisms partly overlapping. However, the color of the isolated barbules is the same as that which they show in the feather.

There is no need of continuing further; it is obvious that Gadow's explanation cannot possibly be correct and that the colors of iridescent feathers are not caused by prismatic dispersion. The properties of these feathers given on subsequent pages only emphasize this. It is unfortunate that Gadow's paper has been so widely quoted without the inadequacy of these theories being perceived by the readers, particularly since the inadequacy ought to be apparent to anyone who subjects them to the least critical examination.

It has been suggested that the colors of iridescent feathers are due to some structure similar to that of a diffraction grating, since grating colors show a marked change with angle and are of considerable brilliancy. However, no trace of the system of fine, regular, parallel, striations characteristic of diffraction gratings is visible on most iridescent feathers, although the rulings of a diffraction grating are readily resolved by the microscope. A diffraction grating requires sensibly unidirectional light for the production of color, and this light must fall across the striations, not parallel to them, while iridescent feathers show their colors from whatever direction the light is coming. A diffraction grating shows no color in uniform light, such as that of a clouded sky, but the iridescent colors of feathers are unaffected by this illumination. The colors of a diffraction grating are visible, not in the path which the directly reflected or refracted rays would take, but considerably to one side of these rays. Thus a grating shows brilliant colors when illuminated from the side and examined from above and gives no color when examined with a vertical illuminator used

in connection with a microscope. On the other hand, the iridescent barbules of feathers show no colors unless at such an angle as to reflect the light which falls on them to the eye of the observer; they give intense colors with vertical illumination under the microscope. Hodgkinson,[1] in an admirable paper, emphasizes these differences. The colors of a diffraction grating approach the red end of the spectrum (increase in "order") as the angle of incidence increases, while those of iridescent feathers approach the blue of the spectrum (decrease in "order") with increasing angle of incidence. The very marked change in color shown by a diffraction grating with change of angle is in marked contrast to the relatively slight change observed in feathers.

The marked differences in properties outlined above make the differences between diffraction colors and the colors of iridescent feathers very apparent. We may conclude that there is no connection between the iridescent colors of feathers and the colors produced by a diffraction grating.

### Interference Colors of Thin Films

More detailed study of the properties of thin films and those of selectively reflecting media is necessary, for sufficient similarity exists to make the distinction very confusing, and indeed, the greatest division of opinion exists as to whether the iridescence of feathers is due to one or the other of these two possibilities.

The colors of thin laminae or films are caused by the destructive interference of certain of the wave lengths of the incident light, part of which is reflected from the outer surface of the film, and part from the other surface, after traversing the film. The portion of the light which traverses the film and is reflected back from the under surface through the film again, suffers a certain amount of retardation, dependent upon the thickness of the film, which may be just sufficient to put certain of the wave lengths out of phase with the same wave

[1] "Manchester Memoirs," [4] 2, 193 (1889).

lengths reflected from the upper surface. Interference as a result of this retardation may result in the destruction of one of the component colors of the reflected light. If the incident light is white, the destruction of any wave length will cause a color due to the remaining components. Examples of this type of color are oil films on water or asphalt pavement, iridescent soap bubles, Egyptian glass, Newton's rings, etc.

Since the film itself must be fairly transparent, these colors are not seen plainly unless most of the light from the opposite side of the film is cut off. Otherwise the light passing through the film to the eye is much stronger than the reflected light, in which the color is found, and the color is obscured. Thus oil films on wet asphalt pavement appear much more brightly colored than oil films on clear water, because the dark background prevents any light from below from lessening the apparent intensity of the colors. The colors of thin films, viewed by transmitted light, are the true complements of those seen in the reflected light, but are not readily seen on account of the admixture of a large proportion of the white light which passes through the film unchanged as to color. The brightest color effects are seen against dark or dull backgrounds. The color seen when the film is illuminated with white light depends on the difference in refractive index between the film and the surrounding medium, on the thickness of the film, and on the angle from which it is viewed. (Dispersion may be neglected in thin films.)

Newton was the first to study these colors and they are often given his name. He arranged them in a series, in order of increasing retardation (or effective thickness) of the film, thus:

Black, white, yellow, red; violet, blue, green, yellow, red; purple, blue, green, yellow red; green, red; greenish blue, red; pale greenish blue, pale red, etc.; the colors corresponding to the thicker films approaching more and more toward white. Such a list of names is of little value, for the colors of the different "orders" (separated by semicolons) cannot be described adequately by naming them. Excellent colored charts of

this series of interference colors have been prepared for use in petrography, and may be found in such books as Johannsen—"Determination of Rock-Forming Minerals," Winchell—"Elements of Optical Mineralogy," Lévy et Lacroix—"Les Minéraux des Roches," Finlay—"Igneous Rocks," and similar works.

Even these charts fail to represent the brilliant "metallic" lustre and intense coloring, which can best be observed with films prepared by allowing a drop of oil to spread on water, wet slate, etc., or by covering a dark object with a thin film of varnish or other material. Permanent films may be made by dipping a plate of black glass (or clear glass coated with a smooth film of India ink) into a *very* dilute collodion or gelatine solution. The excess liquid is allowed to drain off, and the plate is carefully dried. Unless the solution is too concentrated, a series of brilliant colors (Newton's colors) will be observed on the plate, the upper ones corresponding to the thinner part of the film, which is wedge-shaped and increases gradually in thickness toward the lower edge of the plate. By varying the concentration of the solution films of different thicknesses may be obtained and the colors corresponding to different parts of Newton's series may be examined. If the film is prepared on transparent glass the colors will be found to be very faint; the dark background is essential to their brilliancy, and to their distinctly metallic lustre. Thin films may also be prepared by blowing glass into exceedingly thin bulbs, or by cleaving mica. These films should be examined against a dark background to show their colors most plainly. The uncolored character of the transmitted light may be observed when the dark backing is absent.

C. V. Boys[1] in a little book on "Soap Bubbles" discusses the colors in some detail. A film to produce interference colors must be less than about $1.5\mu$ in thickness, while the brilliant colors of the "second order" must correspond to thicknesses between about $0.3\mu$ and $0.7\mu$, for films having a refrac-

[1] "Soap Bubbles," 148, 151.

tive index of 1.5. He points out that the retardation (effective thickness) varies with the cosine of the angle which the refracted ray of light makes with the normal to the plane of the film; if the color of the reflected light from a thin film held perpendicular to the line of vision is compared with the color observed when the film makes an acute angle with the line of vision, the color in the latter position corresponds to that of a thinner film. In other words, increasing the angle of incidence is equivalent to thinning the film, and causes a corresponding change in the color reflected.

The actual color to be obtained at grazing incidence from a thin film may be calculated rather easily from the relationship:

Retardation (effective thickness) = 2 $\Theta$ cosine $r$ where $\Theta$ is the thickness of the film, and $r$ the angle of refraction of the incident light. For a film of thickness $\Theta$, of refractive index 1.5, the maximum angle of refraction (critical angle) is about 42°, and calculating the retardation for $r = 0°$ (vertical incidence) and $r = 42°$ (grazing incidence) the retardation at grazing incidence is found to be about 75% of that at vertical incidence; that is, the effective thickness is less at grazing incidence by about 25%.

From a table of retardations corresponding to the different colors of the series the color at vertical incidence may be recognized, and its retardation noted;[1] the color at grazing incidence will be the color corresponding to a retardation about 75% of this value. This works out very nicely on color-producing films prepared as above.

This change of color with angle, or *iridescence*, is the most striking characteristic of thin film colors. For example, a film which is purple at normal incidence may change through red and yellow to green as the angle of incidence approaches grazing, a yellow film may pass through green and blue to violet, or a green film may change to red. These changes may all be predicted by means of a chart of Newton's colors. In

[1] Johannsen: "Manual of Petrographic Methods," 333 (1918).

the series given above, the colors preceding any given color are those of thinner films, so the color of a given film will always change to colors listed before it, usually through only one or two, or, at the most, three of the colors immediately preceding it in the series. Such a change is often referred to as "lowering of the order of the color," while the reverse change is called a "rise in order." The change in color is slight for inclinations less than about 30° from normal incidence, but as the angle increases toward grazing the colors change in a very striking manner, which is readily observed by the eye.

When the angle of incidence is small, a nicol prism shows no change in color of the reflected light vibrating in different planes. The color change as the angle increases is not affected. At about 60° from normal incidence, however, the reflected light, examined through the nicol in position to transmit the vibrations in the plane of incidence, is seen to decrease markedly in intensity. The light vibrating perpendicular to the plane of incidence is also decreased in intensity. At a definite angle the light vibrating in the plane of incidence almost disappears, and the film appears dark. This angle does not depend on the thickness of the film, for a film of variegated color darkens as a whole at the proper angle, which appears to be in the neighborhood of the "polarizing angle" (the tangent of which is equal to the refractive index of the substance).

If the angle of incidence is further increased, the color of the light vibrating in the plane of incidence appears complementary to that of the light vibrating perpendicular to this plane; it is also complementary to the color seen without the nicol, and to that of the light vibrating in the plane of incidence at angles less than the apparent "polarizing angle" noted above.

The optical properties of thin plates have been rather completely studied from a mathematical standpoint. Preston[1] gives a full discussion of the optical behavior of thin plates, in which he shows that the light reflected, at angles greater than the polarizing angle, is elliptically polarized, and that a

[1] Preston: "Theory of Light," 373 (1912).

complementary change in color takes place at the polarizing angle for vibrations in the plane of incidence.

The elliptical polarization of the light reflected from a thin film at angles greater than the "polarizing angle" may be detected by a "quarter-wave plate," which converts elliptically polarized light into plane polarized light. If the light, reflected at an angle greater than the "polarizing angle" of the thin plate, is passed through such a quarter-wave plate, and then examined through a nicol prism, in position to transmit the vibrations in the plane of incidence, the color observed is that seen without the nicol and quarter-wave plate. In other words, instead of a color *complementary* to that seen without the nicol, or with the nicol at lesser angles, or with the nicol perpendicular to the plane of incidence, the *same* color as that observed under these conditions is seen when the quarter-wave plate is combined with the nicol in position to transmit the vibrations in the plane of incidence. The interposition of the quarter-wave plate under these circumstances, with the resulting change from the complementary to the original color constitutes a very simple means of detecting the elliptical polarization of the light from thin films at angles greater than the polarizing angle. Theoretically, if the reflected light is all elliptically polarized, the quarter-wave plate ought to render it all plane polarized, and it shoud be cut off completely by the nicol in one position. Actually the elliptical polarization of the reflected light is not complete, and rotating the nicol when the quarter-wave plate is in position under these circumstances does not destroy the color.

The above changes in color with change in the angle of incidence may be easily observed by inclining the color-producing film in front of a source of diffuse white light, while viewing it through some sort of telescope combined with a nicol prism. In this work a Fuess Universal Stage Petrographic microscope was used. This instrument permits measured angular rotation of the specimen about a number of different axes, as well as providing a nicol prism and quarter-wave plate for the study of the reflected light. Since the

films as prepared are usually of varying thickness and color, it is necessary to fix the attention upon a very small area of uniform color in order that the changes may be accurately observed. Points of reference may be marked on the film with a needle.

It should be borne in mind that the colored light is reflected from thin films as white light is from a mirror; the angles of incidence and reflection are equal; if the film is smooth images may be seen in it as in a mirror; no scattering takes place, and if the light from a point falls on a thin film only a colored point of light is seen. In order that the whole surface of the film shall appear colored, light from an infinite number of points—that is, diffuse light, is necessary. This is quite the opposite of the diffraction grating, with which a point of light is necessary for maximum color, and no color is seen in diffuse light.

This reflection which is essential to the production of color by thin films is, of course, dependent on the difference in the index of refraction between the film and the surrounding medium; thin films surrounded by a medium of refractive index near their own show no color. Colors of thin films can be completely destroyed by surrounding these films with the medium of the same refractive index. Liquids which do not affect the film itself should be chosen for demonstrating this.

A thin film of gelatine or collodion changes its color to that of a thinner film if subjected to considerable pressure, under a smooth convex surface. More striking effects are obtained by swelling. Gelatine or collodion films may be swelled by breathing on them or by exposing them to steam for a moment. The color produced by swelling is invariably that of a thicker film. Usually the color does not change through more than two colors adjacent in the series, and by examining the swelled film with grazing light (which is equivalent to decreasing its effective thickness) the original color of the untreated film may generally be observed. The color changes from swelling are reversible, and the original color is restored by drying the films.

Although maximum color is obtained from clear, transparent, colorless, thin films, very good effects may be observed with films made from turbid or highly colored material. For instance, black asphaltum varnish forms films on water almost as brilliantly colored as those from pale or colorless oils and varnishes. The asphaltum varnish is far from opaque in films of this thickness, yet the brown color of a thin layer of it is fairly pronounced.

If color-producing films of different refractive indices are superposed, the color produced depends on the relative thicknesses of the films as well as on their refractive indices. If two or more such thin films, each giving the same color, are combined the resultant color is the same in hue but occupies a smaller portion of the spectrum. These "multiple films"[1] except for the increased purity of their colors, have essentially the same properties as the single films. If the films which are combined are of different colors no such purity of color results, but rather a dulling or increase in order toward white.

## Surface Colors

Surface color, which is a result of selective reflection, is possessed by certain substances, such as solid aniline dyes, highly colored crystals, metals, etc., and gives to the substances a peculiar brilliant metallic color, in appearance somewhat like the iridescent coloring of certain feathers.

Thin layers of these intensely colored substances transmit certain of the components of white light, and the light which passes through the substances appears colorless. Those wave lengths which are transmitted compose the "body color" of the substance. Of the wave lengths not transmitted, some are absorbed, while others are reflected from the surface layer of the substance, almost as perfectly as from a mirror. These reflected wave lengths make up the *surface color*, this phenomenon being called selective reflection.[2]

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[1] Rayleigh: Phil. Mag. **26**, 256 (1888).
[2] Wood: "Physical Optics," 439 (1911).

The statement is often made that the selectively reflected light is complementary in color to the transmitted light (Haidinger's Law) but it is evident that reflected light = white light (incident light) − absorbed light − transmitted light, so that unless absorption is negligible, the transmitted and reflected colors are really not complementary, though they often nearly appear so. For instance, solid fuchsine transmits red and reflects greenish yellow, as may be seen by allowing a warm concentrated alcoholic solution of the dye to evaporate on a glass plate. Cyanine, however, transmits purple, and reflects nearly the same color. Wood[1] emphasizes the fact that the wave lengths most reflected are not necessarily the ones most absorbed.

Of the substances which give selective reflection, all which have been studied show anomalous dispersion,[2] that is, the shorter wave lengths (blue) are not refracted as highly as the longer ones (red). This is the opposite of the behavior of the ordinary refracting substances, such as glass, water, etc. This anomalous dispersion is very marked, the refractive index varying greatly with the wave length of the light refracted. Thus cyanine has refractive indices from 0.83 to 2.68. If the selectively reflecting substance were in contact with a transparent substance of the same refractive index as its own for all wave lengths, no light would be reflected by it. It is actually possible to match the refractive index for a particular wave length, which then fails to be reflected, and does not appear in the reflected light. The result is a change in the color of the reflected light. The surface color of fuchsine changes from yellow-green to blue if the surface is covered with balsam or cedar oil.

As a consequence of the high dispersive power the color at grazing incidence will be different from that at normal incidence. In the case of a substance with its refractive index for a certain wave length less than that of air, total reflection may take place for this wave length at large angles of incidence.

[1] "Physical Optics," 440 (1911).

[2] Wood: "Physical Optics," 113 (1911).

with an accompanying change of color, which might be enough to be perceived by the eye. The change in relative intensity of different wave lengths with increasing angle of incidence and of reflection may be calculated from Fresnel's formula

$$\frac{\text{Reflected light}}{\text{Incident light}} = \frac{1}{2}\left[\frac{\sin^2(i-r)}{\sin^2(i+r)} + \frac{\tan^2(i-r)}{\tan^2(i+r)}\right]$$

where "$i$" is the angle of incidence and "$r$" the angle of refraction, but the change in relative intensity for the different wave lengths is not great, and indeed can barely be detected by the eye. It is calculated that the change in color should be toward blue, and this corresponds to what apparent color change is observed, but the effect is so slight that different observers cannot agree as to whether there is an actual change of color or only a darkening of the color seen at normal incidence. If the film of selectively reflecting material is formed on glass the body color may be mingled with the surface color unless care is taken to cut off all transmitted light. In any case, the supposed change of color is not observed except at almost grazing incidence; at angles less than this the change of color observed with the naked eye is almost inappreciable.

Examined through a nicol prism, the light reflected vibrating perpendicular to the plane of incidence shows no appreciable change of color with increasing angle of incidence. The light vibrating parallel to the plane of incidence shows marked change in color, always toward the blue end of the spectrum but never from green to red in any of the cases examined, as it sometimes does in thin-film colors.

To cite a few examples—*Gentian Violet* has a purple body color, yellow-green metallic surface color, which possibly becomes slightly more bluish at grazing incidence. No change in color with angle, examined through the nicol perpendicular to the plane of incidence. With the nicol parallel to the plane of incidence, the color changes to greenish blue at grazing incidence.

*Fuchsine* (magenta).—Body color—red, surface color—yellowish green. Very slight if any change toward blue with

increasing angle of incidence, examined without the nicol or with the nicol perpendicular to the plane of incidence. Surface color changes to greenish blue with increasing angle, if the nicol is parallel to the plane of incidence.

*Aniline Blue.*—Body color purple, surface color reddish brown (bronze). No perceptible change in color with angle, except when examined through the nicol parallel to the plane of incidence, when color changes to dark greenish-bronze.

*Malachite Green.*—Body color green, surface color coppery pink. With the nicol parallel to the plane of incidence surface color changes toward yellow as angle of incidence is increased.

*Cyanine.*—Body color blue, surface color reddish purple. With the nicol parallel to the plane of incidence, surface color changes to greenish blue as angle of incidence increases.

The above examples show how the colors selectively reflected from typical substances showing surface color are not even approximately complementary to those which these substances transmit (body color). The almost inappreciable change in color with angle, except when the colors are examined through a nicol parallel to the plane of incidence, is also worth noting. The change thus observed appears to be always toward blue.

Metallic reflection results in elliptical polarization of the reflected light,[1] the extent of this polarization depending on the angle of reflection. This may be shown in the case of the above selectively-reflecting substances by inserting the quarter-wave plate in front of the nicol set to transmit vibration in the plane of incidence; the color observed without the quarter-wave plate, which is markedly different from that seen without the nicol or with it rotated through 90°, is changed by the interposition of the quarter-wave plate, not to a complementary color but to a color similar to the color without the nicol or with it transmitting vibrations perpendicular to the plane of incidence. This change takes place at any angle where the difference in color between the reflected light vibrating in the

[1] Wood. "Physical Optics," 456 (1911).

two different planes is appreciable, but the color change is by no means a complementary one, nor does it occur only at angles greater than a definite value, as in the case of thin-film colors. Apparently the surface color is elliptically polarized, to a greater or less degree, at any angle, while thin film reflections are elliptically polarized, to about the same extent, at all angles greater than the polarizing angle, but are not even partially elliptically polarized at angles less than this, as shown by the quarter-wave plate. Actually and theoretically, there is no darkening of the light selectively reflected at a definite angle, and no change to a complementary color at slightly greater angle, though, in the case of thin-film colors, the changes are shown both by observation and from theoretical considerations.

The very great absorbing properties of substances showing selective reflection must be emphasized. Even films a fraction of a micron thick show strong color by transmitted light. Films for the study of the transmitted and reflected light of these substances may be prepared by dipping glass plates into their warm alcoholic solutions, and allowing the plates to drain and dry. No matter how thin the film is, its body color is apparent in all cases where the film is thick enough to show any surface color whatever. The surface color is seen best when the film is against a black background. Against a light background the body color is mixed with the surface color, except in the case of very thick, almost opaque films.

All the dye stuffs which we know to give surface color are soluble in water, alcohol, ether, or other organic solvents, and are readily bleached. In the solid state or in concentrated solution in solid material their colors are not affected by pressure. Their optical properties appear to be the same whether they are dissolved in dry films of collodion, or in extremely concentrated solution in some liquid solvent, or simply as a film of the solid dye stuff.

The distinction between the properties of thin, color-producing films, and those of substances showing surface color are marked enough so that, in spite of their superficial similarities, it is possible to decide which is the type of color represented in iridescent feathers.

**Structure and Physical Properties of Iridescent Feathers**

Detailed study of the tail feathers of the peacock, typical iridescent feathers, is of particular interest because of the variety of colors represented in the pattern of a single feather. Examination of the structure is of the utmost importance, both for the detection of any color-producing structure, and because of the influence which structure may have on surface colors, and on tests for their identification.

The iridescent color of the feather is wholly in the barbules; the barbs are a dark, dull brown, and show no color effects. The iridescent color of the barbules is visible from both surfaces; but it is not seen if the feather is held between the eye and the light. Brown is the only color seen in this position, the iridescence not being observable.

The barbules vary considerably in size in the different parts of the feather, but all show the same structure, and appear as thin, narrow, curved, segmented ribbons or elongated plates. In the loose parts of the feather no hooks are found on the barbules, but in the denser parts of the "eye" some of the barbules may have hooklets on their ends. The barbules on the outer surface of the feather in its dense parts present a smooth surface, for they overlap like shingles, and form an approximately plane surface in the general plane of the feather. Actually the surface of the individual barbule is far from plane; they are curved longitudinally, convex-concave in cross-section, and the segments are individually of slightly greater thickness at their ends than at their centers, appearing to overlap somewhat like shingles. The barbules of the peacock feather are much larger than those of any other iridescent feather, being 0.8–3 mm long, 60 to 80 microns wide, 4 to 5 microns thick, with segments 30–50 microns in length.

Cross-section of the barbules, prepared by the paraffin method, were obtained sometimes as thin as about 5$\mu$, though the small size, smooth surface, and brittle nature of the barbules render them very difficult to imbed firmly and to section satisfactorily. While sections thinner than this would be very desirable for accurate interpretation of such a minute

structure, a fairly good idea of the internal structure of the barbule may be obtained, considering that the resolving power of the microscope sets a definite limit to the size of the details which can be studied. Such cross-sections are best examined without freeing them from the paraffin, for otherwise they are likely to lie on their sides rather than standing on end. The paraffin supports the section of the barbules so that their cross-section is readily observable and permanent preparations may be made by simply covering the paraffin sections with xylol-balsam and covering with a cover glass. The paraffin remains in position to support the section of the barbule, while the xylol-balsam partially clears the preparation.

The cross-section shows a central pith or core about $2\mu$ thick, which appears to be of somewhat fibrous or granular character. Enveloping this core are three thin layers or laminae, of equal and uniform thickness, apparently in contact with each other. Since the total thickness of these three layers is only a little more than a micron, they are close to the limit of the resolving power of the microscope, and considerable care has to be taken to avoid incorrect interpretation. However, there seems to be no question but that there are actually three of these thin layers, each about $0.4\mu$–$0.5\mu$ thick, of great uniformity. The inner and outer layers appear dark while the middle layer appears light or transparent. That these are not simply diffraction effects seems to be proved by the fact that they appear in spite of various manipulations of the illumination, and moreover, are sometimes found separated where the broken portion of the barbule has been sectioned.

The barbules may be split by pressure or teasing, often in their principal plane, particularly since the core does not appear to have any great tenacity. Either half of the split barbule may show the iridescent colors. If the barbules are swelled to partial disintegration, by potash, ammonia, or sodium hypochlorite, the thin outer layers swell, pucker, split, and loosen from the core, which has a segmented appearance like flattened, short-joint bamboo. On drying, the loosened envelope shrinks back onto the core again, though not without

considerable puckering and unevenness. Such severe treatment usually destroys the iridescence as well as removing some of the brown coloring.

No differences in structure between barbules of different colors were observed. The above properties fit all the different colored barbules which the peacock feather possesses. Study of other iridescent feathers (bronze-winged pigeon, Monaul pheasant, cock, trogon, etc.) by sectioning, teasing, and swelling, showed essentially the same structure, though the barbules of these feathers are smaller than those of the peacock, and generally are not so highly curved.

The laminated outer layer of the barbules, as shown by cross-section, is particularly characteristic, and is not found on non-iridescent feathers of the same bird where these are available for examination. In all cases a definite structure is associated with iridescence. The barbules are always broad and flattened, distinctly segmented, with blunt ends, and are generally much more heavily pigmented than adjacent, non-iridescent barbules of the same feather.

Newbigin[1] has pointed out the structural differences between iridescent and non-iridescent barbules, which are very noticeable in most feathers where both types of barbules are present. The bronze-winged pigeon, for example, has sharply defined iridescent patches on gray feathers, and microscopic examination shows the boundary of the patches to be very distinct, both types of barbules often existing side by side on the same barb. These structural differences are so apparent, that, after a little practice, it was found possible to pick out from the collection of drawings of barbules in Chandler's paper[2] those which were of the iridescent type, and comparison with the description of the coloring of the feather revealed very few errors, though the drawings cover almost all species, and include many feathers not possessing any non-iridescent barbules for comparison. This shows clearly that the same sort of structural modification occurs in connection

[1] "Colour in Nature," Chap. xiii (1898).

[2] Univ. of Cal. Pub. Zoöl., **13**, No. 11 (1914–16).

with iridescence, irrespective of the species of the bird to which the feathers belong.

The iridescent barbules of feathers do not usually have hooklets developed on them to any considerable extent and when these are present they are usually only on the segments nearest the tip of the barbule. The distal barbules in a feather of dense structure are so placed that, instead of being seen edgewise as the feather is viewed from a point normal to its surface, they present their broad surfaces to the observer, and give a smooth, overlapping "shingled," satiny appearance to the feather, few gaps or openings being visible in this approximately plane surface, even under the microscope; in the looser, more open types of feathers both the distal and proximal iridescent barbules present their flat surfaces to the eye in the above manner, though less closely overlapping. This satiny "shingled" surface is so different from that of a non-iridescent feather that it is not to be wondered at that Altum[1] made the statement that "in the case of the iridescent feathers with metallic lustre, the peculiar color is always accompanied by a peculiar structure. Wherever we find this type of color, we find a feather structure which feels hard, smooth, and metallic. It does not require a delicate sense of touch to distinguish blindfolded those parts of the feathers which show metallic colors, if one runs the hand, for instance, up and down the back and breast of *Cuculus cupreus* or of the different red-breasted trogons, etc. The metallic lustre is always associated with the peculiar, hard, and smooth texture. A blind man could easily pick out all the birds with metallic lustre in a collection of any size. He would even be able to arrange them according to the intensity of the lustre and other peculiarities."

The surface formed is so smooth and so nearly plane in many feathers that it gives them an almost mirrorlike or metallic appearance, and it is noticeable that practically no light is reflected from such a surface unless it is held so that the light may be reflected to the eye as from a mirror, the angles of incidence and reflection being equal.

[1] Jour. Ornithologie, 2, 19 (1854).

**Optical Properties of Iridescent Feathers**

Whatever their colors by reflected light, the barbules of the peacock feather appear brown by transmitted light. The thinness is such that they are fairly transparent under the microscope. The shade of brown does not appear to be different in barbules of different color by reflected light.

By reflected light, the gorgeous colorings show plainly. They include copper-red, brass-yellow, yellow-green, blue-green, and purple, as seen when the plane of the feather is normal to the line of vision. These colors change very markedly with inclination of the feather from this position, an inclination of about 30° from normal causing the red parts to appear green in color, the yellow to appear blue-green, the blue-green to appear purple, and the purple to appear almost reddish. This variation is further increased by increasing the angle of incidence still more.

Microscopic examination by reflected light shows that what appears to the naked eye as a region of uniform color in the feather is really a composite, and that the color of the individual barbules in such a region varies considerably, any color from yellow to green appearing in the brass-yellow part of the feather. The color of the individual barbules is often far from uniform, showing distinct variations in different segments, and some lack of uniformity of coloration is noticeable even within the segments, though the boundaries between the different colors are not sharp, but blend gradually together. The coloring is further complicated by the curvature of the surfaces of the barbules, for, since the line of vision cannot make the same angle with all parts of the curved surface, part may be viewed at normal incidence while another part is seen at an angle as great as 30° from this position. Thus a curved red barbule may appear red at the base and green at the tip, solely on account of this difference in the angle at which these two parts of its curved surface are seen. Flattening the barbules under a cover glass when examining them helps to bring all parts of the barbule into the same plane. The transverse curvature of the barbules, which gives them a convex-concave

cross-section, is more marked than their longitudinal curvature, and results in more noticeable variation of the color for this reason. Sometimes a barbule presents almost a spectrum across its surface, the red being on the part of the surface which is viewed normal, while the colors shade through yellow to greenish-blue on the part of the surface which makes an acute angle with the line of vision. Flattening the barbule brings all parts into approximately the same plane, and this variation of color due to curvature is destroyed.

Examination by means of a microspectroscope shows the light reflected from the barbules to consist of a region of the spectrum rather than being made up of lines or bands. The spectrum in general shifts toward the blue as the obliquity of the barbule to the line of vision is increased. Nothing more significant seems to be revealed by the microspectroscope than can be observed with careful study of the colors by the microscope alone.

On account of this complexity of surface, the color changes with angle can best be studied from single barbules flattened in wax on a slide, but not covered with a cover glass. Even then, the observations are best made on a single point at a time, rather than on the surface of the barbule as a whole, though, if its surface is smooth and approximately plane, good results may be obtained by study of the entire feather. A Universal Stage microscope provides for all possible orientations, while diffuse light may be supplied by an opal glass bulb, with white reflector, behind a white translucent screen, from which light can fall on the barbules from widely differing angles so that, whatever their position may be, it will be reflected in the eye of the observer.

Increasing the angle of incidence from the normal, little change in the color is noted with or without the nicol, at angles less than 30°, but as the angle of incidence exceeds this the color changes are marked. If the nicol is inserted so as to transmit light vibrating in the plane of incidence, the color is seen to darken as the angle of incidence is increased and at a slightly greater angle the complement of this color appears.

The color thus seen at an angle of incidence of about 60° is the complement of that seen at the same angle without the nicol, or with the nicol placed to transmit vibrations perpendicular to the plane of incidence. Also, if a quarter-wave plate is inserted, the color observed in this position is no longer complementary to, but is the same as the color seen without the nicol, or with it in the other position but without the quarter-wave plate. At angles of 60° or greater with the quarter-wave plate in position, rotating the nicol does not cut off the reflected light, showing that not all of the light has been rendered plane polarized by the quarter-wave plate, which means that the reflected light is only partially elliptically polarized.

In all the cases studied the changes in color and polarization with the angle follow the above rules. Indeed, after a little practice, one is able to predict, with considerable success, the color changes which any feather will show with increasing angle of incidence. The color changes of some typical iridescent feathers will be tabulated after the effect of swelling has been discussed.

### Effects of Pressure and Swelling

Since the barbules are composed of fairly dense material, and apparently have no cavities, considerable pressure is necessary to produce any effect on dry, untreated barbules. It is noticeable, however, that their color by reflected light is changed by pressure, and in general this change is toward the blue end of the spectrum, or, more exactly, toward the color seen at grazing incidence. Barbules which have been softened by soaking in water or swelled by alkalies, etc. show much more noticeable changes in color with pressure. In this case the change of color with pressure follows the same rule.

The barbules are swelled markedly and softened by dilute ammonia or sodium hydroxide solutions. If they are mounted in water and the alkali is allowed to diffuse through the preparation the swelling takes place gradually and may be observed under the microscope. The swelling action causes marked

changes in the color of the barbules as observed by reflected light, and all gradations of these changes are sometimes shown on a single barbule, one end of which may have been acted on by the reagent while the other end as yet was not reached by the diffusion. Thus a single barbule may appear blue at one end (its original color), shading through green and yellow to copper-red at the point acted upon longest by the swelling reagent.

In general the colors of the barbules change toward the red end of the spectrum though this is not the case for the barbules of feathers of some other birds than the peacock. The swelled barbules show the color change with angle, and other optical properties, corresponding to the behavior of the untreated barbules. It is always noticed that the color of the swelled barbules seen at grazing incidence is very nearly identical with the color of the untreated barbules seen at normal incidence. In some instances this color is reached at angles of incidence somewhat less than 90° (grazing), when the color of the swelled barbule at grazing incidence is very similar to that of the untreated barbule at an angle of incidence somewhat less than grazing.

The color changes of some typical iridescent feathers may be listed as in the following table:

The above list might be continued but the instances given are sufficient to show the nature and extent of the color change, and to illustrate the generalizations given in the preceding paragraphs. The similar behavior of similar colors in different birds is also worthy of note.

The application of pressure to the swelled barbules restores the original color, the color changes which take place being just the opposite of those passed through during the swelling process. More severe pressure may cause the color to go beyond that of the untreated barbule, generally toward the red end of the spectrum.

Exposure to phenol vapor for a few days causes color changes similar to those brought about by swelling with alkalies, and the swelled feathers have similar properties. Many

**Color Changes from Vertical to Grazing Incidence**

| | Untreated | Swelled |
|---|---|---|
| Monaul Pheasant | Copper-red ⟶ yellow-green<br>Grass-green ⟶ greenish blue<br>Light greenish blue ⟶ blue violet | Purple ⟶ copper-red ⟶ olive-green<br>Copper-red ⟶ grass-green ⟶ bluish green<br>Yellowish green ⟶ greenish blue indigo |
| Wood Duck | Dark blue ⟶ purplish red | Lighter greenish blue⟶ dark blue ⟶ reddish purple |
| Bronze-Headed Trogon | Green ⟶ indigo | Purplish red ⟶ bronze-green ⟶ blue-green |
| Common Pigeon | Green ⟶ red | Red ⟶ green |
| Black Minorca Peacock | Bluish olive-green ⟶ purplish blue<br>Blue-green ⟶ indigo ⟶ reddish purple<br>Greenish yellow ⟶ bright blue | Pinkish brown ⟶ bluish green ⟶ blue<br>Copper-red ⟶ blue-green ⟶ blue<br>Orange ⟶ green ⟶ greenish blue |
| Bronze-Winged Pigeon | Red ⟶ yellowish green | Reddish purple ⟶ red ⟶greenish orange |
| *Ptilopus pulchellus*<br>*P. puella* | Green ⟶ blue | Orange ⟶ green ⟶ bluish green |
| Muscovy Duck (fault bars) | Blue ⟶ purple ⟶ reddish | Yellow-green ⟶ greenish blue |
| (normal) | Green ⟶ blue-green ⟶ purple | Orange ⟶ yellow-green ⟶ green |
| *Nettion brasiliense* | Green ⟶ blue ⟶ purple ⟶ reddish | Orange ⟶ green ⟶ greenish blue ⟶ blue |
| Red King Bird of Paradise | Brilliant green ⟶ blue ⟶ indigo | Red ⟶ yellow ⟶ green ⟶ bluish green |
| Peacock Pheasant | Greenish blue ⟶ purple ⟶ reddish | Orange ⟶ green ⟶ blue ⟶ indigo |

organic liquids also cause swelling and color changes of the same sort, and even soaking for a time in water, or exposure to steam will cause considerable change in color due to the swelling of the barbules. Washing and drying of the barbules swelled by liquids, or simple exposure to the air in the case of those acted upon by vapors, is sufficient to restore the original color and properties perfectly. Care must be taken that only very dilute alkalies are employed, for strong solutions have a solvent and disintegrating effect on the feather, and injure its structure and color permanently.

### Fault Bars in Iridescent Feathers

Riddle[1] shows that fault bars in feathers are caused by some hindrance of the normal development of the feather, either by mechanical injury or restriction, or by a lowering of the anabolic tonus of the bird by illness, starvation, poisoning, or similar cause. The period of this hindrance is recorded on the feather as a transverse mark or bar. The structure of the feather is much more easily affected than its pigmentation, and structural fault bars are very common in both iridescent and non-iridescent feathers, particularly of the denser types. These fault bars appear as gaps or breaks in the plane of the feather and microscopic examination shows that the barbules are stunted and degenerate, or are absent altogether, while the barbs may also be shrunken, the whole leaving an opening in the feather at this point. All degrees of barring may be noted. The dark brown pigment is only affected by extreme impoverishment, which may cause a lighter color to appear, due probably to decrease in pigment production.

In iridescent feathers fault bars are common, and show the characteristics of those found in ordinary feathers. The barbules are seen to be badly dwarfed or absent in extreme cases. At the edges of such bars, where the stunted appearance begins, the iridescent color is different from that of the normal part of the feather. Where the stunting has been

[1] Chicago Univ. Diss., 46; Science, 328 (1907–1908).

relatively slight, so that the structure of the barbules is not noticeably dwarfed, only this contrast in color may serve to indicate the fault bars, which in shape and appearance are otherwise the same as those in which the structure is more markedly injured. These iridescent bars, of different colors from the rest of the feather are very noticeable when present. Without exception, in all the cases examined, where color fault bars are found in iridescent feathers, the color of the fault bars observed at normal incidence is the same as the color of the normal part of the feather as seen at angles approaching grazing incidence. The color of the bar may be quite different from that of the rest of the feather but the above rule always holds. The bars themselves show change in color with angle, and, indeed, have all the properties of typical iridescent barbules.

If iridescent feathers showing color fault bars are swelled moderately, by any of the methods given above, the color of the fault bars of the swelled feather is that of the normal part of the unswelled feather. Further swelling may change their color beyond this point, though the relationship given in the preceding paragraph always holds whether the feathers are swollen or not, the color of the fault bar at normal incidence is the same as that of the rest of the feather at a greater angle of incidence.

Most iridescent feathers show fault bars and in all probability they can be found on any iridescent bird if a sufficient number of specimens are available for examination. Chickens, ducks, pigeons, turkeys, pheasants, trogons, humming birds, Jacamar, *Ptilopus pulchellus*, *Ptilopus puella*, *Lamprocolius phoenicopterus bispecularis*, purple grackle, *Nettion brasiliense*, etc. show fault bars the colors of which are in accordance with the above generalizations.

### Effect of bleaching Iridescent Feathers

The dark brown pigment (melanin), present in varying amounts in all iridescent feathers except those from albinos, may be bleached by various reagents, though it is markedly

resistant to their action. Since all available bleaching agents have deleterious effects upon the structure of the feather, best results are obtained with feathers containing relatively little dark brown pigment, which need not be exposed to the bleaching agent for so long a time. Too concentrated bleaching agents are also to be avoided for the same reason.

Potassium permanganate is a powerful bleaching agent, but is too harmful to the structure of the feather. Sodium hypochlorite is even more active, but swells the barbules badly, as well as rendering them brittle. Hydrogen peroxide (3%) bleaches effectively, with a minimum of injury to the feather, and leaves no harmful products as a result of its action. It is far superior for this work to the methods making use of chlorine, commonly recommended, though it has some swelling action on the feathers, and renders them somewhat brittle. Its action may be stopped at any point by washing with water. Unfortunately, bleached iridescent feathers usually cannot be completely dried without undergoing so much shrinkage and distortion that their structure and color are seriously affected, but they may be studied mounted in water, or permanent mounts may be made in glycerine jelly.

By carrying the bleaching as far as possible without seriously damaging the structure of the barbules, they may be bleached to a pale straw color, almost colorless by transmitted light, yet their iridescent colors resist the action of the bleach, and are changed no more than corresponds to a moderate degree of swelling caused by the soaking to which they are subjected. Such transparent bleached barbules show no appreciable color by transmitted light, but by reflected light against a dark background their iridescent colorings are as brilliant as those of the unbleached barbules. The barbs of the feather are bleached more slowly, but the iridescence of the barbules is very marked when they are held against a dark background. The color changes with angle in accordance with the same rules which apply to the unbleached barbules. Apparently the relatively resistant dark brown pigment of

the barbules is affected by the bleaching agent much more markedly than are the iridescent colors.

Bleaching can usually be carried to completion only when the feather is relatively lightly pigmented. Heavily pigmented barbules are generally disintegrated before they are bleached colorless. . The green feathers of the bronze-headed trogon bleach perfectly without losing their green iridescence, and show their original changes of color very plainly. The brilliantly iridescent feathers of the bronze-winged pigeon also show their original colorings when bleached almost colorless, as seen by transmitted light. Other iridescent feathers show the same effects to a greater or less degree dependent principally upon the amount of dark brown pigment originally in them.

### Effect of Dyeing White Iridescent Feathers

Although only the white iridescent feathers of the neck of the albino and pied (brown and white) pigeon were available for study, there is reason to believe that iridescence is possible in the case of other white feathers from albino or pied varieties of normally iridescent birds, in spite of Chandler's statement[1] that albinism always is accompanied by loss of iridescence and the characteristic structure which accompanies it.

The white neck feathers of the pigeon in mass have a coarse, waxy, appearance, and if examined closely, in bright light, show a slight pearly iridescence.

Microscopic examination shows that the iridescence has the same colors and color changes as seen on normally pigmented pigeons, that is, red at normal incidence to green at grazing, or *vice versa*. These color changes are observed only by careful examination. The white iridescent feathers show exactly the same structure as the pigmented ones, and have the typical, spatulate, segmented barbules which are invariably associated with iridescent colorings. Neck feathers from pied pigeons all show the same structure, and may be all white, or partly white and partly pigmented, or all pigmented. The structure

[1] Univ. of Cal. Pub. Zoöl., 13, No. 11 (1914–16).

is uniform throughout the feather, whatever its pigmentation, but only the pigmented feathers or the pigmented parts of partially pigmented feathers show iridescent colors of brilliancy comparable to those of other birds. Even a single barbule may have some segments pigmented while others are colorless by transmitted light, and the structure is the same; the difference in brilliancy of the iridescence of the pigmented and unpigmented segments is very striking. The presence of pigment appears essential to the production of maximum brilliancy.

It is possible to mix alcoholic solutions of aniline dyes so as to produce a color approximating closely the brown of the pigmented, iridescent feathers of the neck of the pied pigeon. When white iridescent feathers are dyed with this solution, dried, and the excess dye on the surface wiped off, they have a brilliancy of iridescence and metallic colorings equalling those of the best of the naturally pigmented feathers of the pigeon. No effect whatever beyond a plain brown body color is produced when similar white feathers, not possessing the structure characteristic of iridescent feathers, are dyed with the same dye. Black dyes may also be used though they act less readily. They enhance the iridescent colors in the same manner as does the brown dye.

White feathers from the albino peacock and turkey have a distinctly stunted and degenerate structure in the barbules, not of the iridescent type, and show no signs of iridescent colorings. Dyeing does not bring out any iridescence in these feathers.

### Effect on Iridescent Feathers of Immersion in Liquids

If iridescent feathers are immersed completely in liquids the brilliancy of their colorings is always lessened, and the extent to which their iridescence is darkened appears to depend on the refractive index of the immersion liquid. Liquids of refractive index close to 1.60 cause the colors of a peacock feather to darken so that at first glance they would be said to have disappeared. However, microscopic examination shows

that the iridescent colors are not destroyed, but are only much lessened in intensity. If the liquid of refractive index 1.60 is replaced by one of either higher or lower refractive index, the brilliancy of the colors is restored partially. For instance, in alcohol ($n = 1.37$) the colors are very noticeable though still somewhat less brilliant than in air. The most marked disappearance of color appears, in the case of the peacock, in liquid of refractive index 1.60. In general, liquids of refractive indices between 1.55 and 1.60 have the most effect on the colors of feathers, and in many instances careful microscopic examination is required to detect the slight iridescence which remains under these conditions. In all cases, drying the feather restores the original color perfectly.

Most liquids have some swelling action on feathers, and may change their color somewhat, but the brilliancy depends on the refractive index of the liquid, as may be shown by carefully wiping the feather free from all adhering liquid. By thus removing the liquid the effect due to immersion is destroyed, and the original brilliancy is perfectly restored, though if the liquid has swelled the feather exposure to the air for a few minutes is necessary before the original color is regained.

It has not been possible to destroy the iridescent colors by penetrating the feather with cresol or similar liquids. Apparently there are no cavities in the barbules which might be filled by this liquid, even though they are finely divided, and laid open for penetration by sectioning.

### Action of Solvents on Iridescent Feathers

Prolonged extraction of the barbules of iridescent feathers, such as those of the peacock, pigeon, wood duck, Monaul pheasant, chicken, trogon, humming bird, etc., causes no change or diminution of their iridescence. Hot or cold alcohol, alcohol saturated with ammonia, xylene, orthocresol, carbon bisulphide, ether, carbon tetrachloride, acetone, chloroform, and water, have no solvent effect whatever on the iridescent colors during extractions of over 30 hours. The colors of the feathers

are not in the least diminished, and the solvents are not discolored.

Only solvents which destroy the feather affect the iridescent colors. Ammonia, sodium hydroxide in aqueous or alcoholic solution, and similar alkalies disintegrate and dissolve the tissue of the feather and the dark brown pigment, but the iridescence persists until the structure of the barbules is damaged seriously by these powerful reagents. Even when the barbules are dissolved completely by the alkali, their solutions are of the same color irrespective of the original iridescent color of the different feathers. Neutralizing with acid does not precipitate a colored pigment, other than muddy brown.

### Inadequacy of the Surface Color Theory

If the properties of thin-film colors outlined above, and of iridescent colors of feathers are compared in detail, the resemblances between the thin-film colors and the iridescent colors of feathers will be seen to be rather extensive, while surface color as an explanation of the iridescence presents some irreconcilable differences.

As far as optical properties are concerned, anyone who will take the trouble to compare the changes in color with angle shown by thin-film colors, iridescent feathers, and substances possessing surface color, when examined with unpolarized light, cannot but notice the very striking changes which the first two give, as opposed to the almost inappreciable color change shown by surface colors. If surface color is to be considered as the cause of the iridescence, a pigment showing many times as much change in color with angle as is seen in any known substance must be postulated.

Examination of the reflected light with a nicol prism shows some similarities in the color from these different sources, but also reveals the distinct darkening which films and feathers show at a fairly definite angle; this is not shown by surface colors. Also, as the "polarizing angle" is passed, the reflected vibrations in the plane of incidence change to the complementary color in both thin-film and iridescent-feather colors.

This, again, is not shown by surface color. The elliptical polarization of the reflected light is common to all three sources of color, and, in itself, proves nothing one way or the other.

The fact that true iridescence is shown by albino or bleached feathers, which are colorless by transmitted light presents no incompatibility with a theory of thin-film color, while, if surface color is to be considered as the cause of this iridescence, we must postulate a substance which has marked surface color (selective reflection) but little or no power of absorbing light. This is contrary to all experience and to the theory of the nature and cause of surface color. On the other hand, thin films are transparent and almost perfectly colorless by transmitted light, yet may give intense colors by reflected light.

In connection with this, the action of the brown or black dye, which brings out so strikingly the metallic iridescence in the albino pigeon feathers can hardly be explained on the basis of surface color, for it is noted only in the case of feathers of a definite structure. As a dark background to eliminate the dilution of the reflected colors by transmitted or scattered light, its purpose is analogous to the dark background necessary for the display of the full metallic iridescence of thin films.

While pigments showing surface color, yet resistant to bleaching, might be postulated, such pigments could not be colorless and transparent and yet show surface color. Bleaching cannot remove the color from a thin film, but the bleach may destroy the film, and thus destroy the color. Bleaching of feathers does not destroy the iridescence, though the brilliancy is lessened when the dark brown pigment is bleached, just as the brilliant colorings of thin films are lessened when their dark background is removed.

Swelling and pressure do not change the surface colors of any pigments which we know, and to postulate a pigment so affected would require radical modifications in the present theories of reflection and absorption of light. The color changes can hardly be ascribed to chemical action between the swelling reagent and the pigment, when reagents so widely different

chemically all cause the same reversible color change in barbules of a given color, and all cause changes in color which may be predicted on the basis of a thin-film-color theory. Pure water could scarcely change the surface color of a solid pigment from green to red, and this change would hardly be perfectly reversible, yet duplicable by any one of a number of reagents. Thin films, on the other hand, unless made of material not capable of being swelled, are changed readily in color by various swelling reagents; these changes are reversible, and the colors of them may be predicted. Pressure also changes the colors of compressible, thin films; this change is opposite in direction to that caused by swelling, and the colors may be predicted.

The distinctive type of structure found only in iridescent barbules, shows the intimate connection between iridescence and structure in feathers. The structural modification is of such nature that it lends itself to the display of brilliant color very remarkably, and, in its minute details, is in no way incompatible with the presence of thin films as the source of the color.

The modification of the color in fault bars also points to a structural basis of the iridescence, since fault bars are essentially only diminutions in the structures of the feather. The formation of a pigment of different surface color from that of the rest of the feather, in conjunction with the stunting of the growth, seems highly improbable, especially since the color of the fault bars, whatever it may be, is always definitely related to the color of the feather, in the same manner for all colors.

In the preceding paragraphs there are many statements incompatible with the theory of surface color as the cause of the iridescence of feathers. Walter, in an extensive paper,[1] presents among other arguments in favor of the surface-color theory, the statement that thin-film colors "change in intensity, but not in color, with changing polarization of the incident light, while both change in the case of the surface colors." While the second part of this is true, the first is not, for the

[1] "Die Oberflächenfarben oder Schillerfarben" (1895).

change to complementary color at angles greater than the polarizing angle is easily observable, in the case of thin-film colors, and has been demonstrated mathematically.[1]

He admits that thin-film and surface colors have many similarities but fails to bring out their real differences in a very comprehensible manner, finally rejecting the former on the ground that it is inconceivable that films of sufficient regularity should exist. Walter's paper refers particularly to the colors of insects, but he emphasized the fact that many iridescent feathers show a complementary color by transmitted light. Some of his examples are undoubtedly Tyndall blues and greens, the real nature of which was not known at the time of his paper. Because of the yellow color shown by these blues with transmitted light he classes them as lustre (surface) colors on the basis of Haidinger's law, and remarks on the predominance of blues and greens as representatives of this type of color. From this it appears that, in many instances, he did not distinguish between the highly reflecting, metallic, iridescent feathers, and those which we know to be due to Tyndall blue, but perhaps considered them both together.

Michelson,[2] after ignoring Tyndall blue as the cause of the color of non-iridescent blue feathers, states that there are two, important, possible methods of producing color in nature, other than by ordinary pigmentation. These are: A. Interference, including diffraction; B. "Metallic" reflexion (surface color). "The chief characteristics by which 'metallic' reflexion may be distinguished may be summarized as follows:

1. The brightness of the reflected light is always a large fraction of the incident light, varying from 50 to nearly 100 percent.

2. The absorption is so intense that metal films are quite opaque even when their thickness is less than a thousandth of a millimeter.

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[1] Preston: "Theory of Light."

[2] Phil. Mag., [6] 21, 554 (1911).

3. If the absorption varies with the color, that color which is most copiously transmitted will be part of the incident white light which is least reflected, so that the transmitted light is complementary to the reflected.

4. The change of color of the reflected light.....follows the invariable rule that the color always approaches the violet end of the spectrum as the incidence increases. If the color of the normal reflexion is violet the light vanishes (changing to ultra-violet) and if the normal radiation be infra-red, it passes through red, orange, and yellow as the incidence increases."

Michelson has applied these qualitative criteria in the study of the iridescent colors of insects and birds and concludes that they support the surface color theory, mainly on the basis of the change of color with angle, which in the case of surface colors, changes "invariably toward the violet end of the spectrum as the incidence increases."

Even if we ignore the fact that feathers change in color far more markedly than do substances possessing surface color, the color changes exhibited by the neck feathers of the common pigeon constitute an exception to the above rule, for they may exhibit any of the following changes as the incidence is increased.

Purplish green—red—green—yellow-green.
Green—purplish green—red.
Red—green—yellow-green.
Red—purplish green—red.

Of these the first two are observed in most feathers; the other changes are less common.

At any rate here is a case of a feather color behaving in direct opposition to one of the important characteristics of surface colors. Some of the iridescent purples of certain ducks and pheasants, which change to reddish or even yellow-orange at grazing incidence, also are at variance with this property of surface color, though it is to be admitted that in most cases the iridescent colors of feathers do change toward violet as

the incidence increases. (These are not to be separated from the colors which change toward red, however, as will be shown later.)

The iridescence of transparent, albino or bleached feathers is certainly not in accordance with the intense absorption which substances showing surface color possess, while the transmitted color of ordinary iridescent feathers is a plain brown irrespective of their reflected color. As far as the intensity of reflection is concerned, a complex surface such as is presented by a feather would not permit of very conclusive measurements in any case, though quantitative results might be significant if obtained from single, plane, barbules. Anyone who has examined the colors of a thin film backed with black, prepared as directed on a preceding page, will admit that thin films are capable of reflecting as intense colors as those of feathers.

Michelson bases his final conclusion, in favor of "metallic" reflection (surface color) on the similarity in optical properties shown by light reflected from dye stuffs showing surface color and that reflected from feathers or insect wings. Quantitative measurements were made of the "phase differences" in the reflected, elliptically polarized, light, and of the "amplitude ratios," for different angles of incidence. Since the light reflected from thin films is also elliptically polarized, it is unfortunate that similar measurements were not made on it, before thin films were dismissed from consideration as a possible cause of iridescence. Until such measurements are made, the evidence in this quarter leaves much to be desired, and need not be considered as excluding the thin-film theory of the colors of iridescent feathers.

Since the character of the surface influences reflection so pronouncedly, all such measurements, to be comparable, ought to be made on similar surfaces. For instances, the surface colors of dye stuffs painted on dark or neutral-colored feathers might be compared with the iridescent colors of feathers, and with the colors of artificial thin films supported on the uneven surface of dark feathers, and following its irregularities. It

is hoped that measurements of such material may eventually be made at Cornell.

Lord Rayleigh[1] has had about the last word on this subject, and in his paper he points out the exceptions to Haidinger's law (*of the complementary relationship between surface and* body colors) as well as noting that surface colors change too little with angle to correspond with the iridescent colors of feathers and insects. He states that Michelson's four tests for surface color "are as well if not better borne by an interference theory." Rayleigh points out that the absence of a well marked polarization angle may be due simply to the complexity of the surface which produces the color. He also observes that the reflected colors of iridescent feathers and insects are highly saturated as compared with their transmitted colors, while with surface colors the reverse is true. Rayleigh has calculated, on the basis of 1.6 as the index of refraction of the color-producing film, the colors of feathers seen at grazing incidence, from the colors observed at normal incidence, and he remarks upon the very good agreement between the calculated and observed values as a strong point in favor of the thin-film theory. (Cf. p. 422 of this article.) The remarkable variation and range of colors sometimes shown in a small area of the feather, he points out, is easily explicable *in terms of structural variation in the color-producing films,* though making large demands on a surface-color theory. Rayleigh's conclusion is distinctly in favor of the thin-film theory.

Since the theory of surface color as applied to the iridescence of feathers leaves so much to be explained, and presents so many contradictions with the properties observed in feathers, one is forced to exclude this theory, and to consider, as the cause of the iridescence, the other alternative, namely, thin-film colors, as an explanation.

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[1] Phil. Mag., [6] 37, 98 (1919).

**Similarities between Thin Films and Iridescent Feathers**

If the properties of iridescent feathers are compared with those of thin films, the parallelism is very apparent. Perhaps the most striking similarity is that shown with respect to the optical properties studied. The colors of thin films and of iridescent feathers change in the same, very obvious and unmistakable, manner with change in angle of incidence, and all the color changes exhibited in iridescent feathers may be observed with thin films of the proper thickness. This is particularly striking if thin films of gold size, varnish, balsam, asphaltum varnish, etc., are prepared by all owing adrop of the liquid to spread on a smooth water surface. These films are relatively uniform in thickness, and considerable areas often show the same color. Such areas of the film, when hardened by exposure to the air, are strong enough to remain intact when picked up on the surface of a clean non-iridescent feather, and a black or gray feather thus covered by a film requires careful examination to distinguish it from a natural iridescent feather, because the thin film follows closely the complex and uneven surface of the feather rather than remaining as a glassy layer stretched across the tops of the barbs and barbules.

These artificial, iridescent feathers are of importance here because they may be prepared to match any iridescent color found in feathers, and, when thus prepared, show the same color changes with angle as those shown by the natural feather. Their brilliancy and lustre are also quite as intense. Thin films are apparently capable, therefore, of producing colors closely comparable with those of iridescent feathers.

Microscopic study of the colors of individual iridescent barbules also shows the similarity of their colors to those of thin films, for the change of color with angle and with polarization, the existence of a "polarizing angle" at which the color darkens when examined through a nicol, and the elliptical polarization of the reflected light, are alike in feathers and in thin films. The variations of the colors of barbules side by side in the feather correspond to the variations in the colors of thin films due to slight non-uniformity of thickness, and the

same is true of the mottling and blending of colors sometimes observed in a single segment of a barbule. These likenesses are all the more significant because not only do the changes and variations of color exist, but they are the same changes and variations found in thin film colors, from which the colors and properties of iridescent feathers may be accurately predicted.

Pressure and swelling cause changes in the colors of thin films and of iridescent feathers and these changes are observed to be similar for similar original colors. Fault bars exhibit colors in feathers which correspond to the colors shown in thin places in color-producing films.

Destruction of films or of the structures of feathers is necessary to destroy their iridescence. Bleaching does not destroy it and solvents cannot dissolve it. Thin films and iridescent feathers may be actually colorless, showing no colors with transmitted light but distinct iridescence with reflected light, and moreover, both have their brilliancy enhanced and exhibit "metallic" lustre when a dark background is present. Such inherent resemblances, particularly in essential characteristics, cannot be ignored, and point strongly toward the identity of the iridescent colors of feathers and of thin films. One fact which needs to be reconciled with this, however, is the moderate effect which immersion in liquids has on the iridescent colors of feathers. An ordinary, single, thin film produces no color when brought in contact with a liquid of its own refractive index, and, even with liquids of refractive index considerably different from this value, the color is very markedly diminished. However, if we have to deal with two or more thin films, of different refractive indices, in contact with each other, only the color due to the film in contact with the liquid can be destroyed by immersion; the color due to underlying films is not affected. This type of color production by "multiple films," is not essentially different, in other properties, from that of a single thin film and corresponds in behavior with the colors of iridescent feathers, so that if more than one film takes part in the production of the color of an iridescent feather we have no incompatibility in this regard.

## Iridescence of Feathers on the Basis of Thin Films as the Color-producing Structure

It has been shown that, of the various possible explanations of the iridescent colors of feathers, that involving thin color-producing films is the only one which does not present irreconcilable conflicts with the observed properties of the feathers, and since the similarities between thin films and iridescent feathers are so extensive, it seems justifiable to accept this explanation, and to apply it in detail to the properties of iridescent feathers.

On this basis, the colors of iridescent feathers belong to Newton's series of interference colors, being caused by a laminated or plate-like structure of the barbules, where the color originates. These barbules present broad, flat surfaces forming an approximately plane surface which exhibits the colors with great brilliancy. This invariable, spatulate structure of the iridescent barbules serves to display the colors to best advantage. The color originates in the three layers, each about 0.4 $\mu$ thick, which act as a multiple thin film on the surface of the barbule. The thickness of these films is about the value calculated for interference colors of the order observed in feathers, though the whole structure is too small for accurate measurement.

On all the iridescent feathers examined, the colors appear to lie in the upper second or third orders of the series, which include the most brilliant of the interference colors: yellow, red in the upper second order, and dull purple, blue, green, yellow, red, in the third order. Since we have no good method of determining exactly the order of interference and isolated color reflected from a thin film, this was based on matching the colors of feathers with those of artificial films, the colors of which are of known order.

The changes of feathers are summarized in the above series; a feather of given color at normal incidence will appear a color listed ahead of this one when examined at grazing incidence. Hodgkinson,[1] who supports the thin-film theory in

[1] Manchester Memoirs, [4] **2**, 193 (1889).

an admirable paper, was able to predict the color changes of all the humming birds of the Gould collection, South Kensington Museum, and recognized their definite position in Newton's series of colors. In another paper[1] he proposes that the so-called "indescribable" colors of iridescent birds be described as they appear at normal incidence, all their color changes being indicated automatically by the information, in accordance with the above series. The color usually changes through two to three of the colors of the above series, frequently a change "from the blue toward the red end of the spectrum," but these are not spectrum colors, and this generalization does not apply in all cases though it happens to in many. The pigeon, for example, has feathers which change from bluish green through red, to yellowish green with increasing incidence.

Thickening of the color-producing films by swelling results in a color change toward a color listed in the series after the original color, for the thicker the film, the higher the order of color. Thinning by pressure or in fault bars results in a color of lower order (that is, earlier in the series) than the original color of the barbules. Thus the series summarizes the behavior of the colors of feathers on swelling or under pressure.

Bleaching does not destroy the colors, because there is no real color there, but only a structure, and unless this is destroyed the iridescence is uninjured. The "metallic" lustre and brilliancy of iridescent feathers is due to the dark brown pigment in them which serves as a dark background for the thin film colors. The exact distribution of this pigment is not certain, but apparently no special distribution is necessary to give metallic lustre, provided the essential structure is present, for the white iridescent pigeon feathers become metallic by simple dyeing with a brown dye, though detailed study of sections of the dyed barbules does not show any segregation of the dye in one underlying layer, but instead a rather uniform distribution. It is possible that a neutral-

[1] Manchester Memoirs, [4] 5, 149 (1892).

colored, transparent, thin film may serve to some extent as its own dark background, producing brilliant colors and metallic lustre, as does a colorless film on a dark background. This appears to be true in the case of films of asphaltum varnish, a highly colored transparent substance.

When iridescent feathers are held between the eye and the light no colors are seen, because thin films give no colors appreciable to the eye with transmitted light. Only the dark pigment is seen, and this renders the feather more or less opaque.

Since the colors are not destroyed by immersion of the feather in liquid of any refractive index, multiple films must be postulated, and the structure of the barbules, as shown by cross-sections, appears to bear this out. Unless a considerable number of these films are present, the resulting color will have properties essentially the same as that from a single film, except in this one respect of not being destroyed by immersion in liquid.

The polarizing angle is not observable on the feather as a whole, because the curvature of the barbules makes only different parts of them reflect at different angles and no general darkening is observed, though this may be seen under the microscope on the individual barbules.

The curvature of the barbules, with the resultant complexity of the surface of the feather, results in a softening and blending of the garish colors noticed in plane, thin films, because of the different angles at which different parts of the curved surface are viewed. This causes a mingling of the colors seen at normal and at other angles of incidence, causing added softness and richness of color. The slight local variations in the thickness of the color-producing film also contribute to this effect, by causing a mottling of colors, which mingle and appear to the eye as the mean color of all the various hues. The color which we observe on the feather is thus the result of the mingling of a number of colors adjacent in Newton's series, which produce the effect of a single, softer color.

Strong[1] has explained the colors of the iridescent neck feathers of the pigeon as being caused by Newton's ring effects where the spherical pigment granules within the barbules touch the outer surface, but this cannot be the case, for spheres in contact with a more or less plane surface could not produce a uniform color but rather a series of concentric rings of different colors, in this case so small that they would probably be perceived only as white light, and would not exhibit any consistent color changes. Moreover, the iridescence is noted in parts of the barbules where no spherical granules are present. His statement that the feathers present the phenomenon of "anomalous dispersion" because they are "dark brown by transmitted light and light metallic or yellowish brown by reflected light" seems to be rather far-fetched, in view of the fact that anomalous dispersion can only be detected by spectrometric methods, no record of which is given; anomalous dispersion has not been observed in any thin film colors. Altogether his paper presents no consistent theory which would account for the observed facts, on the basis of our knowledge of the behavior of thin films of the type he suggests. The thin films which cause the iridescence of the pigeon are not of this type, but are of the same character as those of all other iridescent feathers.

Variation in the thickness of the color-producing films also explains the different colors often observed on a single feather, either in the form of a pattern, as in the case of the peacock, or in gradations of color, such as are seen in the feathers of the starling, purple grackle, *Lamprocolius phoenicopterus bispecularis*, and other birds. The latter iridescent feathers show bands of colors which remind one very much of the colors surrounding a drop of oil on asphalt pavement. For instance, some of the feathers of the starling are iridescent, reddish purple at the base, shading to yellowish bronze at the tip; others are yellowish green at the base to greenish blue at the tip, while some feathers of the purple grackle shade from red-

[1] "Mark Anniversary Volume," 263.

dish purple at the base to blue, greenish blue, green, yellow-green, to yellow bronze at the tips. These sequences of shades are undoubtedly produced by a gradual variation in thickness of the color-producing films, for the colors are always adjacent in Newton's series, and, moreover, the colors shift with increasing incidence, just as do Newton's rings, the shift or change in position of a given color being toward the thicker part of the film.

The grosser structure of the feather may influence the appearance of the iridescent colors very markedly. Not only the perfection of the surface formed by the overlapping of the distal barbules, but also the visibility of the color, are dependent on this. For example, the blue-green iridescent barbules of the peacock feather are present in the black center of the "eye" but are arranged so that they are seen edgewise and their color does not appear. The iridescent colors of many birds, particularly humming birds, are often visible only from a position in front of the bird, and are quite invisible when the head of the bird is pointed away from the observer. This again, is due to the barbules which are arranged so that instead of having their planes in the general plane of the feather, they are skewed or tilted somewhat, and lie normal to a direction towards the head of the bird, rather than in the plane of the feather, so that from other positions they are seen edgewise, and give little or no color.

The theory of thin films as the cause of iridescence, although it fits all the observed facts, cannot but inspire one to marvel at the perfection of nature's method of producing these colors with such uniformity through successive generations, especially when a slight general variation in the thickness of the films of the feathers of a bird, such as a peacock, would be enough to alter its coloration completely. Thayer's work on "Concealing Coloration in the Animal Kingdom" emphasizes, by many illustrations, the statement that iridescence is one of the potent devices for effecting "obliteration" against a variety of backgrounds and changing lights. Study of this book makes clear the very great usefulness of iridescent

colorings, and throws considerable light on the factors which possibly influenced their development in birds.

The structural foundation of iridescence seems to present a most remarkable case of the regulation of an essential structure within very sharply defined limits of magnitude, not only in numerous individuals but also through many successive generations, and ought to present some interesting problems from a biogenetic standpoint, particularly since very slight structural modifications result in such marked differences in color. Such investigations, however, lie beyond the scope of this paper, as well as outside the training of its author.

## Tests for the Identification of Thin-Film Colors in Iridescent Feathers

For convenience a few simple tests are summarized, to the end that any iridescent feather, the nature of the color of which is in question, may be examined systematically in order to decide whether its colors are due to thin films or to some other cause.

If the color of an iridescent feather is due to thin films it should meet the following requirements to a greater or less degree of perfection.

1. The color should change with increasing angle of incidence, to a color of lower order in Newton's series (frequently towards blue) and should be equivalent to colors of the upper second or third order.

2. The iridescent color should be wholly in the barbules.

3. The barbules should be distinctly spatulate in form.

4. The only color seen by transmitted light should be a neutral brown, more or less opaque.

5. The barbules should retain their iridescence in spite of careful bleaching to partial or complete transparency and colorlessness.

6. The color should be changed by swelling to one of the higher order in Newton's series, and this change should be reversible.

7. Pressure on the softened barbules should change their color to one of lower order in Newton's series.

8. If fault bars are present their color should be of lower order than that of the rest of the feather.

9. The lustre of the feather, if it possesses any dark pigment, should be more or less "metallic."

10. Transparent, non-pigmented feathers possessing the proper structure should become iridescent on being dyed with a dye of neutral brown hue.

11. The barbules, if fairly plane, should show a definite polarizing angle, and at angles greater than this the reflected light should be polarized elliptically, with the vibrations in the two planes complementary in color.

12. No system of fine, regular, parallel striations should be visible.

13. The color should not be lost in uniform diffuse light.

14. The colored light should be reflected regularly as from a mirror of complex surface, the angles of incidence and of reflection being approximately equal.

15. Cross-sections of the iridescent barbules should reveal their laminated structure.

16. Extraction should not remove the iridescence, nor should any but a yellowish or colorless extract be obtained.

### Iridescent Feathers Studied in this Work

The following feathers were studied and found to owe their iridescence to thin films of the type described above:

Black Minorca and Rhode Island Red Chickens, Bronze-winged Pigeon, Common Pigeon, Green Heron, Wood Duck, Mallard, Sommering Pheasant, Monaul Pheasant, Golden Pheasant, Chinese Pheasant, Peacock Pheasant, Bronze-headed Trogon, Peacock, *Musciroia mexicana*, *Ptilopus puella*, *Ptilopus pulchellus*, *Lamprocolius phoenicopterus bispecularis*, Purple Grackle, Jacamar, Ruby-throated Humming Bird, Red King Bird of Paradise, Wild Turkey, *Nettion brasiliense*, Starling, Muscovy Duck.

## Conclusion

The conclusions of this paper are as follows:

1. The iridescence of feathers is caused by thin laminae or films in the barbules, which produce interference colors.

2. No other structural colors and no surface colors due to selective reflection have been identified in iridescent feathers.

*Cornell University*

# THE FREE ENERGY AND HEAT OF FORMATION OF ZINC IODIDE*

BY T. J. WEBB

## Introduction

The directness and definiteness of results obtainable by the employment of the Gibbs-Helmholtz equation in calculating thermal data have given impetus to the measurement of electromotive forces and temperature coefficients of many reversible elements. For the purpose of obtaining the heat of formation of zinc iodide, and for the purpose of subjecting the Nernst Heat Theorem to a still further test (provided sufficient specific heat data are available) the following cell has been set up, and the free energy decrease, as well as the temperature coefficient of the free energy decrease, has been measured—

$$\text{Zn Amalg. (10\%)} \mid ZnI_2 \text{ (saturated soln.)} \mid AgI\text{-}Ag$$

An inspection of the cell will show that the following reaction takes place when current is allowed to flow through an external resistance:

$$Zn + 2AgI = ZnI_2 + 2Ag + Q \text{ cals.}$$

The substitution of the free energy decrease ($E \times F$, E being the voltage of the cell and F a faraday of current) at a given temperature and the temperature coefficient of the free energy decrease, in the Gibbs-Helmholtz equation, $A - U = T\frac{dA}{dT}$, gives immediately the heat of the reaction Q. The addition of the heat of formation of silver iodide (which has been established by various authorities,[1] employing widely differing methods,

* Contribution from the Laboratory of Physical Chemistry, Princeton University.

[1] Braune and Koref: Zeit. anorg. Chem., 87, 175 (1914); O. Gerth: Zeit. Elektrochemie, 27, 287 (1921); Taylor and Anderson: Jour. Am. Chem. Soc., 43, 2014 (1921).

as 15,100 ±50 cals.),[1] to the heat of the reaction Q measured above gives the heat of formation of zinc iodide (solid) from its elements. It is to be recalled at this point that the zinc amalgam employed is a two-phase one, and that consequently there is no heat effect to be taken into account in this calculation.[2] It is to be noted that the system is condensed throughout and employs no substances foreign to the reaction. These conditions eliminate liquid potential calculations as well as other untrustworthy calculations depending upon concentrations of ions.

A direct calorimetric measurement of the heat of formation of zinc iodide has also been made, and satisfactory agreement between this measurement and the calculated value obtained.

The absence of $\beta\nu$ values for zinc iodide as well as any directly determined specific heat data prevents the purposed test of the Nernst Heat Theorem. The obtainance of these data will allow an immediate test of the Theorem. New importance attaches to the thermodynamic data of zinc iodide, since the selection of this substance by Grimm,[3] as a typical one in his calculations of "lattice energies."

## Experimental

The silver electrodes were prepared by rapidly electrolyzing a solution of $KAg(CN)_2$, making a spirally wound platinum wire (sealed into a glass tube) cathode. The electrodes obtained in this way were covered with finely divided silver, and were reproducible to within a few hundredths of a

[1] A recent free-energy study by Gerke (Jour. Am. Chem. Soc., **44**, 1684 (1922)) made in the University of California claims, for a determination of the entropies of the chemical elements studied, a higher order of accuracy than has been hitherto attained. The electrometric studies of silver and lead iodides there made give a generally accepted value for the heat of formation of lead iodide namely 41,860 calories, but, on the other hand, a value for silver iodide equal to 14,814 calories, markedly divergent from the independent and concordant determinations recorded above. Before this latter work can be accepted, calorimetric data in support of such a low value should be advanced.—Hugh S. Taylor.

[2] Hulett and DeLury: Jour. Am. Chem. Soc., **30**, 1826 (1908).

[3] Grimm: Zeit. phys. Chem., **10**, 113, 504 (1922).

millivolt (measured against each other in a solution of silver nitrate). The electrodes prepared by employing currents less than five milliamperes per electrode differed among themselves by amounts as great as one millivolt.[1] The silver iodide was precipitated metathetically in the ordinary way and washed thoroughly. The employment of precipitated silver iodide is advantageous since it is this form which is stable and for which the above quoted thermal data apply.

The zinc amalgam was 10 percent zinc by weight. It was prepared by heating very pure zinc turnings with mercury which had been twice distilled. The zinc was Kahlbaum's pre-war, brown-label variety.

Zinc iodide was prepared by heating together zinc and iodine in the presence of water, but out of contact with air. The resulting dilute solution was evaporated to dryness out of contact with air. In some of the cells, Merck's white-label zinc iodide was employed which had been freed from excess hydriodic acid by solution of zinc. Subsequent analysis of the zinc iodide showed that its purity was sufficient.

The H-type of cell was employed. A platinum wire was sealed into one limb of the cell and covered with the amalgam. A paste consisting of silver iodide and saturated zinc iodide solution was introduced into the other limb. The silver electrode was then embedded in the paste. The cell was then filled with a saturated solution of zinc iodide, care being taken that solid zinc iodide was present in both limbs of the cell.

Measurements of the electromotive forces were made at two temperatures, 25° and 18°. The thermostats contained kerosene baths, and were automatically controlled. They could be regulated so as to keep a temperature constant to within 0.02°. It was found that these cells were extremely slow in coming to equilibrium, it being necessary to keep the cells at a constant temperature for at least six days before constant results could be obtained. This is not unexpected, when it is remembered that 20 cc of water at 25° dissolves

[1] *Cf. Lewis: Jour. Am. Chem. Soc., 28, 166 (1906).*

approximately 80 grams of zinc iodide. The resulting solution was naturally viscous, and diffusion was consequently slow. It is to this cause that the slow attainment of equilibrium is attributed.

Electromotive force measurements were made by means of a Wolff Potentiometer and a Leeds and Northrup high-sensitivity galvanometer. The standard cells employed were prepared by Hulett in this laboratory and were of the saturated Weston type.

### Calorimetric Determination

*Apparatus.*—The apparatus was modelled after that used by Fischer and by Braune and Koref. The calorimeter was a 90 mm. Dewar vessel. It was provided with a felt-lined, wooden cover, provided with holes for the admission of thermometer, stirrer, iodine container, and electric heater. The stirring was so regulated that particles of zinc were kept suspended throughout the solution, but was not sufficiently vigorous as to cause a rise of more than a few thousandths of a degree per minute. For a heater, one end of a piece of 4 mm. glass tubing was bent in the form of a circle at right angles to the tube, upon the bent part of which was wound sufficient constantan wire to give a resistance of ten ohms. Very heavy copper wires served as leads, were put through holes at the bottom of the tube and came up inside the tube. Their resistance was negligible; the constantan wire was completely covered with paraffin. The drop of potential between the leads to the heater was measured by means of a Weston Standard Voltmeter. The current was measured by means of an accurately calibrated ammeter. Both voltage and amperage were constant throughout a heating.

*Procedure.*—Into the calorimeter were placed approximately 700 cc of water and an excess of finely divided zinc. Sufficient iodine to cause a temperature rise of at least 0.5 degree was weighed into the iodine container. The container was placed in the cover, and was so constructed that by raising a stopper, the iodine would drop into the solution. The iodine container was weighed both before and after the experi-

ment. Stirrer, heater, and thermometer were placed in position. The stirrer was rotated by means of an electric motor, and the temperature was noted at intervals of one minute for fifteen minutes. When the temperature was rising by constant amounts (due to stirring), a known quantity of electricity, with a known potential drop across the terminals of the heater, was sent through the heater and the resulting rise in temperature noted. Temperature readings were taken until the rise per minute was the same as (or slightly less than) that which occurred before the heating by the current took place. The iodine was then dropped into the solution. After the temperature was again rising from stirring only, a definite amount of current was again sent through the heater. This gave a double check on the heat capacity of the apparatus for each determination.

The heat of solution of the solid salt was determined in an exactly similar manner, and from the following equations, it is evident that even though the salt is hydrolyzed to some extent in solution, the difference of the two heat effects gives the heat of formation of the solid salt:

(1) $Zn + I_2 = ZnI_2$ (dissolved) $+ Q_1$ cals.

(2) $ZnI_2$ (solid) $+ (H_2O) = ZnI_2$ (dissolved) $+ Q_2$ cals. $+ H_2O$

Subtracting (2) from (1),

$$Zn + I_2 = ZnI_2 \text{ (solid)} + (Q_1 - Q_2) \text{ cals.}$$

## Computation of Results

The cells were put in the 25° thermostat on January first. Consistent results were not obtained until January tenth. The cells were placed in the 18° thermostat on January thirteenth. The results are recorded in the following table.

TABLE I

| Date | Temp. | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| 1–10 | 25° | 0.39875 | 0.39830 | 0.39872 | 0.39825 |
| 1–11 | | 0.39864 | 0.39820 | 0.39874 | 0.39870 |
| 1–12 | | 0.39871 | 0.39820 | 0.39874 | 0.39870 |
| 1–21 | 18° | 0.39933 | 0.39916 | 0.39937 | 0.39943 |

The cells were kept in the 18° thermostat until February fifth, and the voltages measured on that day differed from the mean obtained on the 21st day by not more than 0.1 millivolt. The averages were taken between cells 1, 3, and 4, since cell No. 2 was consistently low throughout the experiments. The average value at 25° was found to be 0.39872 volts; that at 18°, 0.39938 volts.

The temperature coefficient, $dE/dT$, was therefore found to be —0.000094 volt per degree. By substituting in the equation, $E - U = T\, dE/dT$, U, or the heat of the reaction, is found to be 19.7 kg calories. Adding to this the heat of formation of two moles of silver iodide, 30.2 kg calories, gives the heat of formation of zinciodide, which is found to be 49.9 kg calories.

*Thermochemical Data:*

The data taken from a typical experiment are given below:

| | |
|---|---|
| Rise in temperature due to heating | 1.076° |
| Voltage | 8.46 |
| Amperage | 0.800 |
| Time in seconds | 900 |
| Rise in temperature due to reaction | 1.044° |
| Grams iodine added | 5.8682 |

The heat capacity of the apparatus is therefore—

$$\frac{.2394 \times 8.46 \times .800 \times 900}{1.076} = 1355 \text{ calories}$$

The heat of the reaction is then—

$$\frac{1355 \times 254 \times 1.044}{5.8682} = 61.23 \text{ kg calories}$$

Eight determinations were made and an average of 61.4 kg calories was obtained. The error as calculated by the method of least squares is ±0.3 kg calorie.

The value for the heat of solution of zinc iodide was found to be 11.6 ±0.3 kg calories. The value for the heat of formation of solid zinc iodide is therefore 49.8 kg calories.

The agreement between the heat of formation as calculated from the Gibbs-Helmholtz equation and the heat of formation as directly determined is as satisfactory as could be expected. It is hoped that sufficient data on the specific heat of zinc iodide will soon be available, in order that the Theorem of Nernst may be applied to this reaction. The value for the heat of formation of zinc iodide was calculated by Thomsen from purely thermal data and found to be 49.2 kg calories. The divergence between this calculated value and the directly determined values is not unexpected.

**Summary**

A study has been made of the cell, Ag-AgI $ZnI_2$ (Sat. soln.) | -Zn-amalgam. Its e.m.f. at 25° was found to be 0.39872 volts, and its temperature coefficient —0.000094 volt per degree. Employing these data and the value of the heat of formation of silver iodide (15.1 kg cals.) the heat of formation of zinc iodide has been found to be 49.9 kg calories. A direct calorimetric determination has also been made. The value thus obtained was 49.8 kg calories. The agreement is considered satisfactory.

* * * *

I wish to acknowledge my appreciation to Professors G. A. Hulett and H. S. Taylor of this laboratory for their valuable assistance in directing this investigation.

*Princeton, N. J.*

# ELECTROLYTIC PREPARATION OF ORTHO-AMIDOPHENOL

## EFFECT OF CATHODE MATERIALS

BY O. W. BROWN AND J. C. WARNER[1]

Ortho-nitrophenol in alkaline solution, may be reduced to ortho-amidophenol by electrolysis. In a previous paper,[2] we have given the results of our investigations concerning the effect of several factors on this reduction. In this paper, we shall give the results of a study of the effect of various cathode materials.

Many investigators have attempted to find a relation between the efficiency of an electrode in electrolytic oxidation or reduction and some property of the electrode material such as overvoltage, discharge potential or depolarization value. Dony-Hénault[3] thought that depolarization value was a direct indication of whether or not a compound could be oxidized or reduced by electrolysis. He also considered it a means of predicting the products resulting from the reaction. For example, he plotted curves showing the relation between current strength and anode potential using a 3-normal sulphuric acid electrolyte. Ethyl alcohol showed a considerable depolarization value but acetaldehyde practically none. From these data Dony-Hénault concluded that ethyl alcohol could be oxidized by electrolysis, but could be oxidized no farther than to the acetaldehyde stage. Elbs,[4] however claims that this is not a reliable basis for predictions and succeeded in converting acetaldehyde into acetic acid with a current efficiency of 80 percent.

[1] This paper is constructed from a dissertation presented by J. C. Warner to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree Doctor of Philosophy in Chemistry.

[2] Trans. Am. Electrochem. Soc., 41, 225 (1922).

[3] Zeit. Elektrochemie, 6, 70 (1900); 7, 57 (1901).

[4] Ibid., 6, 604 (1900); 7, 341 (1901).

Overvoltage is claimed by many investigators to be a more direct criterion of the usefulness of materials as electrodes. Tafel,[1] one of the chief workers in this field, has accomplished the reduction of such difficultly reducible substances as ketones, pyridine, and various alkaloids of the uric acid group by the use of metals having high hydrogen overvoltages, such as lead, mercury and cadmium. Newbery[2] has considered overvoltage an important factor in electrolytic oxidation and reduction. He has, however, not held to the original Caspari[3] definition of overvoltage since he broke the current at the instant before he measured potential. Caspari's values were obtained by measuring the potential between electrode and solution when, with an increasing impressed E. M. F., the visible evolution of gas at the electrode commenced.

When hydrogen is evolved reversibly at an electrode, the E. M. F. of the combination, metal, solution, normal hydrogen electrode is zero. Caspari found, however, that with practically all cathode materials, the evolution of hydrogen was not reversible and that a greater potential difference was necessary before hydrogen would be evolved. This excess of potential he termed overvoltage. The values determined by Newbery should be termed anodic and cathodic discharge potentials instead of overvoltages.

The catalytic effect and chemical action of the electrode, always important, in some cases become more important than potential considerations. For example; caffeine[4] is much more readily and rapidly reduced at a mercury than at a lead cathode although the hydrogen overvoltage on each is nearly the same. The important factor in this instance is evidently the catalytic action of the electrode material. Many metals, especially in the finely divided condition, act as very vigorous reducing agents. When these metals are used as cathodes, they

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[1] Ber. deutsch. chem. Ges., **33**, 2209 (1900); **35**, 1570 (1902); Zeit. phys. Chem., **34**, 187 (1900); **50**, 712 (1906).

[2] Jour. Chem. Soc., **109**, 1051, 1066, 1107, 1359.

[3] Zeit. phys. Chem., **30**, 89 (1899).

[4] Foerster: "Elektrochemie wässeriger Lösungen," p. 315.

may act upon the substance in a purely chemical manner thereby being converted into ions in the electrolyte. They may thenbe deposited by the current in a finely divided form and again act upon the depolarizer. Lead and zinc seem to act in this manner when used as cathodes for the reduction of ortho-nitrophenol to ortho-amidophenol in an alkaline electrolyte

## Experimental

The method and apparatus employed in these experiments was similar to those used in the study of the reduction at a copper cathode. In all of our experiments, unless otherwise stated the cathode solution consisted of 300 cc of 15 percent caustic soda solution containing 5 grams of ortho-nitrophenol. The container for the cathode solution was a 600 cc pyrex beaker (about 13×10 cm). The cathode in all cases was an 18-mesh wire gauze having a surface of one sq. dcm., counting both sides. The anode solution consisting of about 100 cc of 15 percent caustic soda, was placed in a porous cup[1] (11×5 cm) which was suspended in the cathode liquor. The anode was an iron wire gauze having a surface of 1.2 sq. dcm. counting both sides.

The temperature of the cathode liquor was maintained at 62–64° C by means of an electric hot plate beneath the beaker and glass cooling coils in the cathode compartment through which water could be circulated. A glass stirrer, driven at about 800 R. P. M. by means of a small electric motor, was placed in the cathode compartment, between the cathode and the porous cup. In all experiments, the theoretical number of ampere hours was used. Hence material yield and current efficiency in percent of theory have the same numerical values.

[1] As an objection to processes for the preparation of organic compounds by electrolysis in alkaline solutions, some persons have claimed that no diaphragm can be prepared which will give service for any length of time in strong alkali. In this connection, the authors thought it interesting to make a note of the fact that two Coors' cups were still in serviceable condition after having been used continuously for more than two months in the electrolytic preparation of para-amidophenol in alkaline solutions at temperatures ranging from 50–95° C.

The current strength was read by an ammeter and was kept at a certain value by adjusting the resistance. In experiments at low current densities, the number of ampere hours was determined by use of a copper coulometer.

At the end of each experiment, the cathode, stirrer, porous cup and cooling coils were washed off into the cathode solution and the latter transferred to a 1000 cc graduated flask and diluted to the mark. The quantity of ortho-amidophenol produced was determined by titration with standard sodium nitrite solutions as described in a previous article.

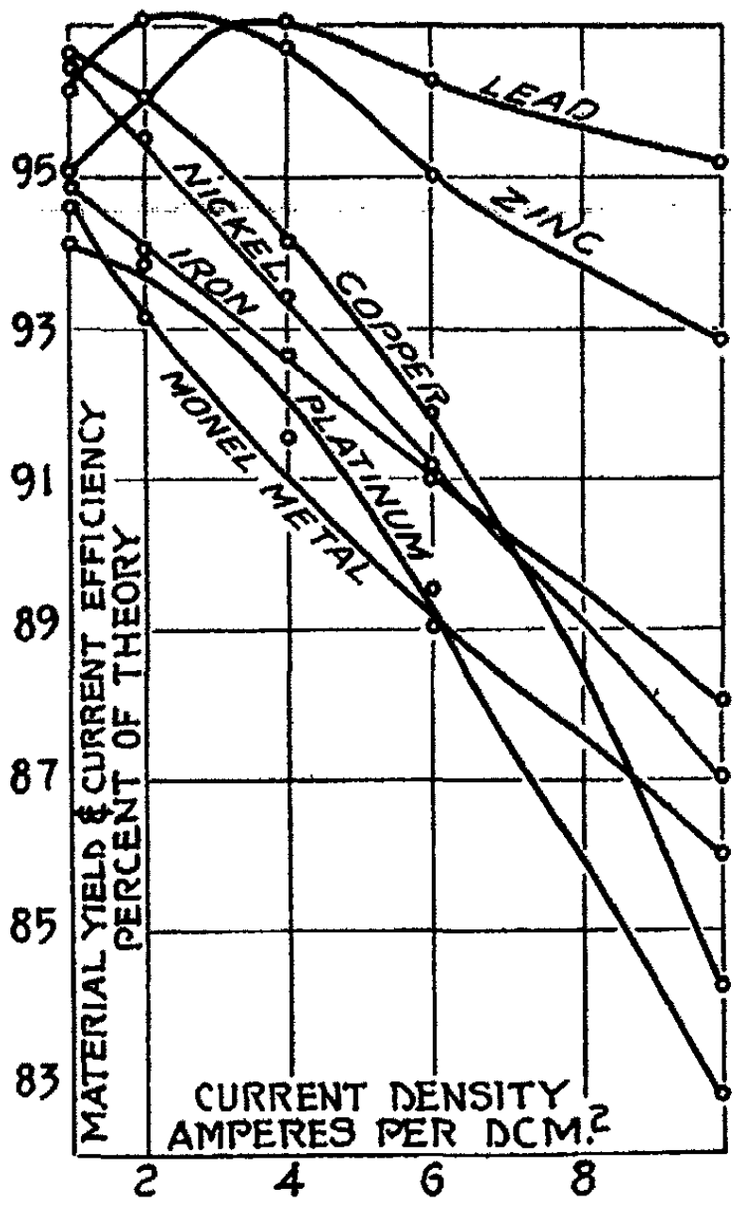



Fig. 1

The effect of current density at the cathode upon current efficiency and material yield was studied for cathodes of copper, nickel, iron, lead, zinc, spongy platinum, monel metal, copper amalgam, zinc amalgam and lead amalgam. The copper, nickel, iron and monel metal cathodes were made of 18-mesh wire gauze. The diameter of the wires in the gauzes was 0.041 cm. The platinum black cathode was made by depositing spongy platinum on a one sq. dcm. 18-mesh copper gauze from a dilute solution of $H_2Pt\ Cl_6$. The lead cathode was prepared by plating lead on a one sq. dcm., 18-mesh copper gauze from a Betts bath and the zinc cathode by plating zinc

on a similar copper gauze from a bath of zinc aluminum sulphate. The amalgam electrodes were prepared by immersing an electrode of the metal to be amalgamated in a solution of mercuric nitrate which contained 2 grams of $Hg(NO_3)_2$ and 5 cc. of concentrated $HNO_3$ in 600 cc of $H_2O$.

The results of all experiments showing the current efficiency and material yield at various current densities with each of the cathode materials are given in Table I. Two experiments were carried out at each current density, the results of both being given in the table.

TABLE I

Material Yield and Current Efficiency in Percent of Theory

| Amp./dcm². | Copper | Nickel | Iron | Monel | Lead |
|---|---|---|---|---|---|
| 1.0 | 96.6<br>96.4 | 96.5<br>96.5 | 95.4<br>94.8 | 94.8<br>95.1 | 94.2<br>94.8 |
| 2.0 | 95.9<br>96.3 | 95.2<br>95.4 | 94.2<br>93.9 | 93.8<br>92.5 | 95.4<br>95.5 |
| 4.0 | 94.1<br>94.2 | 92.4<br>92.9 | 93.7<br>93.2 | 91.2<br>92.4 | 97.2<br>96.9 |
| 6.0 | 91.6<br>92.1 | 91.0<br>91.0 | 91.0<br>91.4 | 89.0<br>89.0 | 96.3<br>96.3 |
| 10.0 | 84.4<br>84.1 | 87.4<br>86.9 | 87.8<br>88.4 | 86.0<br>86.0 | 95.2<br>95.4 |

| | Zinc | Platinum | Cu-Hg | Zn-Hg | Pb-Hg |
|---|---|---|---|---|---|
| 1.0 | 96.6<br>95.6 | 94.1<br>94.2 | 94.8<br>94.8 | 95.7<br>95.0 | 94.2<br>93.9 |
| 2.0 | 97.5<br>96.6 | 94.1<br>93.6 | 93.5<br>93.6 | 96.6<br>96.6 | 94.9<br>94.6 |
| 4.0 | 96.6<br>96.8 | 91.7<br>91.5 | 90.6<br>90.6 | 96.6<br>96.6 | 96.4<br>95.4 |
| 6.0 | 95.2<br>94.8 | 89.9<br>89.3 | 88.2<br>88.1 | 94.5<br>94.5 | 94.2<br>93.9 |
| 10.0 | 92.9<br>92.8 | 82.6<br>83.0 | 83.9<br>83.8 | 93.6<br>93.0 | 93.6<br>93.1 |

The averages of the results obtained when lead, zinc, copper, nickel, platinum, and monel metal were used as cathodes, are shown graphically in Figure 1. In Figure 2, copper, lead and

zinc are graphically compared with their amalgams. In all cases except when zinc, lead and their amalgams were used as cathodes, there was a gradual decrease in current efficiency and material yield as the current density at the cathode was increase The results obtained when zinc, lead and their amalgams are used are unusual since there is first an increase in current efficiency as the current density is increased and then a decrease in efficiency when a still higher current density is used.

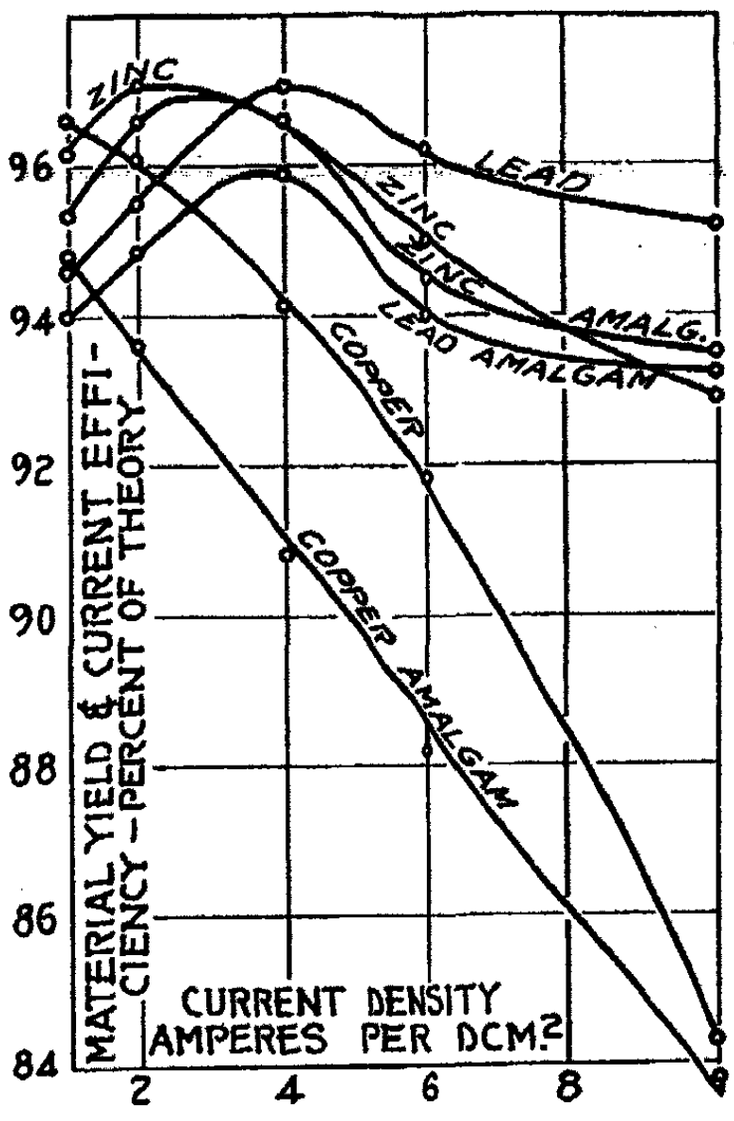



*Fig. 2*

Cathodes of all metals except lead, zinc, and their amalgams undergo no apparent physical change during the electrolysis. Cathodes of the latter, however, after use are covered with spongy metal which can easily be rubbed off. It seems that lead and zinc first go into solution in the caustic soda and are then redeposited on the cathode by the current. There may be some relation between the nature of this deposit at the various current densities and the peculiar shape of the current density curves when these cathodes are used. When the redeposited metal is spongy, the active cathode surface is undoubtedly increased. Hence, any factor which increases the sponginess of the deposit will have an influence similar to a lowering of the current density.

**Overvoltage, Discharge Potential, and Depolarization Value**

From the experiments in which metals without amalgamation were used, it can be seen that they range in usefulness as cathodes roughly in the order of the hydrogen overvoltages on these metals as determined by Caspari. The order of usefulness, however, is not the same at different current densities. The overvoltages of these metals may not be in the same order at different current densities, but it does not seem likely that this is the important factor in this case. It is further interesting to note that in all cases investigated, amalgamation made the metal less useful as a cathode material. This fact is contrary to the suppositions of Newbery[1] who predicts that amalgamated zinc or lead electrodes should be ideal electrodes for accomplishing reductions.

An attempt was now made to find a relationship between discharge potential (the potential difference between electrode and solution at the instant after the circuit is broken) and the usefulness of a material as cathode. The discharge potentials of several cathodes which showed the widest variation in usefulness were measured, first in a 15 percent solution of caustic soda and then in the same solution after the addition of five grams of ortho-nitrophenol to each 300 cc. By taking the difference, the depolarization value of the nitrophenol for each cathode could be determined. In all of these measurements, the normal calomel half-cell was used. Its E. M. F. was taken as —0.56 volts. The results of these experiments are given in Table II.

From these results, it is evident that there is no consistent relationship between discharge potential or depolarization value and the efficiency of the metal as a cathode material in this reduction. Copper amalgam, which shows the highest discharge potential and depolarization value, is the least efficient. Zinc, which is one of the most useful, shows the lowest depolarization value.

[1] Jour. Chem. Soc., 109, 1063 (1916).

Additional experiments were carried out in which the discharge potential at the cathode was measured at regular intervals throughout the reduction process. The results of these experiments are given in Table III.

TABLE II

Discharge Potential and Depolarization Value

Anode; Iron gauze, 1.2 sq. dcm. (counting both sides)
Anode liquor; 15 percent caustic soda
Cathode; 1 sq. dcm. gauze, 18 mesh
Cathodic current density; 6.0 amperes per sq. dcm.
Temperature; 62–64° C
Porous cup separating cathode and anode liquors

| Cathode material | Copper | Copper amalgam | Zinc | Lead |
|---|---|---|---|---|
| Cathodic discharge potential in 15 percent NaOH-volts | +0.81 | +1.50 | +1.07 | +1.01 |
| Cathodic discharge potential in 15 percent NaOH containing 5 gms of *o*-nitrophenol in 300 cc volts | +0.24 | +0.26 | +0.83 | +0.27 |
| Depolarization value—volts | 0.57 | 1.24 | 0.24 | 0.74 |
| Discharge potential after reduction of *o*-nitrophenol-volts | +0.80 | +1.43 | +1.06 | +0.92 |

The results given in Table III are shown by the curves in Figure 3. The relative usefulness of lead, copper, and copper amalgam as cathode materials might possibly be explained by reference to these curves. The discharge potential at a lead cathode remains low until practically all of the nitrophenol is reduced and then rises rapidly to almost the value of the discharge potential at a lead cathode in 15 percent solution of caustic which contains no nitrophenol. With a copper cathode, the rise starts sooner but is much more gradual, reaching a maximum some time after the theoretical number of ampere hours have been passed. With copper amalgam, the discharge potential remains low until the sudden rise considerably before the theoretical number or of ampere hours have been

TABLE III

**Discharge Potentials during the Reduction Process**

**Anode; Iron wire gauze, 1.2 sq. dcm.**
**Anode liquor; 100 cc 15 percent NaOH**
**Cathode; 1 sq. dcm. gauze, 18 mesh**
**Cathode liquor; 300 cc 15 percent NaOH 5 grams ortho-nitrophenol**
**Cathodic current density; 6.0 amperes per sq. dcm.**
**Temperature; 62–64° C**
**Porous cup separating cathode and anode liquors**
**Stirrer in cathode chamber**

| | Ampere hours passed | | | | | |
|---|---|---|---|---|---|---|
| | 0.0 | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 |
| Copper I* | +0.240 | +0.240 | +0.245 | +0.250 | +0.255 | +0.260 |
| Copper II** | +4.5 | +4.2 | +4.2 | +4.3 | +4.2 | +4.2 |
| Cu-Hg I | +0.259 | +0.259 | +0.273 | +0.273 | +0.278 | +0.287 |
| Cu-Hg II | +6.2 | +5.7 | +5.5 | +5.3 | +5.2 | +5.2 |
| Zinc I | +0.829 | +0.829 | +0.829 | +0.876 | +0.922 | +0.968 |
| Zinc II | +5.8 | +5.3 | +5.1 | +5.1 | +5.2 | +5.2 |
| Lead I | +0.273 | +0.273 | +0.273 | +0.273 | +0.273 | +0.273 |
| Lead II | +4.8 | +4.8 | +4.6 | +4.6 | +4.5 | +4.5 |

| | 3.0 | 3.5 | 4.0 | 4.5 | 5.0 | 5.5 |
|---|---|---|---|---|---|---|
| Copper I* | +0.273 | +0.287 | +0.306 | +0.343 | +0.389 | +0.458 |
| Copper II** | +4.2 | +4.3 | +4.7 | +4.7 | +4.8 | +4.9 |
| Cu-Hg I | +0.296 | +0.306 | +0.315 | +0.324 | +1.199 | +1.431 |
| Cu-Hg II | +5.1 | +5.2 | +5.1 | +5.3 | +5.6 | +5.9 |
| Zinc I | +0.977 | +0.991 | +1.000 | +1.014 | +1.037 | +1.060 |
| Zinc II | +5.3 | +5.5 | +5.4 | +5.6 | +5.5 | +5.5 |
| Lead I | +0.283 | +0.283 | +0.296 | +0.310 | +0.324 | +0.690 |
| Lead II | +4.4 | +4.5 | +4.5 | +4.5 | +4.5 | +5.1 |

| | 6.0 | 6.5 | 7.0 | 7.5 | 8.0 | 8.5 |
|---|---|---|---|---|---|---|
| Copper I* | +0.551 | +0.644 | +0.736 | +0.782 | +0.796 | +0.796 |
| Copper II** | +4.8 | +4.9 | +4.9 | +4.9 | +4.9 | +4.9 |
| Cu-Hg I | +1.431 | +1.432 | — | — | — | — |
| Cu-Hg II | +5.8 | +5.8 | — | — | — | — |
| Zinc I | +1.060 | +1.060 | — | — | — | — |
| Zinc II | +5.1 | +5.3 | — | — | — | — |
| Lead I | +0.875 | +0.922 | +0.922 | — | — | — |
| Lead II | +5.1 | +5.1 | +5.1 | — | — | — |

* Discharge potential in volts at cathode.
** Total potential drop in volts through cell.

passed. From this, the low current efficiencies with a copper amalgam cathode might be explained, since it might be supposed that the amalgam ceases to be useful as a cathode while there is still unreduced ortho-nitrophenol in solution. The behavior of zinc, however, destroys the possibility of deriving a general way of predicting the usefulness of a material as an electrode from the discharge potential curve. In spite of the fact that the discharge potential reaches a maximum long before the theoretical number of ampere hours have been passed, zinc is one of the most useful of these metals for carrying out the reduction of ortho-nitrophenol to ortho-amidophenol.

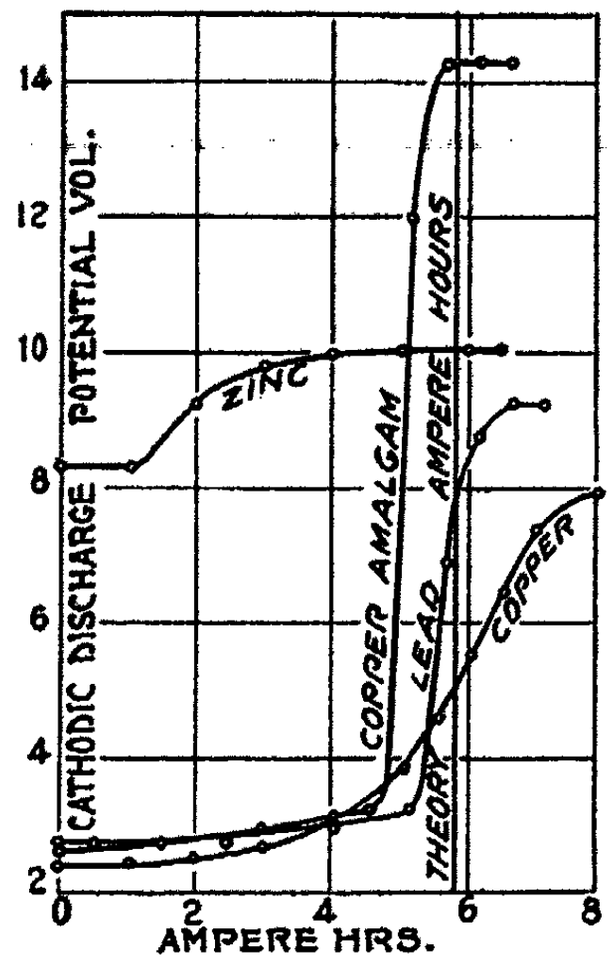



Fig. 3

The results of this investigation lead one to the conclusion that neither overvoltage, discharge potential, nor depolarization value can be taken as an absolute indication of the usefulness of a metal as an electrode, although they are important factors and should always be taken into account.

Purely chemical action of the electrode material upon the substance to be reduced is likewise important. For example: spongy lead will reduce ortho-nitrophenol to ortho-amidophenol in alkaline solutions. When a solution of 5 grams of ortho-nitrophenol in 300 cc of 15 percent caustic soda was treated with an excess of spongy lead and agitated at 70–80° C for a period of one and one-half hours, a 95 percent yield of amidophenol was secured.

Even if each of the above factors could be isolated and

separately studied, they would still be variable depending upon concentrations, temperatures, and current density. It seems therefore, that the most expedient means of determining the usefulness of materials as electrodes would consist of studying the usefulness by actual experiment in carrying out the desired reduction under the varying conditions of concentrations, temperatures, and current density.

## Summary and Conclusions

1. At low current densities, (1–2 amperes per sq. dcm.) copper, zinc, zinc amalgam, and nickel are the most efficient as cathode materials in the reduction of ortho-nitrophenol to ortho-amidophenol. At current densities from 4.0 to 10.0 amperes per sq. dcm., lead gives the highest yields with zinc and zinc amalgam slightly lower.

2. Discharge potentials and depolarization values are not criterions of the usefulness of a material as cathode in carrying out this reduction.

3. Amalgamation decreases the efficiency of a metal as cathode in reducing ortho-nitrophenol to ortho-amidophenol.

4. Since the factors upon which the efficiency of a material as an electrode depends are many and variable, the best method of attack seems to be a study of the performance of practical electrode materials by actual experiment under the various conditions of concentration, temperature, and current density.

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# THE SIZE-FREQUENCY DISTRIBUTION OF GRAINS OF SILVER HALIDE IN PHOTOGRAPHIC EMULSIONS AND ITS RELATION TO SENSITOMETRIC CHARACTERISTICS*

## V. SYSTEMATIC CORRELATION

BY E. P. WIGHTMAN, A. P. H. TRIVELLI, AND S. E. SHEPPARD

### Introduction

We have discussed, in previous papers,[1] the various methods used by others as well as by ourselves of obtaining the size-frequency distribution of the grains of a disperse system, and have given in detail, including the question of the errors involved, the principal method which we have employed in determining such distribution in the case of photographic emulsions.

The sensitometric and size-frequency distribution characteristics of a number of commercial and of a few experimental emulsions were correlated as far as possible experimentally and a tentative general theory of the correlation was proposed, and given a preliminary test.[2]

In the present paper we propose to consider a series of emulsions much more closely related to each other than those previously studied. They were all prepared in a similar manner with the exception of one factor which caused a change in the range of sizes of the grains, and hence in the size-frequency distribution.

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* Communication No. 171 from the Research Laboratory of the Eastman Kodak Co.

[1] E. P. Wightman and S. E. Sheppard: Jour. Phys. Chem., **25**, 181, 561 (1921); Brit. Jour. Phot., **68**, 169 (1921); E. P. Wightman, A. P. H. Trivelli and S. E. Sheppard: Jour. Phys. Chem., **27**, 141 (1923); Jour. Franklin Inst., **194**, 485 (1922).

[2] E. P. Wightman, A. P. H. Trivelli and S. E. Sheppard: Jour. Phys. Chem., **27**, 141 (1923).

By producing these emulsions with extreme care it was possible not only to cause a gradual change in the size-frequency distribution, but likewise in the photographic properties, as will be seen later.

In this connection a paper by M. Miyada,[1] which we had missed previously because of its inaccessibility, on the "Manufacture of Photographic Dry Plates," should be mentioned. He prepared high-speed photographic dry-plates according to Eder's ammoniacal method and studied various well known factors which influence the ripening and speed of the emulsion. The plates thus prepared gave a speed of about 13° Scheiner, i. e., approximately 130 H. and D.

He examined the emulsions of these plates microscopically and showed that in general the faster the plate, the larger the grains in the emulsion, another experimental confirmation of the conclusions of ourselves and others on this question. Indeed, he prepared an emulsion by mixing various emulsions which differed in degree of ripening, and in size of grains. The emulsions thus prepared, contained much greater varieties of sizes of the grains, and gave a considerably higher speed (15° Scheiner, or about 230 H. and D.).

## Experimental Part

Each emulsion in the series, W6C, W7C, W8C, W9C, W10C, W11C, and W12C, was coated onto 12.7 × 17.78 cm² (5 × 7 inch²) plates as in the case of ordinary photographic emulsions, except that the weight of the silver halide coated per unit area of plate was the same in every case.

The photographic properties of these original coatings of the W6C, W9C, and W12C were carefully measured, i. e., speed, latitude and $\gamma_x$, by the usual sensitometric methods employed in this Laboratory,[2] and which need not be described here, except to say that for the exposures a Jones' noninter-

[1] M. Miyada: Jour. Chem. Ind. (Japan), **24**, 884 (1921); Chem. Abst., **16**, 2644 (1922).

[2] *The sensitometric measurements were made by Mr. E. Huse, whom we wish to thank.*

mittent sensitometer was used, and the densities were measured by means of a Martens' photometer, and that all density gamma, and other measurements were carefully checked.

TABLE I

Photographic Properties of WC Series

| Emulsion | Speed | Latitude | $\gamma_{\infty}$ |
|---|---|---|---|
| W6C | 12 | 7.2 | 1.90 |
| W9C | 62 | 8.7 | 2.19 |
| W12C | 112 | 10.0 | 2.27 |

The resulting values are given in Table I, and are shown graphically in Fig. 1. It is seen that in passing from W6C to W12C, i. e., from the smallest to the largest grained emulsion

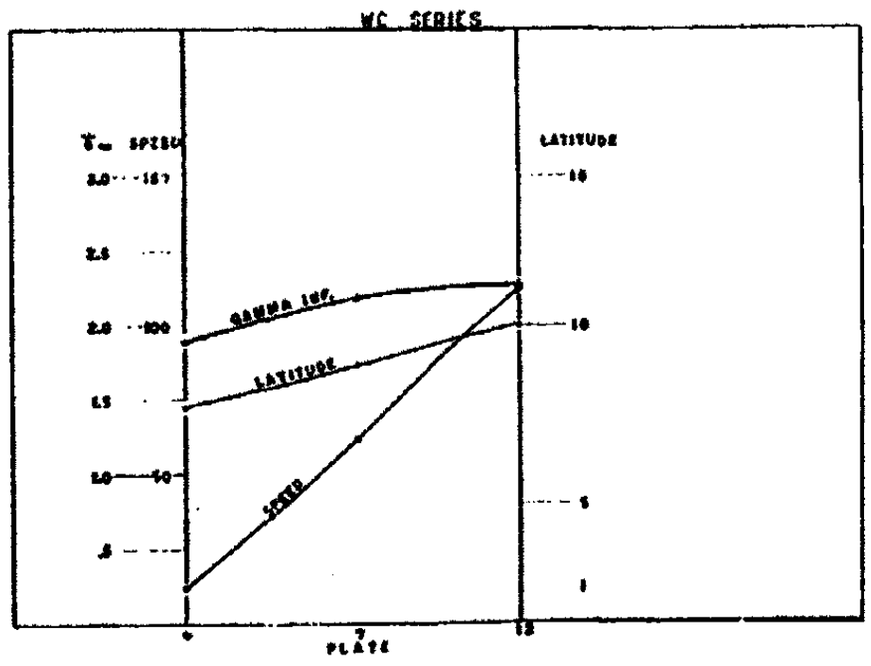



Fig. 1

as will be noted later, there is an increase of the values, and in the case of speed and latitude this increase is linear.

The size-frequency distribution characteristics of each of the emulsions in the series, taken from the coated plates, were determined as described previously.[1] The per thousand frequencies found, together with those calculated by the method of least squares are given in Table II. In Table III are given

[1] E. P. Wightman, A. P. H. Trivelli and S. E. Sheppard: loc. cit.

TABLE II

Size-Frequency per 1000 Grains of WC Series

| Class size in $\mu^2$ | W6C | | W7C | | W8C | | W9C | | W10C | | W11C | | W12C | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. |
| 0.11 | 680.0 | 680.0 | 463.5 | 463.5 | 310.1 | 288.6 | 178.1 | 182.2 | 175.5 | 176.0 | 133.5 | 133.0 | 79.1 | 79.2 |
| 0.3 | 241.0 | 199.5 | 315.5 | 222.6 | 313.0 | 261.9 | 219.2 | 190.8 | 185.1 | 186.0 | 172.5 | 155.5 | 114.5 | 97.0 |
| 0.5 | 58.5 | 58.5 | 141.7 | 106.7 | 185.5 | 210.4 | 198.4 | 179.9 | 172.4 | 175.2 | 164.6 | 165.0 | 117.7 | 111.0 |
| 0.7 | 13.4 | 17.2 | 51.2 | 51.2 | 84.1 | 149.5 | 128.0 | 152.0 | 146.8 | 147.0 | 124.7 | 159.0 | 119.1 | 119.2 |
| 0.9 | 3.8 | 5.0 | 20.6 | 24.5 | 52.2 | 94.1 | 94.4 | 115.1 | 133.0 | 110.0 | 126.6 | 139.1 | 113.0 | 120.0 |
| 1.1 | 1.0 | 1.5 | 4.9 | 11.8 | 22.2 | 52.4 | 60.7 | 78.1 | 66.0 | 73.3 | 84.8 | 110.4 | 96.0 | 113.2 |
| 1.3 | 1.9 | 0.4 | 3.9 | 5.6 | 12.5 | 25.8 | 38.4 | 47.4 | 46.8 | 43.5 | 65.3 | 79.6 | 92.4 | 98.8 |
| 1.5 | | | | 2.7 | 10.6 | 11.3 | 20.2 | 25.8 | 24.5 | 23.0 | 34.1 | 52.2 | 48.0 | 83.0 |
| 1.7 | | | | 1.3 | 3.9 | 4.4 | 20.2 | 12.0 | 12.8 | 10.9 | 31.2 | 31.0 | 48.6 | 64.6 |
| 1.9 | | | | 0.6 | 4.8 | 1.5 | 10.9 | 5.5 | 13.8 | 4.6 | 23.4 | 16.7 | 32.4 | 47.2 |
| 2.1 | | | | | 1.0 | 0.5 | 11.9 | 2.2 | 9.6 | 1.7 | 14.6 | 8.2 | 32.7 | 32.2 |
| 2.3 | | | | | | | 4.7 | 0.75 | 6.4 | 0.6 | 9.7 | 3.6 | 20.6 | 20.6 |
| 2.5 | | | | | | | 5.7 | 0.24 | 2.1 | 0.2 | 2.9 | 1.5 | 18.4 | 12.4 |
| 2.7 | | | | | | | 4.1 | | 3.2 | | 3.9 | 0.5 | 13.0 | 7.0 |
| 2.9 | | | | | | | 1.0 | | 0 | | 0 | 0.2 | 13.0 | 4.4 |
| 3.1 | | | | | | | 1.6 | | 1.1 | | 2.9 | | 12.4 | 2.0 |
| 3.3 | | | | | | | 1.6 | | 0 | | 1.0 | | 8.0 | 0.8 |
| 3.5 | | | | | | | 0 | | 1.1 | | 1.9 | | 7.3 | 0.4 |
| 3.7 | | | | | | | 1.0 | | | | 0 | | 3.2 | 0.2 |
| 3.9 | | | | | | | | | | | 0 | | 3.2 | |
| 4.1 | | | | | | | | | | | 0 | | 1.6 | |
| 4.3 | | | | | | | | | | | 1.0 | | 2.2 | |
| 4.5 | | | | | | | | | | | 1.0 | | 1.6 | |
| 4.7 | | | | | | | | | | | | | 0.3 | |
| 4.9 | | | | | | | | | | | | | 1.6 | |

TABLE III

Frequency × Area Distribution of WC Series

| Class size in $\mu^2$ | W6C | | W7C | | W8C | | W9C | | W10C | | W11C | | W12C | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | nxy $\times 10^{-5}$ in $\mu^2$ | Nxy $\times 10^{-6}$ in $\mu^2$ | nxy $\times 10^{-5}$ in $\mu^2$ | Nxy $\times 10^{-6}$ in $\mu^2$ | nxy $\times 10^{-5}$ in $\mu^2$ | Nxy $\times 10^{-6}$ in $\mu^2$ | nxy $\times 10^{-5}$ in $\mu^2$ | Nxy $\times 10^{-6}$ in $\mu^2$ | nxy $\times 10^{-5}$ in $\mu^2$ | Nxy $\times 10^{-6}$ in $\mu^2$ | nxy $\times 10^{-5}$ in $\mu^2$ | Nxy $\times 10^{-6}$ in $\mu^2$ | nxy $\times 10^{-5}$ in $\mu^2$ | Nxy $\times 10^{-6}$ in $\mu^2$ |
| 0.11 | 53.5 | 764.0 | 33.9 | 193.7 | 17.2 | 49.2 | 4.5 | 25.7 | 5.4 | 15.5 | 3.9 | 11.2 | 1.7 | 5.0 |
| 0.3 | 42.8 | 612.0 | 44.4 | 253.7 | 42.6 | 121.8 | 12.8 | 73.3 | 15.6 | 44.7 | 12.5 | 35.7 | 5.8 | 16.6 |
| 0.5 | 20.9 | 229.0 | 35.5 | 202.7 | 57.0 | 163.1 | 20.1 | 115.1 | 24.5 | 70.2 | 22.1 | 63.1 | 11.1 | 31.7 |
| 0.7 | 8.6 | 123.0 | 23.8 | 136.2 | 56.7 | 162.2 | 23.7 | 136.2 | 28.8 | 82.5 | 29.8 | 85.0 | 16.6 | 47.8 |
| 0.9 | 3.2 | 46.3 | 14.7 | 83.8 | 45.9 | 131.3 | 23.1 | 132.6 | 27.7 | 79.3 | 33.5 | 95.8 | 21.6 | 61.7 |
| 1.1 | 1.2 | 16.9 | 8.6 | 49.3 | 31.2 | 89.3 | 19.2 | 111.0 | 22.6 | 64.6 | 32.5 | 92.9 | 24.9 | 71.4 |
| 1.3 | 0.4 | 5.7 | 4.8 | 27.7 | 18.2 | 52.0 | 13.7 | 78.9 | 15.8 | 45.3 | 27.7 | 79.2 | 25.6 | 73.4 |
| 1.5 | | | 2.7 | 18.6 | 9.2 | 26.3 | 8.6 | 49.5 | 9.7 | 27.7 | 20.9 | 59.9 | 24.8 | 71.3 |
| 1.7 | | | 1.5 | 9.2 | 4.1 | 11.6 | 3.8 | 26.2 | 5.2 | 14.9 | 14.1 | 40.3 | 21.9 | 62.7 |
| 1.9 | | | 0.7 | 4.4 | 1.5 | 4.4 | 2.3 | 13.4 | 2.5 | 7.0 | 8.5 | 24.3 | 17.9 | 51.4 |
| 2.1 | | | | | 0.5 | 1.5 | 1.0 | 5.9 | 1.0 | 2.9 | 4.6 | 13.2 | 13.5 | 38.6 |
| 2.3 | | | | | | | 0.4 | 2.2 | 0.4 | 1.1 | 2.2 | 6.33 | 9.5 | 27.1 |
| 2.5 | | | | | | | 0.1 | 0.8 | 0.1 | 0.5 | 1.0 | 2.9 | 6.2 | 17.7 |
| 2.7 | | | | | | | | | | 0.1 | 0.4 | 1.1 | 3.8 | 10.8 |
| 2.9 | | | | | | | | | | | 0.1 | 0.5 | 2.5 | 7.3 |
| 3.1 | | | | | | | | | | | | 0.2 | 1.2 | 3.5 |
| 3.3 | | | | | | | | | | | | 0.1 | 0.5 | 1.5 |
| 3.5 | | | | | | | | | | | | | 0.3 | 0.8 |
| 3.7 | | | | | | | | | | | | | 0.2 | 0.4 |
| 3.9 | | | | | | | | | | | | | | 0.2 |
| 4.1 | | | | | | | | | | | | | | 0.1 |
| Sum | 130.6 | 1866.9 | 170.6 | 979.3 | 284.1 | 812.7 | 133.4 | 765.4 | 159.3 | 456.3 | 213.8 | 584.6 | 209.6 | 598.9 |

the values of the total areas in each class-size, per $cm^2$ of original plate surface, and also similar values for the one-grain-layer plates, from which the former values were derived.

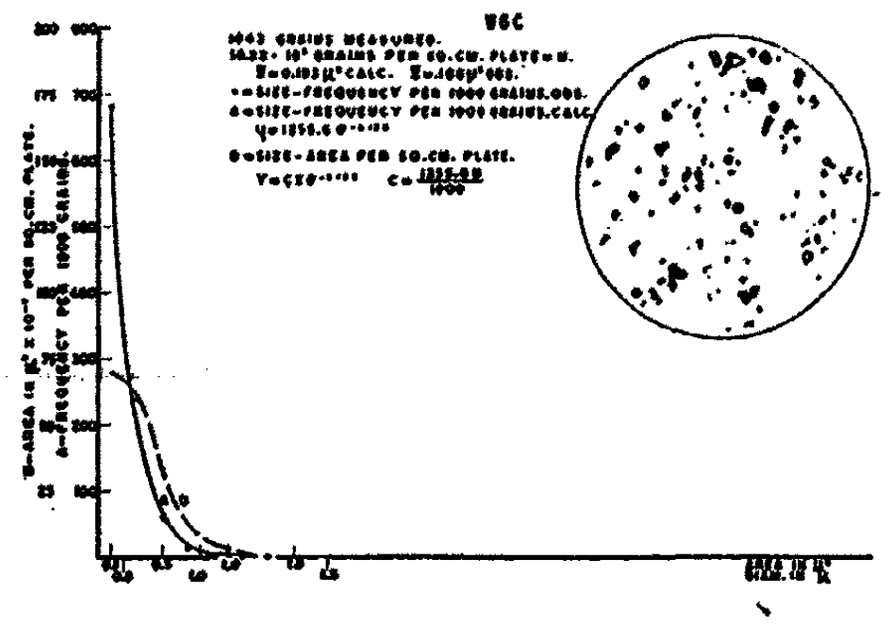


Fig. 2

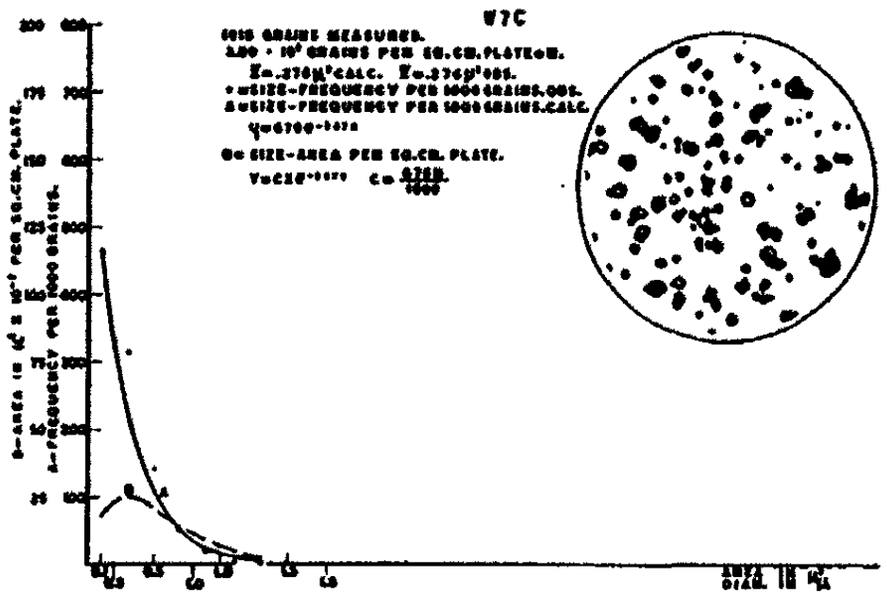


Fig. 3

The curves for each emulsion are shown graphically in Figs. 2 to 8 inclusive, and a photomicrograph of each, made at X2500, is also appended; it is reduced by about one half in the reproduction. It is to be noted that in passing through

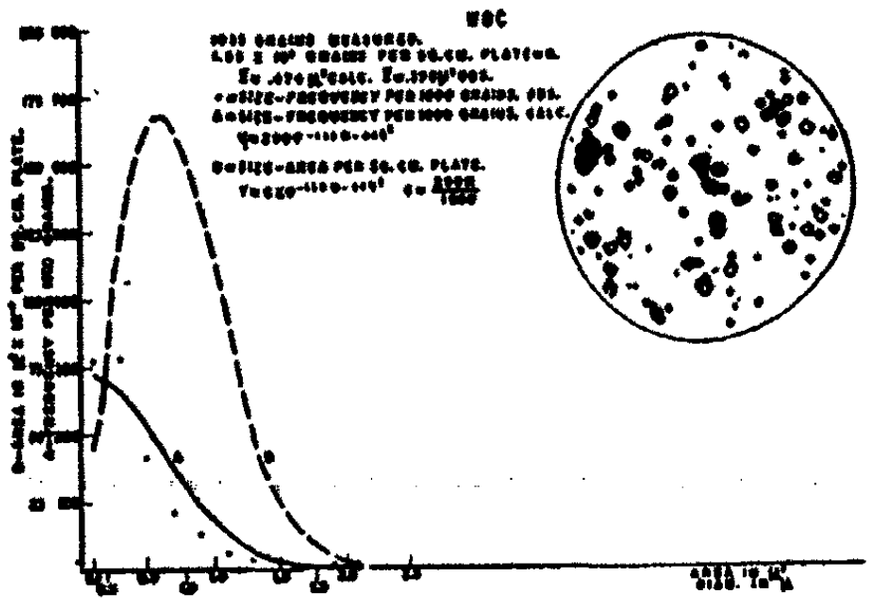


Fig. 4

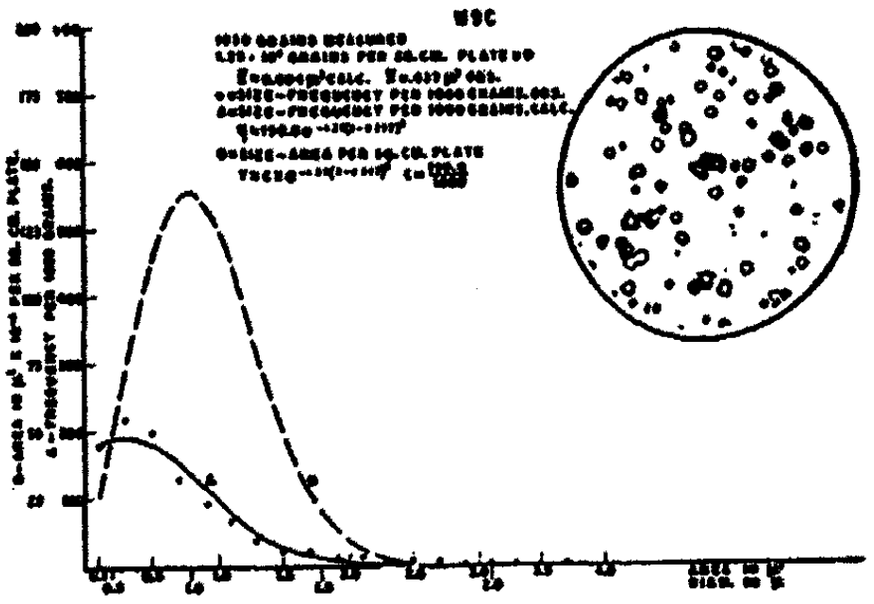


Fig. 5

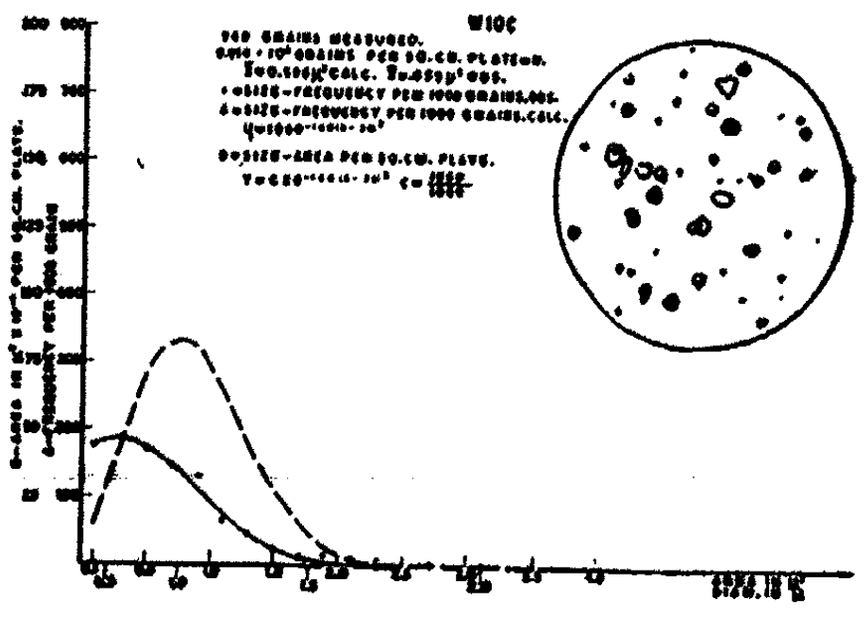


Fig. 6

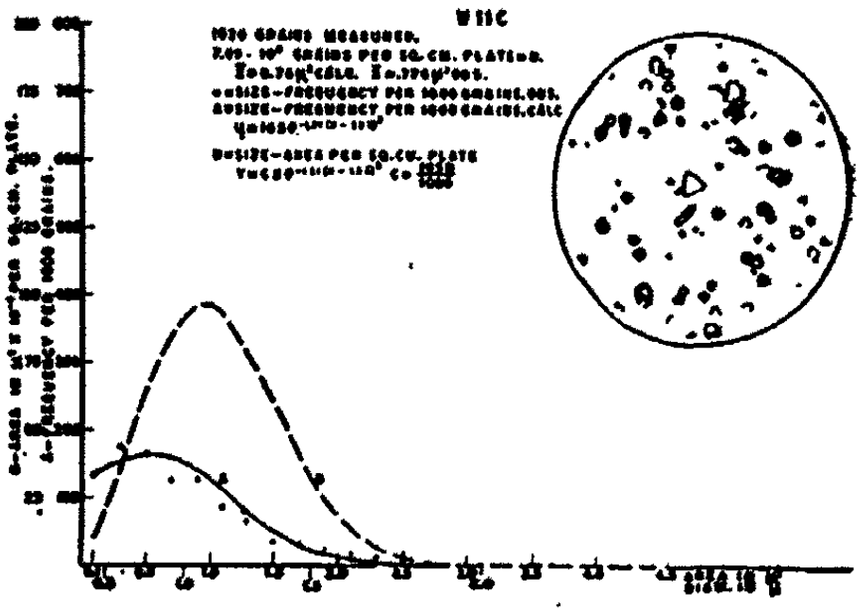


Fig. 7

the series from W6C to W12C, the curves start with the exponential type

$$y = y_0 e^{-kx} \tag{1}$$

and pass by gradations into a modified Gaussian form of error

$$y = y_0 e^{-k(x-\alpha)^2} \tag{2}$$

function and that the latter curves become broader and broader and flatter and flatter.

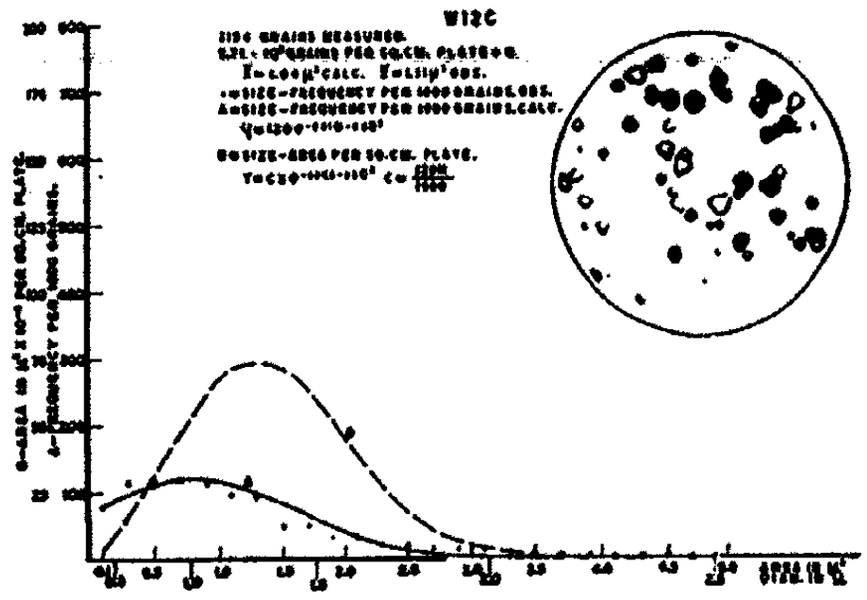



Fig. 8

This relation can also be seen by examining the parameters of these curves given in Table IV — $y_0$ and $k$ decrease and $\alpha$ increases with the emulsion number throughout the series, which is the same as saying, with the increase of speed, since the latter (as seen above in Fig. 1) is a linear function of the former and has a positive slope.

In equation (1), $y_0$ represents the ordinate formed by the intersection of the curve with the y-axis, and $k$ the degree of spread of the curve. In (2), $y_0$ indicates the maximum ordinate, $\alpha$ the position of this ordinate on the x-axis, and $k$ has the same significance as in (1).

Other important grain-characteristics of the emulsions are given in Table IV. The number of grains per cm$^2$ are ob-

TABLE IV

Grain Characteristics of WC Series

| No. | N $\times 10^{-8}$ grains on original | n $\times 10^{-7}$ grains on 1-layer | Gms. AgBr/cm² original plate | % Conc. AgBr per cm² original plate | Average size grain | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $\overline{W}$ in g. $\times 10^{12}$ | $\overline{V}$ in $\mu^3$ $\times 10$ | $\overline{x}$ (obs.) in $\mu^2$ | $\overline{x}$ (calc.) in $\mu^2$ | $\overline{D}$ (obs.) in $\mu$ | $\overline{\tau}$ in $\mu$ plates | $\overline{\tau}'$ in $\mu$ spheres | $\overline{\tau}/\overline{D}$ approx. |
| 6 | 102.2 | 7.15 | 0.001798 | 31.34 | 0.174 | 0.272 | 0.186 | 0.183 | 0.487 | 0.145 | 0.373 | 1:3.5 |
| 7 | 38.0 | 6.65 | 0.001798 | 31.34 | 0.473 | 0.731 | 0.276 | 0.276 | 0.593 | 0.265 | 0.519 | 1:2.2 |
| 8 | 15.5 | 5.42 | 0.001798 | 31.34 | 1.160 | 1.793 | 0.398 | 0.474 | 0.712 | 0.451 | 0.699 | 1:1.6 |
| 9 | 12.8 | 2.23 | 0.001798 | 31.34 | 1.405 | 2.171 | 0.637 | 0.604 | 0.900 | 0.340 | 0.746 | 1:2.6 |
| 10 | 8.01 | 2.80 | 0.001798 | 31.34 | 2.244 | 3.476 | 0.655 | 0.596 | 0.908 | 0.529 | 0.872 | 1:1.7 |
| 11 | 7.65 | 2.67 | 0.001798 | 31.34 | 2.350 | 3.632 | 0.776 | 0.760 | 1.011 | 0.468 | 0.885 | 1:2.2 |
| 12 | 5.71 | 2.00 | 0.001798 | 31.34 | 3.150 | 4.866 | 1.110 | 1.040 | 1.190 | 0.440 | 0.976 | 1:2.7 |

TABLE IV (*Continued.*)

| No. | No. grains meas. | Max. grain size obs. in $\mu^2$ | Total area grains per cm² orig. plate in $\mu^2 \times 10^{-8}$ | | Total area grains per cm² 1-layer plate in $\mu^2 \times 10^{-8}$ | | $\gamma_0$ | $k$ | $\alpha$ | r. p. = Resolving power | $\Delta$ = Turbidity |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | From mean | From Tab. III | From mean | From Tab. III | | | | | |
| 6 | 1042 | 1.3 | 19.01 | 18.67 | 0.131 | 0.131 | 1255.6 | 6.13 | —— | 59 | 8.1 |
| 7 | 1018 | 1.3 | 10.49 | 9.79 | 0.184 | 0.171 | 670.0 | 3.67 | —— | 47 | 8.5 |
| 8 | 1035 | 2.1 | 7.35 | 8.13 | 0.257 | 0.284 | 290.0 | 1.53 | 0.041 | 37 | 9.9 |
| 9 | 1930 | 3.9 | 7.73 | 7.65 | 0.135 | 0.133 | 190.8 | 1.37 | 0.293 | 38 | 9.9 |
| 10 | 940 | 3.5 | 4.77 | 4.56 | 0.167 | 0.159 | 186.0 | 1.44 | 0.300 | 37 | 11.4 |
| 11 | 1026 | 4.5 | 5.81 | 5.84 | 0.203 | 0.214 | 165.0 | 1.21 | 0.523 | 40 | 12.4 |
| 12 | 3154 | 4.9 | 5.94 | 5.99 | 0.208 | 0.210 | 120.0 | 0.81 | 0.820 | 37 | 11.3 |

tained by averaging the counts on a large number of photomicrograms from the one-grain-layer plates, taking into account the area of the photomicrograms, the area of the original plate and that of the one-layer plate, and the dilution factor.[1]

Under the heading "Average Size Grain," $\bar{w}$ signifies the weight of the average grain obtained by dividing the weight of silver halide per unit area of plate by the number of grains in that area.

From the average weight is then obtained the average volume of the grain, $\bar{v}$ in $\mu^3$, by dividing it by the density of AgBr, 6.473, and applying the factor for converting $cm^3$ to $\mu^3$.

We obtained the average projective area, $\bar{x}$, from the frequency data by multiplying frequency per 1000 in each class by the average class size and dividing the sum of these by 1000. For comparison and for use in other calculations we consider the projective area as that of a circle equivalent to the actual projective area of the grain when planimetered. The average projective areas were obtained from both the observed and the calculated data.

$\overline{D}$ represents the average projective diameter of a grain, calculated from $\bar{x}$. If we assume that the grains are spherical we may calculate from $\bar{v}$ the diameter of the sphere, $\tau'$. On the other hand if we assume the grains to be plates instead of spheres, then dividing $\bar{v}$ by $\bar{x}$ gives the thickness, $\bar{\tau}$, of the grains. If the grains were all spheres then $\overline{D}$ would equal $\bar{\tau}'$. But we know from microscopical and other evidence that there are many plates as well as spherical grains, however, the largest ratio of width to thickness that we can get for the average grain is given in the column headed $\bar{\tau}/\overline{D}$.

Besides the average grain size, it is important to know the total projective areas of all the grains per unit area of the plate. In the case of the original plate the grains of course are many layers deep and there must be considerable overlapping of the grains in one layer by those in the layer above

[1] For details of the whole process see Wightman, Trivelli and Sheppard: Jour. Phys. Chem., 27, 141 (1923).

it. To find just what this is for any given number of layers and the distribution of the overlap for the various sizes of grains is a very intricate problem not yet solved. It is all the more so when one considers that some of the overlapping grains lie in such intimate contact with those below that they form a clump which acts as a single unit towards the development action, and perhaps the light action also.

We give in Table IV the total area of the grains on the original plate, without attempting to analyse the data further. Similar figures are given for the one-grain-layer plate. There are two approximate methods of arriving at these data, either to multiply the number of grains per unit area of the plate by the average projective area, or by summing up the products of the frequencies by the average class size. The agreement in the two cases is seen to be fairly good.

The number of grains measured in obtaining the frequency data, the resolving power and turbidities[1] of the original emulsions, and the maximum grain size observed for each emulsion are likewise given in the table.

The data in this table are plotted in Figs. 9 and 10, all against the emulsion number (which, as stated above, may be replaced by the number representing the speed, $\gamma_\infty$, or latitude).

It is seen from these graphs that the number of grains per $cm^2$ of the original plate, and the parameters $y_0$ and $k$ decrease regularly with increase of speed of the emulsion, and this decrease has almost the exponential form. The total area of grains on the original, however, decreases to a minimum and then slightly increases; and the resolving power of the original plates decreases for the first three emulsions and then remains constant for the others. All the other values plotted show a general increase with speed as might be expected except the

[1] F. E. Ross: Astrophys. Jour., **52**, 201 (1920). These values were obtained for us by Dr. Ross whom we wish to thank. For the resolving power the 20 mm fan test object was employed, using violet light and aesculin filter. Development was in MQ Process for 3 minutes at 75. For turbidity white light at violet focus was used, development also in MQ Process but for 3.5 minutes at 70°.

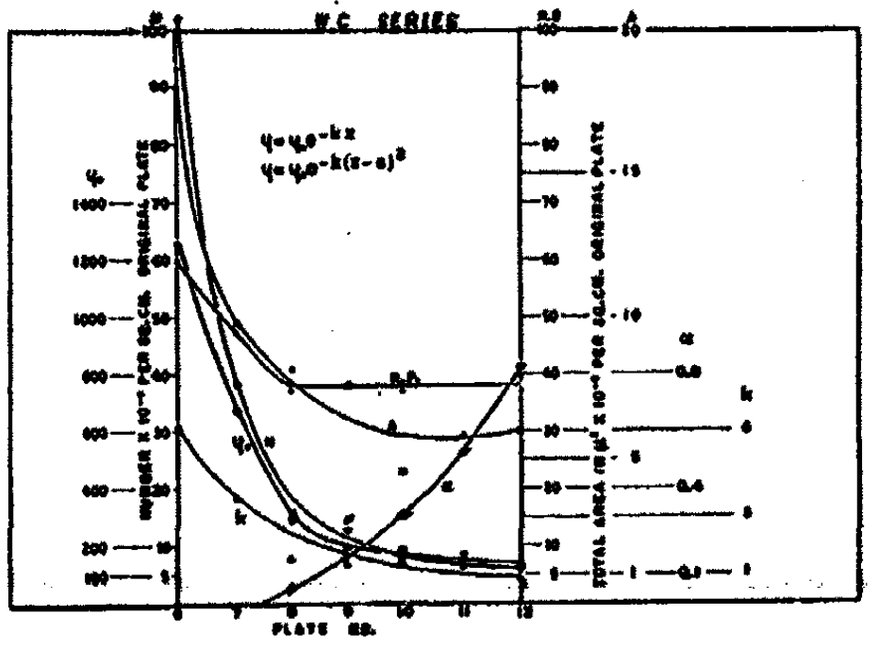



Fig. 9

$y_0$ = □ = parameter
N = ○ = No. grains/cm² orig. plate
R.P. = ▲ = resolving power
A = × = total proj. area grains/cm² orig. plate
$\alpha$ = $\phi$ = parameter
k = △ = parameter

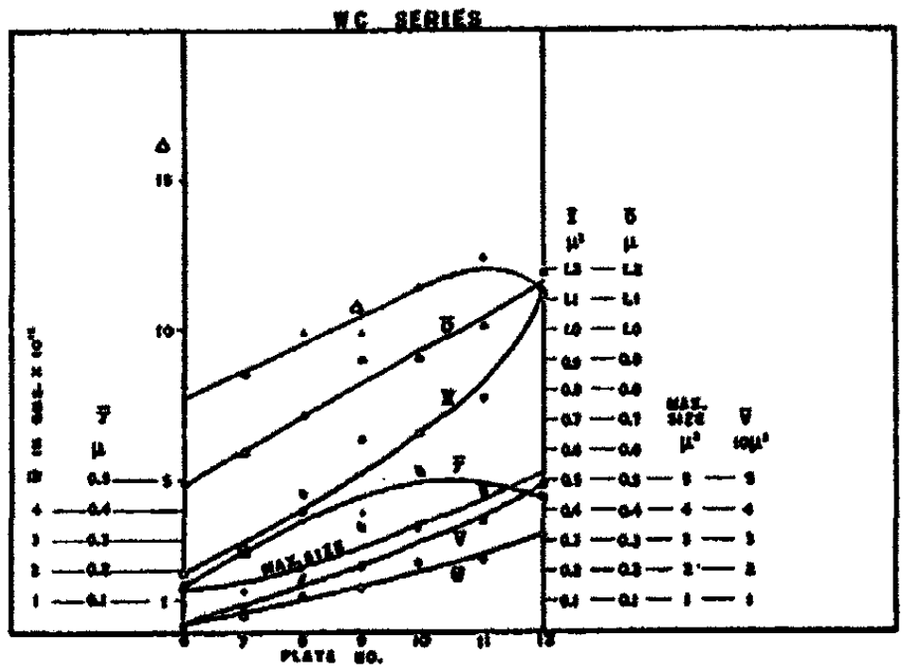



Fig. 10

$\overline{W}$ = ○ = average wt. grains
$\overline{T}$ = $\phi$ = average thickness grains
△ = ▲ = turbidity
$\overline{X}$ = □ = average area grain
$\overline{D}$ = △ = average diam. grains
Max. size = ⊙ = max. size grain obs.
$\overline{V}$ = × = average volume grain

average thickness of the grains which passes through a maximum.

The results so far obtained are for only one series of emulsions and of course should not be accepted as final. To make them of greater value it has been our intention to measure the various characteristics of several similar series in parallel and to take the average of them all.

The present work also covers only the empirical relation of the grain to the sensitometric characteristics of the original emulsions. In another paper we hope to present the results of some work on single-layer plates prepared from such a series.

It should be noted here likewise that work is in progress on a new series of emulsions which differ from the present series in that the frequency distribution of the slowest emulsions as well as the fastest can be represented entirely by exponential curves, the parameters $y_0$ and $k$, however, having a similar relation to each other as in the series above described.

## Summary

1. A series of photographic emulsions has been prepared of which a correlation between the grain and sensitometric characteristics shows an apparently close relationship between the two.

2. These emulsions are strictly comparable because practically all the factors in their preparation were under control, only one being varied so as to progressively increase the speed of the emulsions in the series, and because equal weights of the emulsion containing in every case the same amount of silver halide by weight were coated on the plates.

3. The equations which represent the grain-size-distribution of these emulsions show a steady transition from a steep exponential

$$y = y_0 e^{-kx}$$

to a flat, widely spread Gaussian type

$$y = y_0 e^{-k(x-a)^2}.$$

That is to say, in passing through the series from the slow to the comparatively fast emulsion the parameters $y_0$ and $k$ steadily decrease, while the parameter $\alpha$, which is zero in the first two examples, then steadily increases.

4. Other grain characteristics were determined and they likewise showed the same progressive increase or decrease with the speed.

*Rochester, N. Y.*
*January 10, 1923*

# THE PHYSICO-CHEMICAL PROPERTIES OF STRONG AND WEAK FLOURS. III. VISCOSITY AS A MEASURE OF HYDRATION CAPACITY AND THE RELATION OF THE HYDROGEN ION CONCENTRATION TO IMBIBITION IN THE DIFFERENT ACIDS*

BY ROSS AIKEN GORTNER AND PAUL FRANCIS SHARP**

In the earlier papers of this series[1,2] evidence was presented that strength of gluten is correlated with the colloidal condition of the wheat flour proteins.

Mohs[3] and later Ostwald[4] have discussed the problems of bread making from the colloidal viewpoint.

Lüers and Ostwald[5] studied the viscosity of flour pastes using an Ostwald viscosimeter. The flour pastes were prepared by pouring a suspension of flour-in-water into boiling water thus gelatinizing the starch. They believe that there are two major problems in bread manufacture which should be studied from the standpoint of viscosity. The one has to do with dough formation and the other deals with dough

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Abstracted from a portion of a thesis presented by Paul F. Sharp to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June 1922.

** From the Division of Agricultural Biochemistry of the University of Minnesota.

[1] R. A. Gortner and E. H. Doherty: Hydration capacity of gluten from "strong" and "weak" flours. Jour. Agr. Research, 13, 389–418 (1918).

[2] P. F. Sharp and R. A. Gortner: Physico-chemical studies of strong and weak flours. II. The imbibitional properties of glutens from strong and weak flours. Jour. Phys. Chem., 26, 101–136 (1922).

[3] K. Mohs: Zeit. ges. Getreidew., 7, 239–242, 250–260 (1915).

[4] W. Ostwald: Kolloid-Zeit., 25, 26–45 (1919).

[5] Lüers and W. Ostwald: Kolloid-Zeit., 25, 82–90, 116–136 (1919).

baking. These authors believe that the properties making for a good dough and those making for good baking conditions are distinct.

In an investigation of the different grades of flour they found that the viscosity of flour pastes divided themselves into three classes: the patent flours showed a greater viscosity than did the straight flours, while the clear flours showed the least viscosity. This was found to be true for both wheat and rye flours. They concluded that the viscosity of flour pastes was directly proportional to the starch content and suggested that the viscosity of flour pastes be used as a method for the determination of the starch content of flours. The addition of various amounts of sulfuric acid was found to have little effect on the viscosity of flour pastes.

Suspensions of flour-in-water without heating were investigated, the flour concentrations ranging from 7 to 20 percent. It was found that rye flours of the same grade and concentrations gave relatively much more viscous solutions than did wheat flours, and the authors suggested this as a method of differentiating between the two. In the case of the wheat flour suspension, the lower the grade of the flour the more viscous was the solution. This is just the reverse of the behavior of the flour pastes prepared by heating the flour-in-water suspension so as to gelatinize the starch. Lactic acid was found to markedly increase the viscosity of (unheated) wheat flour suspensions, the effect being more pronounced the higher the grade of the flour. Lactic acid seemed to have no effect in increasing the viscosity of rye flour suspensions.

Lüers[6] studied the effect of acids, bases and salts on solutions of gliadin prepared from wheat and rye flours. With acids the maximum viscosity was attained at 0.0004 to 0.00066 normal hydrochloric acid, with 0.0022 normal sulfuric acid, and with 0.018 to 0.0011 normal lactic acid. With alkali the maximum viscosity was reached at 0.0022 normal sodium hydroxide, and at 0.013 to 0.014 normal barium hydroxide.

[6] H. Lüers: Kolloid-Zeit., 25, 177–196, 230–240 (1919).

Hydrochloric acid was found to increase the viscosity of gliadin dissolved in alcohol. In all of the experiments reported, no essential difference was noted between the gliadin from wheat and rye and the author concluded that they are identical. This confirms the earlier conclusions of Gröh and Friedl.[7]

Lüers and Ostwald[8] studied the viscosity of suspensions of two poor rye flours and found that both gave low viscosity values one having only about one fourth the viscosity of normal rye flour of the same grade. They emphasized that the best flour would probably show an optimum viscosity, neither too high nor too low.

Lüers and Ostwald[9] discuss the work of Upson and Calvin[10,11] on the colloidal swelling of wheat gluten and state that their own conclusions are in essential agreement. While both emphasize that it is the quality and not the quantity of gluten which is important, nevertheless they seem to believe that the quality of the gluten is regulated by the acids and salts present in the flour or added to it in the bread making process. They make no reference to the work by Gortner and Doherty[12] who have shown that the conclusions of Upson and Calvin were based upon insufficient evidence. Lüers and Schneider[13] concluded that the three methods of measuring imbibition as effected by acids, namely the increase in weight of discs, the viscosity method, and the sedimentation method, all lead to the same relative results.

Sharp and Gortner[14] found that drying the washed gluten in a vacuum oven at 45° to 50° C markedly altered the physico-chemical properties of the glutens, the properties of the

[7] J. Gröh and G. Friedl: Biochem. Zeit., **66**, 154–164 (1914).

[8] H. Lüers and W. Ostwald: Kolloid-Zeit., **26**, 66–67 (1920).

[9] H. Lüers and W. Ostwald: Kolloid-Zeit., **27**, 34–37 (1920).

[10] F. W. Upson and J. W. Calvin: Jour. Am. Chem. Soc., **37**, 1295–1304 (1915).

[11] F. W. Upson and J. W. Calvin: The colloidal swelling of wheat gluten in relation to milling and baking. Nebr. Agric. Exp. Sta. Res. Bull., No. **8**, 27 pp. (1916).

[12] Gortner and Doherty: Loc. cit.

[13] H. Lüers and M. Schneider: Kolloid-Zeit., **28**, 1–4 (1921).

[14] P. F. Sharp and R. A. Gortner: Loc. cit.

different glutens becoming more nearly alike. In the same paper data were presented indicating that the optimum hydrogen ion concentration for the imbibition of discs of gluten was the same for the various acids. We concluded that our findings were in complete accord with the earlier postulate of Gortner and Doherty,[12] i. e., "The difference between a strong and weak gluten is apparently that between a nearly perfect colloidal gel with highly pronounced physico-chemical properties, such as pertain to emulsoids, and that of a colloidal gel in which these properties are much less marked."

In continuing the investigation of the colloidal properties of wheat flours, the viscosity of flour-in-water suspensions was studied to determine its suitability as a method for the determination of the imbibitional powers of the flour proteins as affected by acids.

The viscosity method of measuring imbibition offers distinct advantages over the increase-in-weight-of-discs method. The viscosity method is more rapid, results are reproducible within a smaller experimental error, less material is required, and the inconvenience of washing out the gluten is avoided.

Lüers and Ostwald appear to conclude that the greatest baking strength of flour is associated with a medium viscosity of simple flour-water suspensions. Our finding is that the strength of the flour is not so much related to the original viscosity of the simple flour-water suspension as it is to the change in viscosity effected by treating such a suspension, with an acid or alkali, that is, to the imbibitional power of the protein as influenced by acids or alkalis. If it were true that the greatest baking strength is associated with a high viscosity of a simple flour-water suspension then we should expect rye flours to have markedly greater baking strength than wheat flours, for according to the data of Lüers and Ostwald, rye flours yield suspensions which are much more viscous than are wheat flour suspensions of the same concentration. On the other hand if the flours which yield simple flour-water suspensions of medium viscosity are the strongest (this is the belief of Lüers and Ostwald) then we should expect the weak

rye flours cited by Lüers and Ostwald, to have the greatest baking strength inasmuch as they show viscosity values intermediate between those of their strong rye flours and the wheat flours. If, on the other hand, the baking strength of a flour is associated more or less with the increase in viscosity produced by acids, then we would expect rye flour to be an extremely weak flour as compared with wheat flour, for, according to the work of Lüers and Ostwald, the imbibitional powers of rye flour are not increased by treatment with acid while the imbibitional powers of the wheat flours increased markedly. The weakness of the rye flours cited by Lüers and Ostwald may be due to a low protein content, this supposition cannot be verified from their published work for no protein determinations were given.

We have pointed out in the preceding paper[14] that weakness of flour may be divided into three classes, (1) weakness due to an adequate quantity of gluten but of inferior quality, (2) weakness due to an inadequate quantity of gluten of good quality, and (3) weakness due to factors influencing yeast activity, diastatic and proteolytic enzymes, hydrogen ion concentration, etc. It is believed that the first two types of weakness are the ones most frequently met with although the data by Rumsey[15] indicates that the soft wheats may also be low in diastase. The work of Pauli and Handovsky[16], Handovsky[17] Fischer[18] and others indicates that the various acids influence the imbibition of proteins to markedly different degrees. Loeb[19] advanced the claim, supported by his experiments with gelatin, casein and albumin, that maximum imbibition occurs with all acids at the same hydrogen ion concentration and that the same high point is reached regardless of the acid used. Sulfuric acid, because of its ability to function as a dibasic acid

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[15] L. A. Rumsey: The diastatic enzymes of wheat flour and their relation to flour strength. Amer. Inst. Baking, Bull. 8, 86 pp. (1922).

[16] W. Pauli and H. Handovsky: Biochem. Zeit., 18, 340–371 (1909).

[17] H. Handovsky: Kolloid-Zeit., 7, 183–193, 267–277 (1910).

[18] M. H. Fischer: Oedema and Nephritis; 2nd Ed. (1915).

[19] J. Loeb: Proteins and the theory of colloidal behavior, 292 pp. 80 figs. (1922).

at the hydrogen ion concentration of maximum imbibition, produced only about half the effect of a monobasic acid.

Gortner and Doherty, and Sharp and Gortner found that different acids did not produce the same maximum imbibition of gluten discs but the later authors did conclude that the maximum imbibition of discs produced by various acids occurred at practically the same hydrogen ion concentration. The investigation here reported was undertaken to further investigate this point, and to ascertain which acid would be the best suited for the measurement of the imbibitional capacity of flours by the viscosity method.

## Experimental

In this work no attempt has been made to distinguish between viscosity and plasticity, nor to determine the plasticity constants for those mixtures which were undoubtedly plastic. The term viscosity has been used in a rather loose sense throughout, to indicate all resistance offered by the suspensions to the shearing force applied.

In this investigation we worked with the same flours used in the previous study.[20] Flour B-780 was taken as an example of a strong flour and flour B-783 as an example of a weak flour.

Flour analyses and baking tests of these flours were reported in Tables I and II of the preceding paper[20] and will not be repeated here. We need only mention that the crude protein (N. × 5.7) in these flours is almost identical (B-780 = 12.13%: B-783 = 12.15%); ash values are fairly low (B-780 = 0.44%: B-783 = 0.53%).

The value of such an extended investigation on the same flours might be questioned due to the fact that flours are known to change in baking strength with age. It is believed, however, that the effect of age did not exert an appreciable influence on the results of this investigation. The flours were stored at ordinary room temperature for about six months

[20] P. F. Sharp and R. A. Gortner: Loc. cit.

before the investigation was started, from then on they were stored in air tight containers in a cold storage plant at a temperature of about 3° C. The imbibitional power of the gluten was determined by the increase in weight of discs both at the beginning and at the end of the investigation and no difference in the imbibitional power of the gluten could be detected by this method after the flours had been kept in storage for two years.

Preliminary determinations were first carried out with 20 percent flour-in-water suspensions using an Ostwald viscosimeter according to the method advocated by Lüers and Ostwald. Several difficulties were encountered and the method was finally abandoned. Successive readings with the same flour-in-water suspension gradually decreased. Difficulty was encountered in preparing duplicate suspensions which would have the same viscosity values. The time of outflow through the capillary tubes became for some flours excessively long. After accumulating considerable data by this method it was finally abandoned for a viscosimeter of the torsion wire type.

The data from which we have drawn our conclusions were all obtained with a MacMichael[21] viscosimeter of the original type. A very definite experimental procedure was adopted and rigorously adhered to; by so doing duplicate results could be obtained which agreed within a small experimental error.

The moisture in the flour was determined, and enough flour taken to make 25 grams on the dry basis, to this amount of flour sufficient water was added to make a total of 100 grams of water counting that already in the flour. The mixture was allowed to stand for one hour with occasional shaking. All determinations were carried out in a room electrically controlled where the temperature was maintained at approximately 25° C. The viscosity of 100 cc of the mixture was first determined and then normal solutions of the various acids were added in gradually increasing amounts up to 10.0 cc of the normal acid. Quadruplicate readings were taken after each

[21] R. F. MacMichael: Jour. Ind. Eng. Chem., 7, 961–963 (1915).

addition. The effect on the viscosity of diluting mixtures of various viscosities was determined and from the results so obtained the viscosities were corrected for dilution by the assumption of a linear interpolation. The effect on the viscosity of the addition of the following total amounts of a normal acid

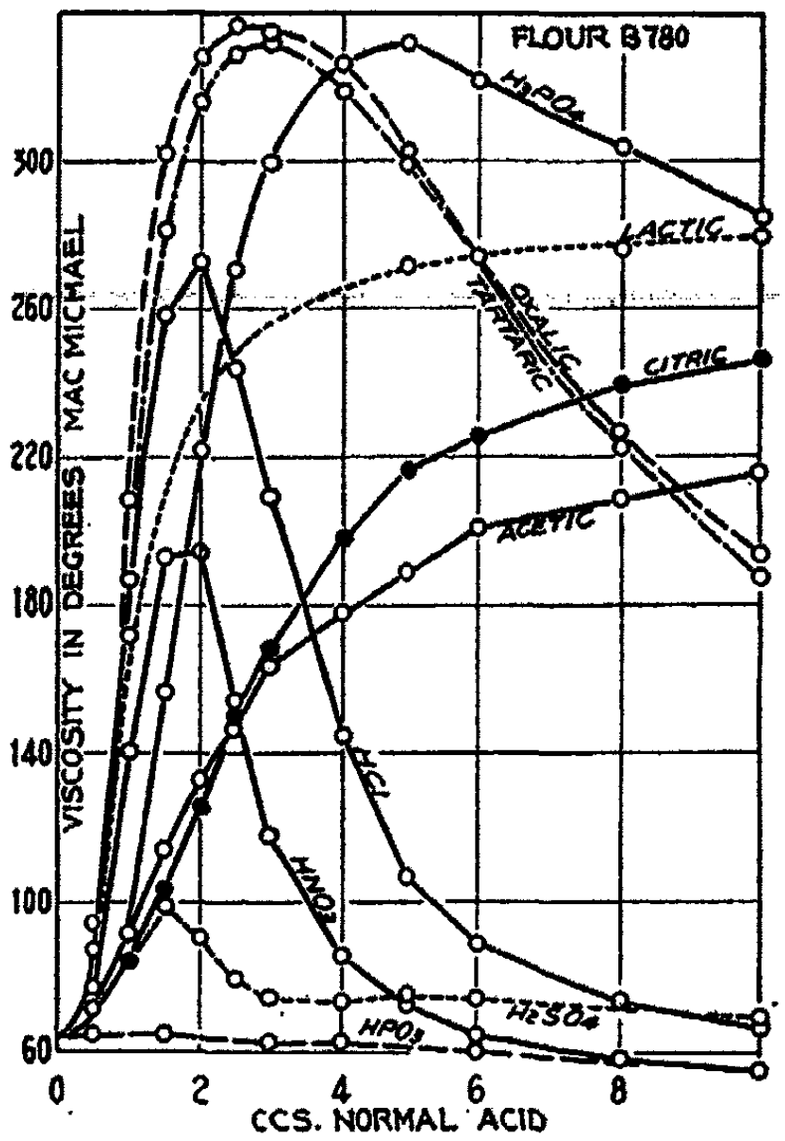



Fig. 1

Viscosity of 100 cc of 20% flour-in-water suspensions of strong flour B-780 as affected by different amounts of various acids.

solution was determined: 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, 1.00, 1.20, 1.50, 2.00, 2.50, 3.00, 4.00, 5.00, 6.00, 8.00, and 10.00 cc. The readings are all expressed in degrees MacMichael (M°) and are comparable only among themselves. Any resetting of the wire in the viscosimeter

was found to displace the readings for the flour mixtures one way or the other, although the viscosimeter showed exactly the same reading with a standard sucrose solution. The values obtained are probably a combination of the effects which go to make up both viscosity and plasticity. For these reasons the attempt to express the results in the terms of absolute viscosity units would be of doubtful value. The speed of the motor was adjusted so that, with the wire used in this work, a sucrose solution, whose absolute viscosity was 5.73 centipose, gave a reading of 14.3 degrees MacMichael.

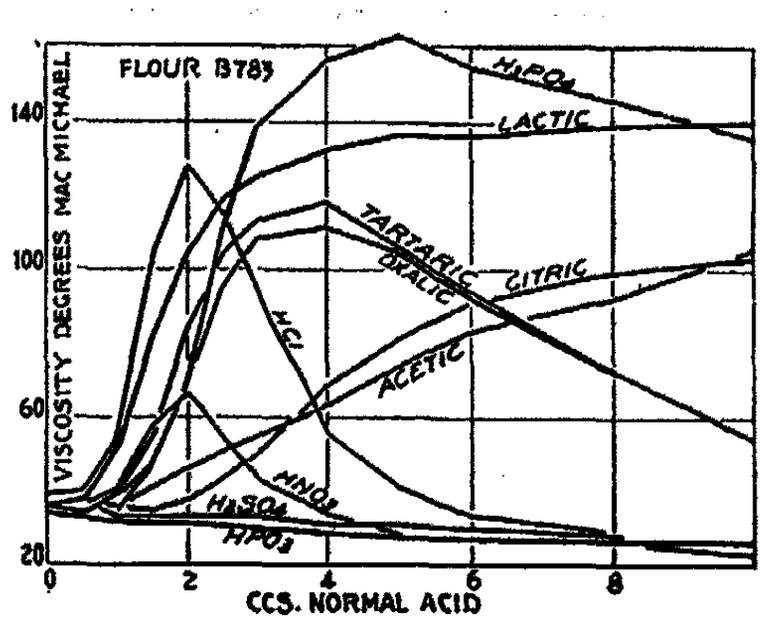



Fig. 2

Viscosity of 100 cc of 20% flour-in-water suspensions of weak flour B-783 as affected by different amounts of various acids.

The results obtained with flour B-780 are expressed graphically in Figure 1 and those with flour B-783 in Figure 2. It will be noted that the same maximum is not reached with the different acids and that if the acids are arranged in the order of their ability to produce maximum imbibition this order is not the same with the two flours. Meta-phosphoric acid produces no increased imbibition with either flour, while sulfuric acid produces increased imbibition with flour B-780 but not with flour B-783.

The hydrogen ion concentration was determined electrometrically on 20 cc aliquots of the flour-in-water suspension to which had been added the proportionate amount of acid to correspond with the various points on the imbibition curve. The imbibitional data plotted against the pH of the flour-in-water mixture are expressed graphically in Figures 3 and 4. The curves in these last two figures are all similar in shape and

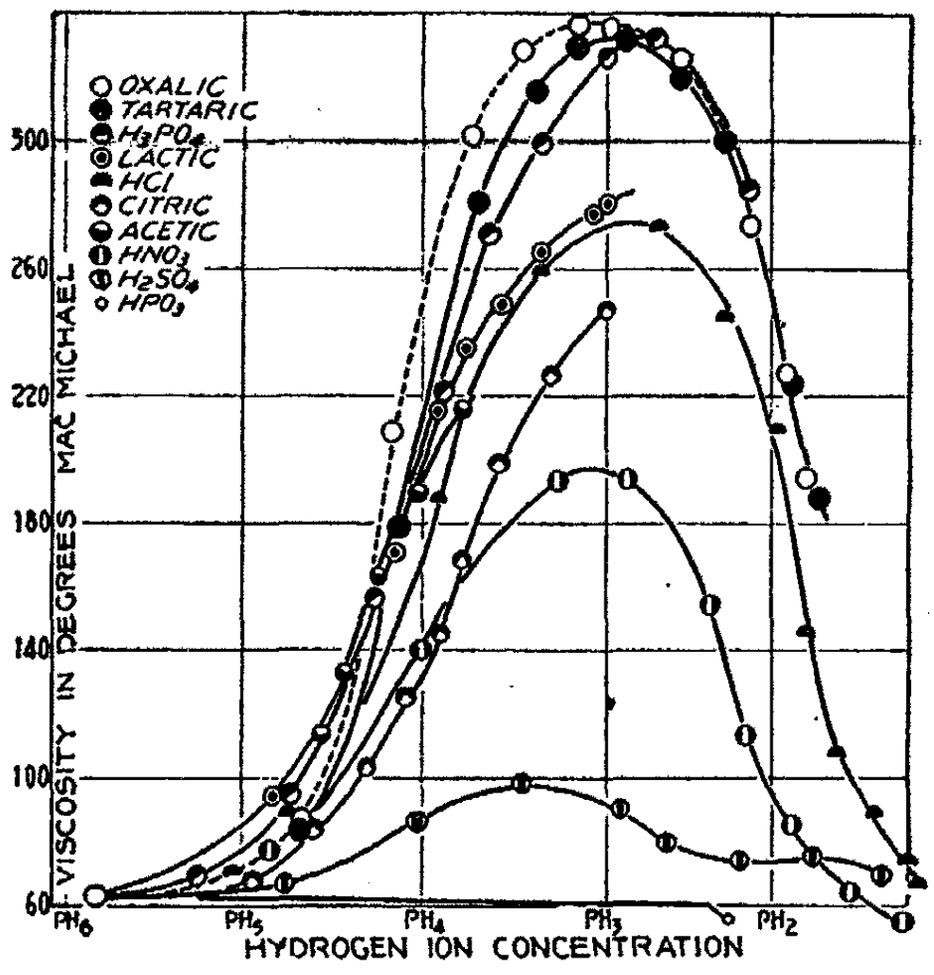



Fig. 3

Viscosity of 100 cc of a 20% flour-in-water suspension of strong flour B-780 at different hydrogen ion concentrations produced by various acids.

all tend to reach a maximum in the neighborhood of a pH of 3.0 which agrees with our earlier conclusion in regard to the swelling of gluten discs. The curves shown in Figures 3 and 4 do not all reach the same maximum viscosity. A flour-in-water suspension is a complex colloidal system and it is perhaps not surprising that a relationship which Loeb found to hold

for a highly purified and perhaps altered protein material does not hold in such a mixture.

From the shape of the curve it can be seen that lactic acid effects the least change in viscosity per unit of actual acid concentration and is therefore probably best suited for the

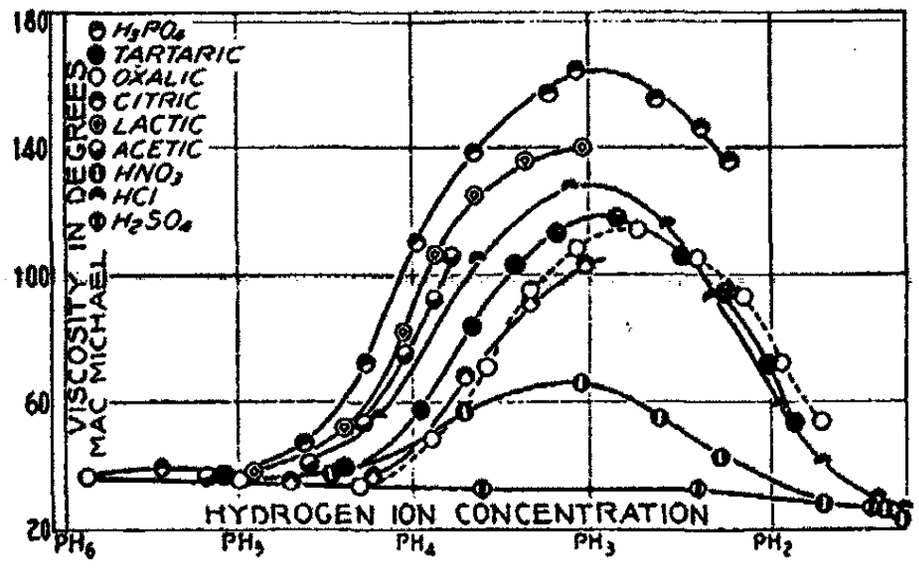



Fig. 4

Viscosity of 100 cc of a 20% flour-in-water suspension of weak flour B-783 at different hydrogen ion concentrations produced by various acids.

measurement of the imbibitional capacity by the viscosity method. This agrees with the results of Gortner and Doherty using the increase in weight of discs as a method of measuring the imbibitional capacity of the gluten.

## Summary

1. The viscosity method offers a rapid and easily duplicable method for the measurement of the relative imbibitional capacity of the gluten colloids of flours. It is far superior to the method of weighing gluten discs.

2. Our earlier observations that there are marked differences in the imbibitional capacity of the gluten colloids from strong and weak flours are confirmed.

3. The same maximum viscosity is not reached when mixtures of flour and water are treated with various amounts of different acids.

4. The order of the acids arranged according to their ability to produce maximum imbibition is different with the two flours. This indicates a different Hofmeister series for each flour.

5. The hydrogen ion concentration at which the various acids produce their maximum imbibition is approximately the same, and is roughly at a pH of 3.0 ($C_H \times 10^{-3}$).

# NEW BOOKS

**The Examination of Hydrocarbon Oils and of Saponifiable Fats and Waxes.** *By D. Holde. Translated by Edward Mueller. Second edition. 23 × 15 cm; pp. xix + 572. New York and London: John Wiley and Sons, Chapman and Hall, 1922. Price: $6.00.*—The second English edition is based on the fifth German edition. There are nine chapters: general methods of examination; petroleum and petroleum products; natural asphalt; ozocerite; hydrocarbons (tar) obtained by distillation of coal, shale, resins, and wood; vegetable and animal fats and oils; industrial products prepared from fats; waxes; physico-chemical tables.

The question of static electricity comes up on p. 122. "When woolen fabrics are agitated in ether or in naphtha an electrical excitation results. Richter has shown that in each case the exciting liquid (ether or naphtha) assumes a negative charge; the woolen material becomes charged positively. These charges may reach such a value that sparks may result if a workman approaches or touches the material with his hand, and if the proper air and combustible vapor mixture is present, a serious fire may be started. Conflagrations in chemical cleansing establishments have been due to such sparks. Richter proved that such fires might be prevented by dissolving in the naphtha a small amount (as little as one-twentieth of one percent) of magnesium oleate. However, the action of this material was not understood.

"Richter showed that fires might also result from sparks due to charges generated by the frictional flow of inflammable liquids (ether or naphtha) through narrow pipes either under their own pressure or that of a force pump. In this case also he suggested a practical solution of the difficulty. He found that sparks did not form if the liquids were run through non-conducting earthenware or glass funnels instead of metal funnels, or if a metal funnel seemed to be necessary all trouble was avoided by having a metal chain attached which could make good electrical connection with the earth. If metal funnels were used without earthing electrical charges might build up, and, on the approach of a workman, a spark might pass with disastrous results."

On p. 165 we read that "the use of oils to lay the dust on streets depends on the very slow evaporation of the heavier components, on the ease of oxidation to asphaltic bodies, and on the disinfecting action of the tar and tar oils. The tar applied hot, is brushed into the street or an emulsion of oil and water is used. The materials best suited for laying the dust are crude oils, heavy asphaltic oils, oil residues, tars, liquid asphalts, or a mixture of tar and clay.

"In printing establishments and type foundries, the floors are oiled regularly, since after one treatment with non-drying oil they can be swept without raising the dust. In some respects this is not satisfactory, because the floors become slippery and are thus likely to lead to injury. . . .For oiling wood floors pure mineral oil should be used to prevent rancidity, and to avoid slipperiness an oil of specific viscosity 30 to 40 at 20° is advisable. The oil should not get sticky after several weeks. Krist thinks that floor oils should be pure mineral

oils of not too high viscosity so that they may penetrate the pores of the wood readily and conversely rise easily by capillarity to the dust layer and bind it." The idea of adding oil so as to bind the dust to the wood floor is not one that seems likely to appeal to the housewife.

On p. 255 is the statement that "in order to obtain a uniform terminology for pitch-like and asphalt-like bodies, it is advisable to restrict the term asphalt to those products which are found already formed in nature and which contain at the most only traces of added mineral oils (these latter being added only to increase the usefulness industrially). The less valuable substitutes which are formed during the treatment of petroleum should be known as artificial asphalt or better still as pitches (for example, according to their origin as petroleum pitch, fat-pitch, lignite pitch, coal-tar pitch)."

"According to Engler the asphalts are derived from petroleum hydrocarbons through polymerization, free oxygen acting as a catalyzer of the change. It has been shown experimentally that the formation of asphalt takes place much more rapidly in the presence of air, and yet the amount of oxygen absorbed is too small to explain the formation of the asphalt through oxidation," p. 278.

Freundlich is quoted, p. 233, as having found that most of the particles in oilbag are less than 1$\mu$ in diameter, only a fraction running 1–6$\mu$. At 1200 magnifications the graphite particles seemed scaly and not spherical. On p. 167 it is stated that "only liquids with great tendency to adhere to solids are suited for lubrication since only these have the property of penetrating by capillarity where journal and bearing are the closest and where the danger of contact and wear is the greatest. The lubricating oils prevent direct contact of the metal surfaces because of their adhesion to these surfaces and because their viscosity keeps them from being squeezed out by the pressure on the oil." On p. 304 is the interesting fact that stearine (with a different index of refraction) is added to paraffin candles to make them white and opaque.

The physical chemist will be interested in double melting points, p. 346. "A characteristic of solid glycerides is the phenomenon of so-called double melting point which was first noticed by Heintz in the case of stearin. This was at first thought to be due to the formation of different isomeric modifications, but recently Guth assumed that the glycerides went into a labile condition like that of super-cooled water. According to Bömer the phenomenon is due to physical dimorphism as in the case of sulphur and of silicic acids. Since the glycerides crystallized from solvents have only one melting point, the stable modification is assumed to be present in them while the modification obtained on rapid cooling of the melted material consists of the labile form which passes into the stable condition at the so-called first melting point. The same transformation takes place gradually at room temperature. The existence of these two modifications of the glycerides which might be attributed to polymorphism, polymerism or a subtle isomerism has not yet been definitely explained."

The author is quite frank in admitting, p. 358, that the drying of oils, such as linseed oil "is no more clearly understood than is the rancidity of fats. Common to both processes there is an increase in the amount of oxy-acids (shown by an increase in the ester value); a polymerization takes place which (as does the oxidation of the unsaturated bodies) causes an increase in specific gravity and viscosity. The oxidation and polymerization in the drying process take place,

not only with the compounds with one double bond, but also with those glycerides and acids containing two double bonds (linoleic, linolenic, etc., acids), the changes of the latter bodies giving rise to the oxidized, polymerized and partially dehydrated substances, more or less hard, insoluble in ether and naphtha, only soluble in alcoholic solutions of alkali."

The reviewer was interested in learning about montan wax, p. 528. "In lignite (brown coal) is found a variable amount of bitumen (from 3 to 30 percent). When the lignite is extracted with naphtha or benzol the bitumen is obtained in the form of montan wax. . . .The crude montan wax is purified by distillation with superheated steam in a vacuum. The montan wax is used for the preparation of shoe polish, phonograph records, insulating material for cables, floor wax, and composition greases, and to a small extent in the candle industry. The origin of the montan wax is uncertain. It has been thought that the material was produced by certain algae. Others have supposed that it originated from the resins of coniferous and deciduous trees; but the comparison of montan wax with retinit, a fossil resin found in deposits of lignite, does not lend probability to this view. The fatty and waxy components of plants have been considered by some investigators as the possible source. The occurrence of both waxy and resinous material in montan wax has led others to believe the montan wax to be derived from such substances."

On p. 369 is given a summary of the situation in regard to fats during the war. "The question of finding substitutes for fat became a serious problem for Germany during the war. Fats have not been prepared synthetically by methods satisfactory for quantity production. The prospect of an immediate solution of this problem did not seem promising, so that more attention was paid to stock-raising and the judicious use of chemical fertilizers as a means of increasing the amount of fat available. As a means of meeting the requirements partially, the following measures were adopted in Germany wherever possible:

1. Butter and margarine were rationed; in this way the decreased amount available was apportioned uniformly among the population. The use of marmalades was encouraged as the sugar contained might well be considered as a fat substitute, since sugar provides over four large calories per gram consumed.

2. Hydrolysis of fat for the production of soap was forbidden. In this way no fat, which might have been used for margarine was used for soap; furthermore for making soap only fatty acids from which glycerine has been completely removed were used.

3. The use of oils (such as linseed) which might be used as food was not permitted for varnish, linoleum, or paints. As a substitute for varnish was suggested the use of cumarone resins or synthetic resins made from phenol and formaldehyde; the production of linoleum was suspended for the time being.

4. The use of clay washing compounds, of washing powders containing little soap, and of various colloidal inorganic soap substitutes was encouraged; this reduced the consumption of fat for washing purposes to a minimum.

5. Fish oils were hydrogenated by the catalytic method; in this way were obtained solid fats usable as food.

6. Much oil was obtained by extraction from the embryos of wheat, rye, barley, and oats (which represent from 2 to 4 percent of the grain, in the case of corn from 10 to 14 percent) which are separated by mechanical milling

processes from the rest of the grain. The embryo of corn contains 12 percent of fat and 35 percent of protein, the former being used as a salad oil and for the production of margarine, the latter being a valuable food for cattle.

7. Oil was recovered from various seeds and fruits which during a time of normal import could not be economically treated for fat: sunflower seed, beech nuts, cherry stones, grape seeds, plum stones, walnuts. Cherry stones yielded about 3.25 percent, plum stones 4.3 to 6.8 percent, grape seeds (4850 tons collected in Germany and Austro-Hungary) gave 8 to 20 percent of oil.

8. Increased cultivation of plants gave increased yields of rape seed, linseed, hedge mustard, and soja beans, all capable of yielding oil.

9. Recovery of fat from waste waters of slaughter houses, sausage factories, barracks, hospitals, and hotels was accomplished by various devices. The material collected contained about 40 percent of fat.

10. Fat was also recovered from the sewage of large cities; this was done in the clarification tanks or by special mechanical separators. Before the war there was needlessly lost from 3 to 4 kilograms of fat per person per year (in Berlin this went as high as 7 kilos). With a diminished use of fat in the household these figures do not hold. The fat recovered contains unsaponifiable material, due to the considerable amounts of lubricating oils and other mineral oils which originate in various industrial establishments.

11. Very important was the recovery of fat from bones. This recovery was carefully organized. The fresh bones from slaughter houses contained about 16 percent of fat; the bones were pulverized, heated with steam under 4 to 5 atmospheres pressure, whereby a soup stock was also collected. The residue was used as a fertilizer. In the invaded territories the recovery of fat was carried on systematically. From the bones which were not obtained in a fresh condition, bone oil was obtained by extraction with solvents, this material being worked up into stearin, olein, glycerine, and pitch.

12. Fat was obtained by P. Lindner by the growth of a fungus obtained from a sample of the sap of the birch. The fungus converted the sugar of the sap into fat; it converts other sugars into fat, without alcoholic fermentation, but part of the sugar is used in the formation of protein and mucins. An attempt was made to grow this fungus in quantity.

13. Fats and oils were replaced in various industrial uses by various substitutes. In greases, soap was replaced by montan wax soaps, in the manufacture of leather, fish oils were displaced by mineral oils. Mineral oils were also used as cutting oils, and in tempering metals.

14. Attempts were made to produce fatty acids from lignite-tar oils by ozonizing them. Paraffin is said to have been oxidized at high temperatures into fatty acids. The yield has not been stated."

One point which strikes a colloid chemist in regard to this book is the haziness of the author in regard to emulsions. He speaks of them continually; but it is very hard to tell, as in the case of degras, whether he is discussing an oil-in-water or a water-in-oil emulsion. *Wilder D. Bancroft*

**The Theory of Emulsions and Emulsification.** *By William Clayton. 22 × 14 cm; pp. viii + 160. Philadelphia: P. Blakiston's Son and Co., 1923. Price: $3.00:*—In the foreword Donnan says that "the study of emulsions and

emulsification is of very great theoretical and practical interest. From the standpoint of pure science it throws great light on the problems of surface tension, surface concentration and adsorption, surface films, electrical double layers, adsorption of ions, Brownian motion, and the general theory of disperse systems and colloids. The study of emulsions and emulsification is also of great importance in biological science, e. g., the adsorption of fats, the permeability of membranes, etc.

"When we consider industrial and applied science, it is remarkable how many subjects of interest and importance are dependent on a knowledge of the formation, behaviour, and stability of emulsions. In this connection one has only to think of milk (and 'synthetic' milk), butter, margarine, the emulsions and ointments of pharmacy, emulsified disinfectants and lubricants, rubber latex, spraying fluids, soaps and other detergents, flotation processes, and a host of other things, in order to realise the extremely important *rôle* of emulsions in practical life. The engineer who wants to prevent emulsification of his lubricating oil, or to remove oil from his condensed water, is dependent on the physical chemistry of emulsions for the methods which he employs."

The subject is treated under the following heads: emulsions and emulsifying agents; the properties of emulsions; earlier theories of emulsions; adsorption at liquid-liquid interfaces; dual emulsions and the inversion of phases; the modern adsorption film theory; physical measurements in emulsions; emulsification; de-emulsification.

There is no question as to where Mr. Clayton stands in regard to general theory. "In order to prepare concentrated stable emulsions of either the oil-in-water or the water-in-oil type, besides the two liquids, a third substance is necessary, known as the emulsifier or emulsifying agent. On the nature of the emulsifying agent depends the type of emulsion promoted. Water-soluble colloidal substances promote emulsions of the oil-in-water type, whilst oil-soluble colloids promote the reverse type," p. 2.

"Without the presence of an emulsifying agent, emulsions of oil in water may be made up to a maximum concentration of 2 percent. Usually, however, pure oil-in-water emulsions are very dilute, the oil content being of the order of 1 in 10,000. Apart from condensed water in engineering practice, such emulsions are of little or no significance technically. They have a very important bearing, however, on the theoretical side, owing to their great similarity to colloidal suspensions, and because several interesting facts have been established for which no satisfactory explanation is yet available.

"In the first place, with pure oil and pure water only, but one type of emulsion is known, viz., that in which the oil is dispersed in water. Groschuff claimed to have prepared very dilute emulsions of water in benzene and mineral oils by heating the water and oil in a sealed vessel and then cooling down to 18° C. The emulsion in benzene was stable for a few minutes, that in petroleum for one hour, whilst paraffin oil, and particularly transformer oil, gave stable emulsions. Very similar results have been published by Hall. The noteworthy feature in the results of both of these workers is that the purer the materials, the less stable were the emulsions. The more stable emulsions were in each case in oils where colloidal matter is in all probability present. Consequently, with pure oil and water we only know stable emulsions of the oil-in-water type. No

observer has ventured an explanation for this fact, and an excellent line of research is open for an investigation on the possibility of making water-in-oil emulsions, using materials beyond suspicion," p. 14.

"The essential difference between Fischer's theory and the present theory of an adsorbed film enveloping the emulsion globules is that in the former case the emulsifying agent is supposed to be evenly distributed throughout the aqueous phase as some sort of chemical compound with the water; the oil globules are dispersed in this aqueous phase because of its viscosity or 'covering power.' The modern theory believes that a *concentration* of the emulsifying agent occurs at the interface between the oil globules and the aqueous phase. Strangely enough, this very idea of adsorbed film protection of emulsion particles has to be resorted to by Fischer in order to explain the formation of emulsions with finely-divided solids as emulsifying agents, and also to account for the stability of milk when diluted with water. Critical reading of Fischer's work does not establish a strong case for his hydration theory, which seems particularly one-sided in its treatment of emulsions," p. 44.

On p. 121 we read that "very little creaming takes place in the case of homogenised milk, whilst raw milk creams rapidly. Homogenised milk cannot be churned into butter, and homogenised cream cannot be whipped; the addition of a colloid, such as gum tragacauth is necessary, if a permanent foam is desired. The Brownian movement is very marked, and there is a measurable decrease in the surface tension."

Under de-emulsification, p. 127, the author speaks of Cottrell's electrical dehydration process which uses an alternating current. "The theory underlying the Cottrell process and its modifications is that the emulsion serves as a multitude of electrical condensers, the electrodes or poles being the water globules and the continuous oil phase serving as the dielectric. Under the influence of a high-potential alternating field the charged water particles rupture the enveloping oil films and coalesce, forming larger drops. According to W. G. and H. C. Eddy, who followed such a test by the aid of the micro-photographic cinema film, this action of stress and strain, attraction and repulsion on the conducting water particles continues until all the microscopic drops of water in the original emulsion have broken the bonds of the entrapping oil film, the larger droplets serving as nuclei until the entire water content is freed into large drops which readily settle out."

On p. 130 the author says that "of other hydrophile colloids recommended in the de-emulsification of crude oils may be mentioned gelatin (glue) and starch. It is possible to prepare a concentrated gelatin mixture in fuel oil, which readily 'breaks' these emulsions. Starch added in suitable oil-soluble form also acts very effectively, although starch is not usually considered a strong protecting colloid for oil-in-water emulsions."

He then quotes from Ayres to the effect that "nothing of value can be said in regard to the percentages of such hydrophile reagents required to break these emulsions, because, in practice, the effects of the reagents are progressive. Taking, for example, an emulsion which can be separated in a given continuous centrifugal at the rate of five barrels an hour, the addition of 0.001 percent of oil-soluble sodium soap, glue, or starch, several hours before centrifuging will cause the rate of separation to be increased to fifteen barrels an hour. The

same increase may be obtained by the addition of 0.01 percent of hydrophile colloid thirty minutes before centrifuging, or the addition of 0.1 percent at the time of centrifuging. Within practical limits, the more reagent is used the further will coalescence proceed in a given time. An absurdly small percentage of hydrophile colloid is enough to insure complete coalescence by contact if the emulsion is given time to come to equilibrium."

The reviewer does not believe that the Trent process of cleaning coal, p. 131, involves the formation of the reverse type of emulsion. It is essentially a case of bulk-oil flotation in which the oil is loaded so heavily with coal that it becomes more dense than water.

The chief criticism on this book is that it is too short. Since Thorpe's Dictionary of Applied Chemistry does not contain the word emulsion as a separate heading, it would have been a good thing if the author had talked more at length about technical emulsions including his own specialty, which is margarine. By so doing, he would have increased the value of the book to the general reader very much. Three W. Ostwalds have been too much for Mr. Clayton's historical discrimination. He mixed those Ostwalds up; however, could he do it?

*Wilder D. Bancroft*

**The Theory of Spectra and Atomic Constitution.** *By Niels Bohr. 22 × 15 cm; pp. x + 126. Cambridge: Cambridge University Press, 1922. Price: $3.00.*—The book consists of three essays: the spectra of hydrogen; the series spectra of the elements; the structure of the atom and the physical and chemical properties of the elements.

Bohr assumes, p. 12, that "the radiation of light corresponding to a particular spectral line is, according to our assumption, emitted by a transition between two stationary states, corresponding to two different frequencies of revolution." On p. 32 we read "just as we have assumed that each emission of radiation is due to a transition from a stationary state of higher to one of lower energy, so also we must assume absorption of radiation by the atom to be due to a transition in the opposite direction. For an element to absorb light corresponding to a given line in its series spectrum, it is therefore necessary for the atom of this element to be in that one of the two states connected with the line possessing the smaller energy value. If we now consider an element whose atoms in the gaseous state do not combine into molecules, it will be necessary to assume that under ordinary conditions, nearly all the atoms exist in that stationary state in which the value of the energy is a minimum. This state I shall call the normal state. We must therefore expect that the absorption spectrum of a monatomic gas will contain only those lines of the series spectrum, whose emission corresponds to transitions to the normal state. This expectation is completely confirmed by the spectra of the alkali metals. The absorption spectrum of sodium vapour, for example, exhibits lines corresponding only to the principal series, which as mentioned in the description of the figure corresponds with transitions to the state of minimum energy."

"In spite of the great formal similarity between the X-ray spectra and the hydrogen spectrum indicated by these results a far-reaching difference must be assumed to exist between the processes which give rise to the appearance of these two types of spectra. While the emission of the hydrogen spectrum, like the

emission of the ordinary optical spectra of other elements, may be assumed to be connected with the binding of an electron by an atom, observations on the appearance and absorption of X-ray spectra clearly indicate that these spectra are connected with a process which may be described as a reorganization of the electronic arrangement after a disturbance within the atom due to the effect of external agencies. We should therefore expect that the appearance of the X-ray spectra would depend not only upon the direct interaction between a single electron and the nucleus, but also on the manner in which the electrons are arranged in the completely formed atom," p. 69.

On p. 86 the author states that the experiments by Franck and his coworkers showed that "the impact of electrons could bring helium into a 'metastable' state from which the atom cannot return to its normal state by means of a simple transition accompanied by the emission of radiation, but only by means of a process analogous to a chemical reaction involving interaction with atoms of other elements. This result is closely connected with the fact that the binding of the electron can occur in two different ways, as is shown by the occurrence of two distinct spectra."

"Our ordinary electrodynamic conceptions are probably insufficient to form a basis for an explanation of atomic magnetism. This is hardly to be wondered at when we remember that they have not proved adequate to account for the phenomena of radiation which are connected with the intimate interaction between the electric and magnetic forces arising from the motion of the electrons. In whatever way these difficulties may be solved it seems simplest to assume that the occurrence of magnetism, such as we meet in the elements of the fourth period, results from a lack of symmetry in the internal structure of the atom, thus preventing the magnetic forces arising from the motion of the electrons from forming a system of closed line of force running wholly within the atom," p. 106.

*Wilder D. Bancroft.*

**Practical Physical Chemistry.** *By J. B. Firth. 18 × 12 cm; pp. xii + 178. New York: D. Van Nostrand Co. Price: $1.25.*—This book was reviewed when it first appeared (20, 814). Except for the one line "First published in 1915," there is nothing to show the date of this issue or whether it is in any way a new edition. The titles of the chapters are the same and so is the number of pages. This is not the way to treat the reading public. *Wilder D. Bancroft*

# HYDROUS OXIDES. V

BY HARRY B. WEISER

## Hydrous Cupric Oxide

The gelatinous precipitate obtained by the addition of dilute alkali to a cupric salt is usually considered to have the composition $Cu(OH)_2$ or $CuO.H_2O$. This is because the precipitate washed rapidly until free from the mother liquor and dried over $H_2SO_4$ has the composition corresponding to a monohydrate. Spring and Lucion[1] recognized that the freshly precipitated oxide contains more water and assigned it the formula $CuO.2H_2O$ or $CuO.3H_2O$. Van Bemmelen[2] found however that the oxide forms neither a di- nor a trihydrate. The freshly precipitated blue substance is highly hydrous, containing more than 20 mols of water to one of CuO even after pressing it between porous earthenware for two hours. The water, at least in excess of one $H_2O$, is adsorbed and not chemically combined in the usual sense. When the precipitate is exposed at ordinary temperatures to an artificially dried atmosphere, it loses water continuously until the vapor pressure is equal to that of the aqueous vapor in the atmosphere. From $\pm 2H_2O$ to $\pm 1H_2O$ the water is held more firmly than above $\pm 2H_2O$ and on standing at a pressure of zero the composition approaches the properties and composition of a crystalline hydrate $CuO.H_2O$. Van Bemmelen considers the evidence insufficient to establish the existence of a definite amorphous oxide of the composition $CuO.H_2O$; so that the gelatinous substance must be looked upon as hydrous cupric oxide rather than hydrous hydrated cupric oxide. However, a number of investigators have claimed to get a crystalline hydrate. Bec-

[1] Zeit. anorg. Chem., 2, 195 (1892).
[2] Ibid., 5, 466 (1894).

querel[1] prepared it by the action of dilute KOH on a basic cupric nitrate and Böttger[2] obtained it by the action of concentrated NaOH on crystalline basic cupric sulphate.[3] Péligot[4] hydrolyzed crystalline blue-violet copper ammonium nitrate; while Villiers[5] claimed that a crystalline hydrate was formed from the amorphous hydrous oxide by suspending the latter in water which was subsequently frozen and allowed to stand several hours. Villiers' observation supports van Bemmelen's view noted above that the amorphous hydrous oxide goes over gradually to a crystalline monohydrate on standing.

When the blue hydrous oxide is allowed to dehydrate slowly in the cold or rapidly at 100° a brown substance is obtained to which Sabatier[6] assigned the formula $4CuO.H_2O$. This loses water slowly in dry air and approaches the composition of $7CuO.H_2O$. Schaffner and Rose[7] thought the brown oxide was a hydrate of the formula $3CuO.H_2O$. In the light of van Bemmelen's observations on the dehydration of the hydrous oxide, it seems altogether unlikely that the brown oxide is a definite hydrate. This view is strengthened by the more recent work of de Forcrand[8] and of Chemanov.[9] The former obtained several so-called hydrates, among them a brown oxide which had a composition corresponding to the formula $CuO.0.35H_2O$; while the latter found that the mineral atacamite was changed by KOH into a dark brown substance of the approximate composition $4CuO.H_2O$, while soluble copper salts $CuCl_2$, $CuSO_4$, etc. are changed by alkali, according to the conditions, to one or the other of the following compounds; $7CuO.H_2O$, $8.5CuO.H_2O$ and $9CuO.H_2O$. Of course none of these substances was a definite hydrate.

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[1] Comptes rendus, **34**, 573 (1852).
[2] Jour. prakt. Chem., **73**, 491 (1839).
[3] Cf. Habermann: Zeit. anorg. Chem., **30**, 318 (1906).
[4] Comptes rendus, **53**, 209 (1861).
[5] Ibid., **120**, 322 (1895).
[6] Ibid., **125**, 301 (1897).
[7] Schaffner and Rose: Gmelin-Kraut Handbuch des Chemie, **3**, 598.
[8] Comptes rendus, **157**, 442 (1913).
[9] Jour. Russ. Phys. Chem. Soc., **47**, 1268 (1915).

Lorentz[1] devised the interesting method of preparing the blue hydrous oxide by electrolyzing a solution of an alkali nitrate or sulphate with a copper anode. Müller and Spitzer[2] electrolyzed an alkaline copper ammonium solution with a platinum anode and obtained a black deposit that contained 95.5% CuO, 4.2% $H_2O$ and 0.5% higher oxides of copper. In the latter case dehydration took place at the same time as the precipitation. Müller and Spitzer showed further that the blue oxide could be suspended in alkali solution for an hour without darkening; but, if a current was passed through the solution, the particles moved to the anode and darkened at once. In one experiment the black oxide had the composition $CuO.0.128H_2O$. This is an interesting example of partial dehydration of a hydrous oxide at the anode by electric endosmose. The experiments were repeated with the blue so-called "crystalline" cupric oxide and a similar dehydration took place though it required about three times as long. Müller and Spitzer do not believe that chemically combined water can be removed by electrical endosmose and suggest that the chemical hydrate, so-called, goes over to an adsorption compound that does dehydrate; or that an unstable peroxide results at first which later decomposes to the ordinary oxide containing less water. It seems to me that neither suggestion is very plausible. What seems more likely is that the so-called crystalline hydrate is not a true hydrate at all but is a granular hydrous oxide in which the particles are matted closer together giving a denser structure that retains the adsorbed water more strongly than a gelatinous precipitate. In line with this Kohlschütter and Tüscher[3] showed that solid copper salts as the basic nitrate, vitriol and Schönit can undergo pseudomorphous transformations to hydrous oxide or hydroxide, as they say, and finally to oxide. The transformation products from a given crystal of salt were shown conclusively to have the same shape as the

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[1] Zeit. anorg. Chem., **12**, 438 (1896). Cf. Elbs: Zeit. angew. Chem., **1903**, 291.

[2] Zeit. Kolloidchemie, **1**, 44 (1906); Zeit. anorg. Chem., **50**, 322 (1906).

[3] Zeit. anorg. Chem., **111**, 193 (1920).

original, a circumstance that indicates that the so-called crystals of copper oxide are really pseudo-crystals that do not result from its own power of crystallization.[1] Kohlschütter and Tüscher claim however that both the gelatinous and granular products are made up of particles of cupric hydroxide, $Cu(OH)_2$, and not of hydrous cupric oxide as I have suggested. The real difficulty is that the vapor pressure of hydrous copper oxide becomes practically zero at a composition of approximately $CuO.H_2O$ so that it cannot be determined by pressure measurements whether or not a definite hydrate exists. Bancroft[2] has pointed out that if a definite compound, $CuO.H_2O$, existed with a practically zero pressure, it should form from cupric oxide in the presence of water; but it is well known that the reverse process is the one that actually takes place. Kohlschütter and Tüscher consider that the failure of CuO to take up water is due to the chemical mechanism of the process of dehydration. Their view is that the dehydration is not due to a molecular splitting off of water that may be represented by the equation $Cu(OH)_2 \longrightarrow CuO + H_2O$ but depends on intramolecular neutralization of the $H^{\cdot}$ and $OH'$ ions resulting from an amphoteric dissociation. The process is represented by the equations:

$$Cu(OH)_2 \rightleftharpoons Cu'' + 2OH'$$
$$Cu(OH)_2 \rightleftharpoons CuO_2'' + 2H^{\cdot}$$
$$OH' + H^{\cdot} \rightleftharpoons H_2O$$
$$CuO_2'' + Cu'' = 2CuO$$

I shall come back to this again in a subsequent paragraph.

Kohlschütter and Tüscher electrolyzed solutions of $KNO_3$ with a copper anode using varying concentrations of solution at varying current densities and found that "the use of a small current density corresponds to precipitation in dilute solutions. As usual smaller particles are obtained in this way which can form a denser clump so that the precipitate as a whole settles down further and it can be shown that at a current density of

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[1] Cf. Kohlschütter: Zeit. anorg. Chem., 105, 1 (1919).

[2] "Applied Colloid Chemistry," 246 (1921).

0.04 amp/cm² larger 'primary particles' and so more voluminous 'secondary particles' are formed whereas the smaller particles formed at 0.01 amp/cm² deposit denser packed larger individuals. On the other hand, continuing the electrolysis leads in both cases to larger and looser secondary bodies and flocks since the first-formed smaller particles serve as kernels or centers of accumulation for the condensation of the particles formed later on."

*The Colloidal Oxide.*—With but one exception, stable colloidal solutions of hydrous cupric oxide have been prepared only by the aid of a protective colloid. Graham[1] obtained a colloid by adding KOH to a cupric chloride solution containing sugar. The solution was deep blue at first but changed to green after dialyzing. Most of the KCl was removed and the colloid contained approximately one part of copper to two of sugar together with some $CO_2$ from the air. Graham called the preparation "copper saccharate." It was precipitated readily by boiling or by adding salts and acids forming a bluish green precipitate. A colloid that is much more stable than Graham's colloid can be prepared using Paal's[2] sodium salts of protalbinic or lysalbinic acids as protective colloid. The colloid moved to the cathode under electrical stress and was therefore positively charged. The oxide can be obtained in the colloidal state also in the presence of casein.[3]

Biltz[4] attempted the preparation of the colloidal oxide by dialysis of a solution of copper nitrate; but found that the salt was too little hydrolyzed and passed unchanged through the dialyzer. Ley[5] hydrolyzed the copper salt of succinimide and obtained a very satisfactory colloid that changes in color slowly at room temperature but rapidly at 70° from a blue-green to yellow-brown and finally dark brown. The course of the hydrolysis was followed by cryoscopic observations and found

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[1] Phil. Trans., **151**, 183 (1861); Comptes rendus, **59**, 174 (1864).
[2] Ber. deutsch. chem. Ges., **39**, 1550 (1906).
[3] Rittenhausen: Jour. prakt. Chem., [2] **5**, 215 (1873); **7**, 361 (1874).
[4] Ber. deutsch. chem. Ges., **45**, 4431 (1902).
[5] Ibid., **38**, 2199 (1905).

to be complete after $^1/_2$ hour at 70°. If the succinimide formed by the hydrolysis was removed by dialysis the colloid precipitated; so it is probable that succinimide acts as a protective colloid.

Kohlschütter has prepared a colloidal solution without the use of a protective colloid by what he terms "discharge electrolysis."[1] In this process a passivifying layer of oxide was deposited on the anode and the layer was dispersed in the liquid by a rapidly oscillating discharge. In this way a very finely divided uniform colloid was obtained which was perfectly clear in transmitted light. The color was bluish green to green at the outset but later on went over to brown oxide. Ultramicroscopic observations of the latter disclosed particles varying in size from 0.05 to 0.08$\mu$. The transformation to brown oxide took place more slowly the diluter the colloid and the lower the temperature. At 12° a fairly high concentration of the green colloid was obtained but this gradually clouded up and settled out. By heating to 40° the colloid became brown quickly and the degree of dispersion increased. At lower temperatures the sedimentation not only came to a standstill as the green oxide (hydroxide) changed to brown but the latter formed a very stable colloid that did not coagulate in a month.

*The Color of Cupric Oxides.*--It is well known that a clear blue hydrous cupric oxide can be obtained only by precipitation in the cold. It was demonstrated by Schaffner,[2] Harms,[3] Tommasi,[4] Spring and Lucion[5] and by van Bemmelen[6] that the pure blue oxide could be obtained only at temperatures below 18° and even at low temperatures it retained its color only when freed from the mother liquor as rapidly as possible. The color alters slowly at room temperature but very rapidly at high tem-

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[1] Zeit. Elektrochemie, 25, 309 (1919).
[2] Ann. Chem. Pharm., 51, 168.
[3] Arch. Pharm., [2] 89, 35 (1858).
[4] Bull. Soc. chim. France, 37, 197 (1882).
[5] Loc. cit.
[6] Zeit. anorg. Chem., 5, 468 (1894).

peratures going from blue through various shades of green to brown and black. The transformation to the black oxide is accompanied by a decrease in volume of the precipitate and a loss of most of the water. Van Bemmelen[1] prepared 5 samples of the hydrous oxide below 15° that varied in color from sky-blue through dark blue and green to dark green, the green colors resulting from too slow washing. He noted that the composition of the several samples dried over $H_2SO_4$ was approximately the same in spite of a rather marked variation in color.

Unlike the amorphous hydrous oxide the blue granular oxide prepared by Becquerel, Böttger and Péligot is said by these investigators to be stable in boiling water and to maintain its blue color when heated at 100°.[2] De Forcrand[3] studied the effect of heat on Péligot's blue oxide and found that it changed in color from blue to green at 85° without loss of water. Dehydration did not start until after it had become green and de Forcrand concludes that the blue compound is a metastable substance that does not lose water. At 100° the green oxide loses water becoming olive at a composition $CuO.0.8H_2O$ and brown at $CuO.0.35H_2O$. It is difficult to reconcile de Forcrand's observation that Péligot's oxide changes color at 85° with the observations of Becquerel, Böttger, and Péligot that the blue compound does not change color even at 100°. De Forcrand's oxides seemed to behave more like the amorphous precipitated substance.

De Forcrand dissolved the blue, green, olive and brown hydrates, so-called, and the black anhydrous oxide prepared at 140° in sufficient $HNO_3$ to form the nitrate and Sabatier[4] and Joannis[5] carried out similar experiments on the oxides dehydrated at 440° and at red heat. From these data de Forcrand concludes that the blue and green hydrates are isomers, the transformation from the former to the latter involving

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[1] Loc. cit.
[2] Péligot: Comptes rendus, **53**, 213 (1861).
[3] Comptes rendus, **157**, 441 (1913).
[4] Loc. cit.
[5] Comptes rendus, **102**, 1161 (1895).

+0.261 Cal. Between 85° and 140° the oxide loses water and undergoes progressive polymerization. He concludes further that there is a second isomeric change between 140° and 440° involving +0.181 Cal. and a third between 440° and red heat involving +2 Cal. It seems to us that thermochemical evidence of this sort is insufficient to establish the existence of definite isomers. The oxide undergoes a progressive change and the data do not establish definite inversion temperatures. Wöhler[1] has shown that the sudden decrease in the surface energy of a number of hydrous oxides when heated quickly is sufficient to raise the temperature of the whole mass to incandescence. Thermochemical data obtained before and after glowing might be interpreted to mean that an isomeric transformation had taken place; but such a conclusion would be erroneous. I think it quite unlikely that the different colored cupric oxides are definite allotropic or isomeric forms of the oxide. The slow change in color of the hydrous oxide on standing at ordinary temperatures is doubtless caused by a change in the character and size of the particles. Kohlschütter and Tüscher are of the opinion that the blue compound is amorphous or pseudocrystalline $Cu(OH)_2$ while the black compound is CuO. I have already called attention to their observation that the blue colloidal hydrous oxide consists of rather large particles whereas dehydration of these particles by heating or by standing for some time results in the formation of a stable colloid made up of distinctly smaller particles of CuO. They point out further that the blue compound kept under cold water gradually becomes denser whereas the opposite is true with the anhydrous product. On the basis of these observations and the further fact noted by Berczeller[2] that the black oxide adsorbs more alkali than the blue hydroxide under certain conditions, Kohlschütter and Tüscher conclude that the blue substance is made up of larger particles than the black. This conclusion seems to have been reached without taking all the

[1] Zeit. Kolloidchemie, **11**, 241 (1913); Cf. Weiser: Jour. Phys. Chem., **26**, 404 (1922).

[2] Biochem. Zeit., **93**, 230 (1919).

facts into consideration. Every one knows that copper oxide *can* be obtained in quite large particles which are black and the hydrous oxide in very much smaller particles which are blue. Moreover, it is very probable that particles of the blue hydrous colloid observed by Kohlschütter and Tüscher, were in reality clumps of very finely divided blue particles that had adsorbed water strongly forming a gelatinous mass. On heating, this relatively large gelatinous clump is broken down and the particles constituting it agglomerate to larger particles that appear black. These larger black particles are small only in comparison with the gelatinous clump and, because of their physical character, are more readily peptized than the continuous mass of hydrous particles. Unfortunately Kohlschütter and Tüscher have given the wrong impression by calling attention to Berczeller's experiments which tend to show that the black compound adsorbs more alkali than the blue without mentioning the further fact observed by Berczeller, that the blue compound adsorbs more iodate ions than the black. The work of Bancroft on the color of cupric oxides is merely mentioned by Kohlschütter and Tüscher and the results are entirely disregarded. The former believes that the dehydration of hydrous cupric oxide is attended by an increase in size of particles with the resulting change in color from blue through various shades of green to brown and finally black. From this point of view anhydrous cupric oxide would be blue and not black if agglomeration during dehydration were prevented. In support of this Schenck[1] observed that a mixture of the hydrous oxides of Cu and Al containing 5% CuO remained blue even after ignition. His explanation was that agglomeration of the blue oxide was prevented by the large excess of alumina. These experiments have been repeated recently[2] in Bancroft's laboratory by Parsell who dissolved out the excess of alumina from the blue mixture of CuO and $Al_2O_3$ with NaOH. In this way a distinctly blue powder was obtained containing CuO and $Al_2O_3$ in the proportion of approxi-

[1] Jour. Phys. Chem., **23**, 283 (1919).
[2] Ibid., **26**, 501 (1922).

mately 4 to 1. In the light of these observations it is evident that Kohlschütter and Tüscher are not justified in their conclusion that the individual particles of black oxide are more finely divided than the blue. As a matter of fact it seems very unlikely that peptization of a light blue substance should yield a black product. The other hypothesis that the blue compound is a definite hydrate while the black is anhydrous CuO stands or falls on the correctness of the unproven assumptions that there *is* a definite amorphous hydrate and that this dehydrates not by the molecular splitting off of water in the usual way but by a process termed "internal neutralization as a result of amphoteric dissociation," to which I have already referred.

*The Dehydration of Hydrous Cupric Oxide and the Effect of Salts on the Process.*—Attention has been called to the fact that the pure hydrous oxide maintains its blue color only when precipitated below 18° and freed from the mother liquor as rapidly as possible. Tommasi[1] precipitated and washed the oxide at 0° and then suspended it in a number of salt solutions which were subsequently heated. He made the interesting observation that in a number of cases salts retarded rather than hastened the blackening. As a notable example the suspended precipitate did not blacken even at 100° in contact with a dilute solution of manganous sulphate. Bancroft[2] considers that the blue hydrous copper oxide is stabilized by the hydrous oxide of manganese so that the former does not blacken at 100°. Since wool fibre is colored green by boiling with a solution of copper salts Knecht, Rawson and Löwenthal[3] are positive that a hydrate is not formed in mordanting wool with copper salts since a copper hydrate would blacken at the boiling point. But Bancroft answers this argument by pointing out the stabilizing action of manganese sulphate on hydrous copper oxide and concludes that wool has a similar stabilizing action on the hydrous oxide. Reasoning from analogy Ban-

[1] Bull. Soc. chim. France, **47**, 197 (1882).
[2] Jour. Phys. Chem., **18**, 149 (1914); **26**, 512 (1922).
[3] "A Manual of Dyeing," **1**, 59 (1910).

croft arrives at the important conclusion that the instability in solution of a free color base like that of fuchsine does not mean that it is instable when adsorbed by silk.

Blucher and Farnau[1] repeated and extended Tommasi's experiments and report that hydrous copper oxide remains blue in the presence of small amounts of the sulphates of Mn, Zn, Ni, Al, Cr and the chlorides of Co and Mg. Since such small amounts of the salts are effective it is concluded that hydrous cupric oxide adsorbs the hydrous oxides of Mn, Al, etc., and that these adsorbed oxides act as protective colloids preventing agglomeration and the consequent blackening of the blue oxide.

Kohlschütter and Tüscher discuss the effect of salts on hydrous cupric oxide in the light of their theory of the mechanism of the dehydration process. In order to present their theory in accurate detail as well as to emphasize the absence of experimental proof of their fundamental assumptions, I quote at some length from their paper: "The results of our observations have lead to the view that the intermolecular splitting off of water by inner neutralization does not take place with a single molecule of $Cu(OH)_2$ or between two simple $Cu(OH)_2$ molecules but between complex molecules already of colloidal dimensions. This is subject to the further limitation that a definite degree of dispersity must be assumed to account for the reaction taking place, for it does not take place at all or is retarded both with very finely divided and with coarse varieties; and so in common with many other properties of disperse systems it has a maximum in a mean region of dispersity. Further, a certain concentration or agglomeration of the particles is necessary since obviously the distance between them must be reduced to such an extent that they come within the common sphere of action. From this viewpoint then, the nature of the subdivision and grouping or in other words the structure of a form is occasionally of paramount importance.

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[1] Jour. Phys. Chem., 18, 629 (1914).

"With the aid of these conceptions the observed phenomena will be understood and in order to show their accuracy, the single results which, in part, were obtained by detailed comparison and observation, will be summarized briefly; while at the same time, a few facts already known will be fitted into the bounds of the theory and certain conclusions of a general character will be drawn.

"In addition to the chemical considerations, the formation of CuO by oppositely directed migration of particles in connection with the cataphoresis of finely divided hydroxide sols, as well as the permanence of a preparation that has once dried, speaks for the conception that the dehydration comes about as a result of neutralization based on the amphoteric nature of $Cu(OH)_2$. That it takes place between particles follows from its non-existence under conditions where $Cu(OH)_2$ exists in a molecular state of division. Thus CuO never separates out from salt solutions in which are present $Cu(OH)_2$ molecules formed by hydrolysis, and it never results from crystalline basic salts which contain hydroxide if these, either dry or under water, are subjected to temperatures and other influences which give rise to the splitting off of water from hydroxides of a colloidal degree of dispersity.

"However, alkali solutions in which either only a little hydroxide is dissolved at first or the separation of oxide has taken place until a definite amount is present, give no oxide although they unquestionably contain $Cu(OH)_2$ which, in part, is molecularly dissolved in equilibrium with an anion containing Cu and, in part, is in a highly dispersed form.

"In this an indication can be seen that a very high colloidal degree of dispersion likewise suppresses the reaction. More conclusive proof of this is that hydroxide sols prepared with the high frequency discharge at high potential remain chemically unchanged at concentrations where sols prepared by other methods change rapidly and spontaneously into oxide at ordinary temperatures.

"On the other hand a dispersed hydroxide is stable in which, considering the method of preparation, larger particles

can or must be assumed. Such obtains in the case of the transformation product of basic nitrate in consequence of the close packing of the reacting material from the outset; also in the hydroxide frozen according to Villiers; and in the precipitation from alkali solution.

"Between the extremes of least reactivity the stability first increases and then decreases with the degree of dispersity. Of particular interest in this connection is the increase in the capacity to dehydrate in the series of polymorphic hydroxides from basic nitrate, vitriol and Schönit and also its increase with decreasing dispersity in the electrically prepared sols.

"Likewise one observes an increasing tendency to split off water in consequence of decreasing dispersity in the adsorption layers according as they are formed with or without cooling; although here the second factor, the concentration of the particles, plays a rôle.

"This influence of the concentration of the particles is particularly marked in the electrical colloids. However the action of adsorption in the boundary surface is at the basis of this and shows itself further in the condensing by cataphoresis of the colloidal hydroxide in the highly dispersed alkaline solution and in the reaction at Cu anodes where the rapid increase of potential caused by the formation of CuO occurs, the more rapidly the greater the strength of the current, that is when the more particles in the same time are deposited on the electrode.

"The differences in the possibility of reaction at a given concentration must not be traced exclusively to the size of the particles as such, for one has to deal with various orders of magnitude of the particles which may be designated as primary and secondary. The structure therefore plays a rôle.

"Like primary particles can in different ways build up larger individuals in which they are grouped together in a looser or denser fashion. A loose structure obviously promotes the dehydration since it affords room for the forcing out of the layer of solvent and therewith provides the opportunity for amphoteric electrolytic dissociation and reaction

to the particles themselves, present in sufficient amount; while a dense grouping prevents both.

"In the pseudomorphous bodies one must perhaps attribute the difference in behavior more to these factors than to the size of the particles; at all events it appears decisive in the electrolytically produced precipitates. A small current leads to the formation of small primary but to denser secondary particles, and thereby increases the stability of the hydroxide. On the other hand, products of greater looseness result if, under otherwise constant conditions, a larger amount of precipitate is obtained by longer electrolysis; the dehydration capacity is increased in consequence of this.

"The structural relations must play a large rôle also in the promoting of the reaction by raising of the temperature and addition of electrolytes and these have therefore been considered from this point of view. Here appears to be a connection with the investigation especially of Spring and Lucion whose qualitative results were that the presence of a salt calls forth an action which is comparable to a raising of temperature while from a quantitative view the process may be described thus: that time has a resistance to overcome, as it were, before the reaction can take its course.

"It is suggested to look upon the process which this action of time adjusts, as a swelling which the hydroxides can undergo in different amounts and with different velocity according to their structure. The swelling is hastened by warming and by the addition of electrolytes; its effect consists in increasing the dispersity by loosening up of the secondary particles. In this way is obtained the freedom for reaction of primary particles since they are unable to come in contact with the layers of solvent which are necessary for their transformation by means of amphoteric dissociation and self-neutralization. And so is explained the action which temperature and salt solutions have on the formation of CuO. To follow this influence with a characteristic series of ions and thereby to prove it without objection as the promoting of a process of swelling was unfortunately not feasible on account of a secondary

chemical reaction with the swelling material; still the investigations of Spring and Lucion contain indications for the validity of such a view.

"Finally the point of view that has been followed clears up the counterpart to the accelerating action of many materials, namely, the retarding and suppressing of the splitting off of water by the presence of others.

"The latter may be treated in two groups: first, those materials which can react chemically with the $Cu(OH)_2$ forming difficultly soluble products on the surface; and second, adsorbed colloidal substances which include everything from a pure surface adsorption to almost homogeneous mixtures of the nature of adsorption compounds.

"Thus, carbon dioxide, especially, prevents the formation of oxide to a marked degree by the surface formation of basic salts; and traces of different anions often act in a quite similar manner as is occasionally observed, immediately on the appearance of the hydroxide precipitate.

"The already long known stabilizing influence which the presence of larger amounts of other heavy metal salts has on precipitated $Cu(OH)_2$ rests, on the other hand, on the adsorption or mixing of foreign hydroxides. These manifestly suppress the amphoteric dissociation and neutralization of the surface molecules of the copper oxide in the aqueous adsorption layer since they hold apart the particles capable of reaction or make the greater part inaccessible for a swelling. The action can be shown very clearly if the electrically prepared green colloid consisting essentially of hydroxide particles is treated with a protective colloid. It remains green after the time when an unprotected portion has changed to brown by the formation of oxide; and its particles are dehydrated by electric cataphoresis and by warming."

This survey of the work that has been done on the effect of salts on the stability of hydrous copper oxide raises a number of questions. Blucher and Farnau found that small amounts of certain salts are effective in preventing blackening at 100° thus supporting Bancroft's hypothesis that hydrous cupric

oxide adsorbs the hydrous oxides of manganese, aluminium, etc. and that these adsorbed oxides act as a protective colloid preventing agglomeration and the consequent blackening of the blue oxide. When wool is brought in contact with a copper salt it adsorbs hydrous cupric oxide and according to Bancroft the latter is stabilized by adsorption so that it does not blacken at 100°. These two cases are not the same. In the first instance the hydrous cupric oxide is the adsorbing phase and in the second, the adsorbed phase. While there is no *a priori* reason why hydrous cupric oxide may not be stabilized both by being adsorbed and by adsorbing a protective agent, it seems to me that neither conclusion necessarily follows from the other. It will be recalled that Kohlschütter and Tüscher accept Bancroft's hypothesis that heavy metal salts stabilize $Cu(OH)_2$ by adsorption of the hydrous oxides of the metals; but they seem to have gotten the impression that a fairly large concentration of salts is necessary. It should be pointed out that we have no independent confirmation of the hypothesis that the hydrous oxides of chromium, aluminium and manganese are strongly adsorbed by hydrous copper oxide and that such adsorption stabilizes the blue form. Kohlschütter and Tüscher conclude that the presence of electrolytes in small amounts favors dehydration by promoting the swelling and consequent peptization of the larger clumps of hydrous oxide. In this connection I have been unable to find any reference to direct experimental evidence of such swelling or peptization. It would seem that if such a phenomenon took place it would not be difficult to detect. Some experiments bearing on these points were accordingly undertaken. I was assisted in carrying out the experiments described in the next section by Mr. Allen Bloxsom a student in my laboratory to whom I am greatly indebted.

## Experimental

*The Stability of the Granular Oxide.*—As noted above Péligot, Böttger, and Villiers claimed to get a crystalline hydrate that remained blue on heating to 100°; whereas de Forcrand obtained a similar compound that darkened gradually on heat-

ing. In order to determine whether a compound exists that will stand a temperature of 100° for an appreciable length of time without darkening, the following experiment was carried out:

Bonsdorff[1] claims to get a crystalline hydrate by precipitating a solution of copper ammonium nitrate with sodium hydroxide. I have followed his procedure. Crystals of copper ammonium nitrate were first prepared and a solution of the salt was precipitated by the addition of slightly more than the equivalent amount of NaOH free from carbonate. This precipitate stood in a corked flask in contact with the mother liquor for two weeks without darkening. A sample of this preparation in contact with the mother liquor was placed in a test-tube which was suspended in boiling water. Darkening was observed in ten minutes. A second sample was washed thoroughly by the aid of the centrifuge and suspended in pure water. This sample remained blue after heating 2 hours at 100°. A third sample was washed thoroughly, filtered and placed in an oven at 100°. No blackening was observed after heating 3 hours. The product was distinctly granular in character but repeated microscopic observations failed to reveal a definite crystalline form.

From the observations it is evident that a granular cupric oxide can be prepared that remains blue after prolonged heating at 100°. De Forcrand's sample seemed to possess properties intermediate between the usual hydrous oxide which blackens promptly at 100° and the granular compound that is stable at 100°. There are doubtless an indefinite number of such intermediate compounds since Villiers and van Bemmelen have each observed the gradual transformation from the precipitated gelatinous hydrous oxide to the granular product on standing. The observations support Kohlschütter and Tüscher's view that the granular product is not truly crystalline. The absence of definite crystalline structure eliminates the proof that has usually been offered in support of the exis-

[1] Zeit. anorg. Chem., **41**, 132 (1904).

tence of a definite hydrate of copper oxide having a zero vapor pressure.

In the course of these experiments it was observed that the hydrolysis of a small amount of the copper ammonium salt in the presence of a large excess of water resulted in the formation of a highly dispersed oxide that appeared very much lighter than the usual blue precipitate. By standing or by centrifuging the precipitate was agglomerated into larger masses that were distinctly blue. The results show that increasing the degree of dispersion of the blue gelatinous compound results in the formation of a lighter product rather than a black one. It will be recalled that this is the reverse of Kohlschütter and Tüscher's conclusion.

*The Action of Salts on Hydrous Copper Oxide.*—Blucher and Farnau[1] took 1 cc of N $CuSO_4$, diluted it to 8–10 cc with distilled water and then added 1 cc NaOH from a burette. To the suspensions of hydrous cupric oxide prepared in this way were added normal solutions of several salts in drops from a pipette. The test-tube was shaken thoroughly and then placed in a beaker of boiling water. Observations were made with varying amounts of the "stabilizers," so-called.

In the interest of greater accuracy, the method of procedure followed by Blucher and Farnau was modified slightly. N/10 solutions rather than normal were employed, the precipitation was carried out between 5° and 8° rather than at room temperature and the precipitate was washed to remove excess sulphate. The method was as follows: 10 cc of exactly N/10 NaOH was mixed with 10 cc of N/10 $CuSO_4$ at 5–8° in a hard glass test-tube. This test-tube was placed in a centrifuge immediately and the precipitate thrown down by centrifuging for one minute at 3000 r.p.m. The supernatant liquid was poured off and 20 cc of cold water added after which the precipitate was shaken thoroughly and the centrifuging repeated. By this procedure most of the sulphate was removed.

[1] Loc. cit.

Finally cold water was pipetted on the precipitate and the salt solution added. The total volume of solution was 10 cc. The salt solutions which were N/10 were measured with a 2 cc Ostwald pipette graduated in tenths of a cc. After thorough shaking, the test-tube was clamped in an upright position in boiling water. Observations were made each minute for 5 minutes and then at the end of 10 minutes. The results for $MnSO_4$ that are significant are recorded in Table I.

TABLE I

*Experiments with Manganese Sulphate*

| Time, min. | Observations | | |
|---|---|---|---|
| | Hydrous cupric oxide suspended in 10 cc. of | | |
| | Solution containing | | Water |
| | 0.25 cc N/10 $MnSO_4$ | 0.50 cc N/10 $MnSO_4$ | |
| 1 | Light greenish blue | Light greenish blue | Light greenish blue |
| 3 | Light greenish blue | Light greenish blue | Dark gray |
| 5 | Greenish gray | Light greenish blue | Dark gray |
| 10 | Dark gray | Light greenish blue | Brown |

The above results confirm the observations of Tommasi and of Blucher and Farnau that the blackening of hydrous cupric oxide is prevented by the presence of only a small amount of $MnSO_4$. The necessary concentration is less than half that found by Blucher and Farnau. The latter investigators recorded "no change" in the hydrous oxide in the presence of a suitable amount of $MnSO_4$. This notation should have been "no blackening" for there is a very distinct change in color. The usual clear blue gelatinous precipitate first becomes light blue (baby blue) and later greenish blue as the heating is continued. At the same time the character of the precipitate changes from a highly gelatinous form to a less bulky, granular condition. The experiments were repeated with the sulphates of Cr, Al, Zn, and Co with the results recorded in Tables II, III, IV, and V.

TABLE II

Experiments with Chromic Sulphate

| Time, min. | Observations | |
|---|---|---|
| | Hydrous CuO suspended in 10 cc solutions containing | |
| | 0.25 cc N/10 $Cr_2(SO_4)_3$ | 0.50 cc N/10 $Cr_2(SO_4)_3$ |
| 1 | Light bluish green | Light bluish green |
| 3 | Gray | Light bluish green |
| 5 | Dark gray | Light green |
| 10 | Dark gray | Light green |

TABLE III

Experiments with Aluminium Sulphate

| Time, min. | Observations | |
|---|---|---|
| | Hydrous CuO suspended in 10 cc solutions containing | |
| | 0.25 cc N/10 $Al_2(SO_4)_3$ | 0.50 cc N/10 $Al_2(SO_4)_3$ |
| 1 | Light greenish blue | Light greenish blue |
| 3 | Light greenish blue | Light greenish blue |
| 5 | Light gray | Light greenish blue |
| 10 | Gray | Light greenish blue |

TABLE IV

Experiments with Zinc Sulphate

| Time, min. | Observations | | |
|---|---|---|---|
| | Hydrous CuO suspended in 10 cc solution containing | | |
| | 0.25 cc N/10 $ZnSO_4$ | 0.50 cc N/10 $ZnSO_4$ | 0.75 cc N/10 $ZnSO_4$ |
| 1 | Greenish blue | Light greenish blue | Light greenish blue |
| 3 | Light brownish green | Light greenish blue | Light greenish blue |
| 5 | Brown | Light greenish blue | Light greenish blue |
| 10 | Chocolate brown | Light bluish gray | Light greenish blue |

TABLE V

Experiments with Cobalt Sulphate

| Time, min. | Observations | |
|---|---|---|
| | Hydrous CuO suspended in 10 cc solution containing | |
| | 0.25 cc N/10 $CoSO_4$ | 0.50 cc N/10 $CoSO_4$ |
| 1 | Light greenish blue | Light greenish blue |
| 3 | Light greenish blue | Light greenish blue |
| 5 | Grayish green | Light greenish blue |
| 10 | Dark gray | Light greenish blue |

The results recorded in the preceding tables show that the limiting concentration of the various sulphates necessary to prevent blackening of hydrous cupric oxide is very nearly the same. If the hydrous oxides of Al, Cr, Zn, Mn, and Co stabilize the blue oxide it means that the hydrous oxides have the same stabilizing power, which is interesting. To test this point some experiments were carried out with colloidal solutions of the hydrous oxides of Al, Cr and Sn. Colloidal alumina was prepared by prolonged boiling of a solution of hydrous aluminium oxide peptized by acetic acid;[1] colloidal chromic oxide by the hot dialysis of a solution of hydrous chromic oxide peptized by $CrCl_3$;[2] and colloidal stannic oxide by boiling a solution of hydrous stannic oxide peptized by $NH_4OH$.[3] The colloidal alumina and chrome were positive colloids while the stannic oxide was negative. As previously noted, the evidence seemed to indicate that the hydrous oxides of the metals stabilized the blue oxide. Since the metallic salts are effective in such low concentration it was thought that but little of the colloidal oxides would be required. It was found however that the presence of the colloidal oxides had but little effect in preventing darkening even when present in high concentrations. In every case the colloid precipitated on heating and the color of the copper oxide was modified.

[1] Weiser: Jour. Phys. Chem., **24**, 638 (1920).
[2] Ibid., **26**, 417 (1922).
[3] Ibid., **26**, 682 (1922).

This was of course most noticeable in the presence of the dark green chromic oxide. In no case, however, was there any very marked retarding of the darkening. As an example of the results of these experiments, I have set down in Table VI the observations of the effect of heating the blue oxide suspended in an excess of the colloidal solutions.

TABLE VI

Experiments with Colloidal Oxides

| Time, min. | Observations | | |
|---|---|---|---|
| | Hydrous CuO suspended in 10 cc of colloidal solutions of | | |
| | Hydrous $Al_2O_3$ 1.2 g per liter | Hydrous $Cr_2O_3$ 3.65 g per liter | Hydrous $SnO_2$ 4.32 g per liter |
| 1 | Light bluish green | Bluish green | Light greenish blue |
| 3 | Light gray | Grayish green | Light greenish blue |
| 5 | Dark gray | Dull grayish green | Light grayish green |
| 10 | Dark gray | Dull grayish green | Gray |

The results recorded in Table VI tend to show that the effect of salts on the stability of blue copper oxide is not due to the action of the hydrous oxides of the metals. This conclusion is supported by the observations with $CuSO_4$ recorded in Table VII.

TABLE VII

Experiments with Cupric Sulphate

| Time, min. | Observations | |
|---|---|---|
| | Hydrous CuO suspended in 10 cc solution containing | |
| | 0.25 cc N/10 $CuSO_4$ | 0.50 cc N/10 $CuSO_4$ |
| 1 | Light greenish blue | Light greenish blue |
| 3 | Light gray | Light greenish blue |
| 5 | Gray | Light greenish blue |
| 10 | Dark gray | Light greenish blue |

Comparison of the results given in Table VII with those in Tables I, II, III, IV and V shows that cupric sulphate is quite as effective as other sulphates in preventing the darkening of cupric oxide. This result completely eliminates from

consideration the effect of the hydrous oxides of the metals; for by no stretch of the imagination can blue hydrous cupric oxide be considered to prevent blue hydrous cupric oxide from darkening at 100°.

With the effect of the hydrous oxides eliminated, it seemed possible that the anion was the important thing. If so, then alkali sulphates should behave like the sulphates of Mn, Cu, etc. This seemed unlikely in view of the observations of Harms, Spring and Lucion and others that alkali salts favor rather than retard the spontaneous dehydration of hydrous cupric oxide. This is borne out by the results recorded in Table VIII.

TABLE VIII

Experiments with Sodium Sulphate

| Time, min. | Observations | | |
|---|---|---|---|
| | Hydrous CuO suspended in 10 cc solution containing | | |
| | 2 cc N/10 $Na_2SO_4$ | 6 cc N/10 $Na_2SO_4$ | 10 cc N/10 $Na_2SO_4$ |
| 1 | Light greenish blue | Light greenish blue | Light greenish blue |
| 3 | Light gray | Light gray | Greenish gray |
| 5 | Gray | Gray | Gray |
| 10 | Dark gray | Dark gray | Dark gray |

Some experiments were next carried out on the effect of heating hydrous cupric oxide in the presence of chlorides. The results are similar to those with sulphates as indicated by the data for $CuCl_2$, $CoCl_2$ and $MgCl_2$ recorded in Tables IX, X and XI.

TABLE IX

Experiments with Cobalt Chloride

| Time, min. | Observations | |
|---|---|---|
| | Hydrous CuO suspended in 10 cc solutions containing | |
| | 1.25 cc N/10 $CoCl_2$ | 1.50 cc N/10 $CoCl_2$ |
| 1 | Light greenish blue | Light greenish blue |
| 3 | Light greenish blue | Light greenish blue |
| 5 | Gray | Light greenish blue |
| 10 | Dark gray | Greenish gray |

TABLE X

Experiments with Cupric Chloride

| Time, min. | Observations: Hydrous CuO suspended in 10 cc solution containing | | |
|---|---|---|---|
| | 0.50 cc N/10 $CuCl_2$ | 0.75 cc N/10 $CuCl_2$ | 1.00 cc N/10 $CuCl_2$ |
| 1 | Light greenish blue | Light greenish blue | Light greenish blue |
| 3 | Light gray | Light bluish green | Light bluish green |
| 5 | Gray | Light bluish green | Light bluish green |
| 10 | Dark gray | Light bluish green | Light green (color of Paris green) |

TABLE XI

Experiments with Magnesium Chloride

| Time, min. | Observations: Hydrous CuO suspended in 10 cc solution containing | |
|---|---|---|
| | 5 cc N/10 $MgCl_2$ | 10 cc N/10 $MgCl_2$ |
| 1 | Light greenish blue | Light greenish blue |
| 3 | Greenish gray | Grayish green |
| 5 | Gray | Light gray |
| 10 | Dark gray | Light gray |

The chlorides of cobalt and copper prevent the blackening of hydrous cupric oxide at 100° in much the same manner as the corresponding sulphates. A slightly higher concentration is required and the oxide takes on a distinctly greener color than was observed in the presence of sulphates. Contrary to the observations of Blucher and Farnau, $MgCl_2$ does not prevent the darkening at 100° even when an amount equivalent to the copper oxide is present. It was thought that Blucher and Farnau might have used the sulphate instead of the chloride; but this was not the case since preliminary experiments carried out in the usual way with $MgSO_4$ showed that between 8 and 9 cc of N/10 solution in 10 cc was required to prevent darkening.

## Discussion of Results

At the outset of this investigation there seemed to be two possible explanations of the action of small quantities of salts in preventing the darkening of hydrous cupric oxide at 100°. The first of these, that the blue oxide is stabilized by adsorption of the hydrous oxides of the metals, was shown to be untenable in the light of the investigations described above. It is a significant fact however that the solutions of those salts which are most effective are hydrolyzed giving an acid reaction. The extent of this hydrolysis is increased by shaking with hydrous cupric oxide since Tommas[1] found that solutions of alkali salts like sodium chloride and sodium sulphate show an alkaline reaction after such treatment. This is due to the fact that hydrous cupric oxide adsorbs acids more strongly than bases thereby displacing to the right the equilibrium represented by the equation $2Na^{\bullet} + SO_4'' + 2H_2O \rightleftharpoons 2Na^{\bullet} + 2OH' + 2H^{\bullet} + SO_4''$, and leaving an excess of $OH'$ ions in the solution. This tendency of hydrous cupric oxide to adsorb acids more strongly than bases is in line with our conclusions that the effect of certain salts on gelatinous cupric oxide is not due to stabilization of the blue compound by adsorption of hydrous oxides. According to Spring and Lucion[2] and Mailhe[3] basic copper salts are formed in the presence of alkalies.

Having eliminated the hypothesis of stabilization by adsorption of hydrous oxides, we can consider the second hypothesis that the blue copper oxide reacts with certain salts forming basic copper salts that retain the blue color when heated to 100°. In support of this hypothesis, I have noted that the bright blue color of hydrous cupric oxide changes when heated with a suitable concentration of certain salts to a greenish blue, bluish green, or grayish green, the color varying slightly with the nature of the salt employed. Spring and

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[1] Comptes rendus, 92, 453 (1881).
[2] Loc. cit.
[3] Bull. Soc. chim. France, [3] 27, 167 (1902).

Lucion[1] investigated the action on blue cupric oxide of solutions containing an excess of sulphate and halogen salts; and was convinced that definite basic salts are formed to which he assigned the formulas: $Cu_2X_2.CuO.3H_2O$ where X = chlorine, bromine, or iodine; and $CuSO_4.2CuO.2H_2O$. As noted above Spring and Lucion claim that Tommasi also obtained basic salts of this character. While we cannot say with certainty that Spring and Lucion's products were definite basic salts,[2] there is no doubt that such compounds can be prepared. Thus Sabatier[3] prepared crystalline compounds having the formulas: $Cu(NO_3)_2.3Cu(OH)_2$; $CuCl_2.3Cu(OH)_2$; $CuBr_2.3Cu(OH)_2$; $Cu(ClO_3)_2.3Cu(OH)_2$; $CuS_2O_6.3Cu(OH)_2$; $CuSO_4.3Cu(OH)_2.H_2O$. Miller and Kenrick[4] by the aid of the phase rule established the existence of a basic chloride $CuCl_2.3CuO.2H_2O$ formed by adding N/5 KOH to N/5 $CuCl_2$ at 85°; and Werner[5] obtained basic salts of the general formula $[Cu(Cu(OH)_2)_3]X_2$. Although hydrous cupric oxide may react with an excess of certain salts, e. g., sulphates to form definite basic sulphates which do not darken at 100°, it seems to us altogether improbable that this explanation will account for our observations. It will be recalled that 0.50 cc of N/10 sulphates of Zn, Mn, Cu, Co, Al and Cr in 10 cc was found sufficient to prevent the hydrous oxide prepared from 10 cc of N/10 copper salt from turning black when heated. If all the sulphate reacted with the hydrous oxide to form a basic salt the composition would be represented by the formula $(CuO)_{20}.SO_4.XH_2O$. The improbability that such a compound should exist disproves the hypothesis that the entire precipitate is converted over to basic salt. On the other hand it does not eliminate the possibility that a film of protective basic salt forms on the surface of the oxide. This explanation is untenable since relatively large concentrations of alkali salts

[1] Zeit. anorg. Chem., **2**, 209 (1892).

[2] Cf. Young and Stearn: Jour. Am. Chem. Soc., **38**, 194 (1916).

[3] Comptes rendus, **125**, 101 (1887).

[4] Trans. Roy. Soc., Canada, [II] **8**, part 3, 35 (1901–2); Jour. Phys. Chem., **7**, 259 (1903).

[5] Ber. deutsch. chem. Ges., **40**, 444 (1917).

are not effective and Spring and Lucion found such solutions to act on the hydrous oxide in much the same way as solutions of salts of the heavier metals.

Since the experimental results fail to establish either the adsorption or the basic salt hypothesis we were led to conclude that the stability of the cupric oxide may be due in large measure to a change in the physical character of the compound in contact with certain salts. I have pointed out that the oxide can be prepared either in a gelatinous form which darkens on heating or in a denser, granular form that does not darken readily at 100°. That the gelatinous form actually does go over into a less bulky granular form when heated with dilute solutions of certain salts was noted at the outset of this investigation and I have called attention to it in an earlier paragraph. The significance of this transformation was not appreciated at the time; but it seems that therein lies the explanation of the stabilizing action of certain salts. In an earlier communication[1] I have pointed out that a gelatinous precipitate may be destroyed and the particles agglomerated into denser clumps in the presence of a substance having a slight solvent action. One might expect to get the necessary solvent action on hydrous cupric oxide with a solution having a small hydrogen ion concentration such as obtains with dilute solutions of salts of strong acids that undergo appreciable hydrolytic dissociation. In line with this we find that the blue oxide does not darken when heated with relatively low concentrations of the sulphates of Co, Cr, Al, Zn and Cu, and the chlorides of Co and Cu. Other similar salts are doubtless equally effective if one wishes to extend the list. In contrast to the behavior of the salts listed above are salts of the alkalies and the alkaline earths, sodium sulphate, magnesium chloride, and magnesium sulphate which are hydrolyzed much less and so are not effective in low concentrations. From Table VII it is seen that 10 cc of an N/200 solution of cupric sulphate is sufficient to prevent the darkening of the hydrous oxide obtained from 10 cc of N/10 copper salt. With

[1] Weiser: Jour. Phys. Chem., **24**, 306 (1920).

sulphates more highly hydrolyzed than cupric sulphate, the latter will tend to form so that it is not surprising that the sulphates of aluminium and chromium which are more hydrolyzed than cupric sulphate must be present in approximately the same concentration. It follows further that the concentration of sulphuric acid and of hydrochloric acid necessary to prevent darkening will be the same as that for the corresponding copper salts. This is verified by the results in Table XII and XIII.

TABLE XII

Experiments with Sulphuric Acid

| Time, min. | Observations | |
|---|---|---|
| | Hydrous CuO suspended in 10 cc solutions containing | |
| | 0.25 cc N/10 $H_2SO_4$ | 0.50 cc N/10 $H_2SO_4$ |
| 1 | Light greenish blue | Light greenish blue |
| 3 | Light greenish blue | Light greenish blue |
| 5 | Gray | Light greenish blue |
| 10 | Dark gray | Light greenish blue |

TABLE XIII

Experiments with Hydrochloric Acid

| Time, min. | Observations | | |
|---|---|---|---|
| | Hydrous CuO suspended in 10 cc solutions containing | | |
| | 0.25 cc N/10 HCl | 0.50 cc N/10 HCl | 0.75 cc N/10 HCl |
| 1 | Light greenish blue | Light greenish blue | Light greenish blue |
| 3 | Light greenish gray | Light grayish blue | Light bluish green |
| 5 | Gray | Light grayish green | Light bluish green |
| 10 | Dark gray | Light grayish green | Light bluish green |

In view of the change in physical character of the hydrous oxide which is not identical in all cases and the slight interaction of salt and oxide, it is not surprising that the final products should show slight variations in color.

In the nature of things it is quite evident that the free hydrogen ion concentration must vary at different stages of the process. N/200 $CuSO_4$ say, has a definite $H^{\cdot}$ ion concentration at the moment of formation; but when this solution is added to the hydrous oxide, a part of the $H^{\cdot}$ ions is adsorbed. Under constant conditions the amount adsorbed is constant; but the physical character of the precipitated oxide changes during the experiments from a highly gelatinous to a granular form and this affects the adsorbability of the compound. Wagner[1] has shown that when salts of aluminium, iron, etc. are hydrolyzed, the oxides adsorb the free acid; but that as the oxides age this adsorption decreases so much that practically all the acid is set free.[2] Gilbert[3] has observed that the physical character of cupric oxide has a marked influence on its adsorption of eosin.

It will be recalled that Harms, Spring and Lucion, and van Bemmelen found that solutions of alkali salt favor rather than retard the spontaneous dehydration of hydrous cupric oxide. In order to account for this, Kohlschütter and Tüscher assume that the salts cause a swelling or peptization of the precipitate. I have been unable to detect such an effect; on the contrary, the reverse appears to be the case from the moment the salt solution is brought in contact with the hydrous oxide. Kohlschütter and Tüscher cite no evidence to support their assumption and point out that the swelling cannot be detected because other factors come in. It is necessary to make some such assumption however, in order to explain the facts in terms of their theory of the mechanism of the dehydration process. As a matter of fact, the effect of salt solutions on the hydrous oxide is exactly what one would expect from the well-known properties of the oxide. It is known that the finely divided particles adsorb water sufficiently strongly to give a gelatinous precipitate but not so strongly but that spontaneous dehydration takes place very rapidly unless

[1] Monatsheft für Chemie., **34**, 95 (1913).
[2] Cf. Freundlich and Schucht: Zeit. phys. Chem., **10**, 290 (1906).
[3] Jour. Phys. Chem., **18**, 586 (1914).

the compound is kept at a low temperature. It is known also that the hydrous oxide adsorbs salts very strongly indeed so that they cannot be removed completely from the precipitate by even prolonged washing. In the presence of a salt solution then, the adsorption of the salt by the oxide decreases the capacity to adsorb water so that the loss of water is slightly more rapid in the presence than in the absence of a salt solution. It seems quite unnecessary to resort to the interesting but rather fantastic theory of Kohlschütter and Tüscher to account for this and other properties of hydrous cupric oxide.

## Summary

The results of this investigation may be summarized as follows:

1. No hydrates of cupric oxide are known with certainty. Since a hydrous oxide having approximately zero vapor pressure approaches the composition $CuO.H_2O$, it is usually concluded that a monohydrate exists. This conclusion is negatived by the fact that the anhydrous oxide does not take up water at ordinary temperatures in contact with water; but, on the contrary, the hydrous oxide loses water under these conditions. A "crystalline hydrate" has also been described but this has been found to consist of pseudo-crystals or granular particles that do not result from its own power of crystallization. Loss of water takes place more readily from the gelatinous oxide than from the granular because of the compact structure of the latter.

2. Highly dispersed hydrous cupric oxide is very light blue in color. The gelatinous oxide in mass possesses a characteristic clear blue color which alters slowly at room temperature but rapidly at higher temperatures, going through various shades of blue to green, brown and finally black. The continuous change in color is due to agglomeration of the particles which accompanies the spontaneous loss of water.

3. Blue gelatinous cupric oxide kept at 0° goes over spontaneously to a denser and bluer granular product. It is thus

possible to obtain any number of hydrous oxides that vary continuously in composition from $CuO. \pm 20H_2O$ (van Bemmelen) to $CuO. \pm H_2O$.

4. Hydrous cupric oxide adsorbs ions strongly. If shaken with solutions of neutral salts like NaCl or $Na_2SO_4$, hydrolysis takes place and the solution becomes distinctly alkaline owing to stronger adsorption of acid than of base.

5. On account of the strong adsorption of hydrous cupric oxide for certain ions the presence of certain salts frequently accelerates slightly the spontaneous loss of adsorbed water.

6. Hydrous cupric oxide may be heated to 100° without darkening in the presence of very small amounts of salts such as $MnSO_4$, $CoSO_4$, $Al_2(SO_4)_3$, $Cr_2SO_4$, $ZnSO_4$, $CuSO_4$, $ZnCl_2$ and $CuCl_2$.

7. The stability (absence of darkening) of hydrous cupric oxide at 100° in the presence of certain salts is not due to adsorption of the hydrous oxides of their metals as suggested by Bancroft and reaffirmed by Blucher and Farnau. The evidence against this stabilization theory is (1) that hydrous cupric oxides adsorb acids more strongly than bases, (2) that relatively high concentrations of the colloidal hydrous oxides are not effective and (3) that $CuSO_4$ is as effective as $MnSO_4$, $Cr_2SO_4$, etc. This latter observation is conclusive since it is inconceivable that adsorption of blue hydrous cupric oxide should stabilize blue hydrous cupric oxide.

8. The absence of darkening cannot be due to the formation of basic cupric salts since the effective concentration of electrolyte is so low that the ratio of oxide to sulphate in the salts could be no less than $\pm 20CuO : 1SO_4$, which is altogether improbable; and it is not due to the formation of a protecting film of basic salt since alkali salts which give basic salts under certain conditions hasten rather than retard the blackening.

9. Darkening of the hydrous oxide at 100° does not take place in the presence of suitable concentrations of certain salts owing to a change in the physical character from the highly gelatinous to the granular form of the oxide. Only

those salts which hydrolyze appreciably are effective in low concentrations since the slight solvent action of the $H^+$ ion destroys the gelatinous structure and the denser, granular modification which forms, loses water and darkens less readily than the loose voluminous mass.

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# STUDIES IN THE HYDROGENATION OF BENZENE

BY GREGG DOUGHERTY AND HUGH S. TAYLOR

## Introduction

In the field of contact catalysis, attention has recently been directed anew to the problem of reaction mechanism as revealed by kinetic studies. Especially in the field of catalytic hydrogenation is this true.

During the past two years, a number of researches dealing with this problem, more particularly the hydrogenation of liquid compounds, have been published with results not entirely in harmony with one another. Thus, Thomas[1] concludes that the addition of hydrogen at constant pressure to unsaturated glycerides, in the presence of nickel catalysts, is a reaction of the first order. The rate of saturation of the glyceride was also shown to be proportional to $p^{1.5}$ where $p$ is the hydrogen pressure. This result could be explained, according to Thomas, on the assumption that the hydrogen was absorbed by the nickel to an extent proportional to the square root of the partial pressure, a relationship which was established by Sieverts for the solubility of hydrogen in nickel. From the temperature coefficient of the rate of reaction, which was small, it was concluded that the reaction was similar to photochemical reactions and that olein molecules became activated by absorption of infra-red radiation.

This viewpoint concerning the action of a nickel catalyst towards hydrogen has been amplified subsequently by Lewis,[2] who also makes use of Sieverts' solubility data for hydrogen in nickel and other catalysts, to determine the relative catalytic activities of several metals. The theories developed by Thomas and Lewis in respect to catalytic hydrogenation overlook an important fact which has recently been established

[1] Thomas: Jour. Soc. Chem. Ind., **39**, 10T (1920).
[2] Lewis: Jour. Chem. Soc., **117**, 623 (1920).

experimentally in this laboratory, namely that *nickel of the form used by Sieverts in his measurements of solubility is catalytically inert.* Moreover, it has been shown by direct measurements, that the adsorption of hydrogen by a nickel catalyst in the neighborhood of 200° C is as much as 25 times greater than the hydrogen dissolved by nickel at such temperatures. Furthermore, the experimental evidence already obtained tends to show that the adsorptive power of an active nickel catalyst for hydrogen is not a simple square root function of the hydrogen pressure but that the adsorption isotherm is similar in nature to other adsorption isotherms, the variability with pressure being different at different absolute pressures.[1]

The researches of Armstrong and Hilditch[2] on the hydrogenation of liquid unsaturated compounds conflict with the results of Thomas in that the initial rate of hydrogenation according to their experiments is linear for as much as 40 to 80 percent of the total absorption of hydrogen, after which a falling away in reaction velocity is noted. The explanation offered by Armstrong and Hilditch that what was actually measured by them was the rate of decomposition by hydrogen of an unstable complex formed between nickel and the unsaturated compounds is shown to be in accord with their experimental facts. The deviation from linearity of initial action, obtained by others, was ascribed by Armstrong and Hilditch to the accumulation in the gaseous system of by-products exerting a definite influence upon the activity of the nickel and the speed of the reaction.

The experiments outlined in the present paper were started, prior to the publications of the foregoing investigations on the hydrogenations of unsaturated liquids, with the object of studying the mechanism of a strongly catalysed reaction, which was susceptible to reaction velocity measurement owing to the pressure change involved. Since the hy-

[1] See Taylor: Jour. Ind. Eng. Chem., **13**, 75 (1921); H. S. Taylor and R. M. Burns: Jour. Am. Chem. Soc., **43**, 1273 (1921).

[2] Amstrong and Hilditch: Proc. Roy. Soc., **96A**, 137, 322 (1919); **97A**, 259, 265 (1920); **98A**, 27 (1920).

drogenation of benzene vapor in the presence of nickel is accompanied by a volume diminution,

$$\underset{\text{(vapor)}}{C_6H_6} + 3H_2 = \underset{\text{(vapor)}}{C_6H_{12}}$$

the velocity of change might be followed manometrically. Moreover, the choice of reaction was determined by the definite nature of the reactants which could readily be obtained in a high state of purity, and, in moderate concentrations, existed in the vapor state at ordinary temperatures, a circumstance which facilitates manometric study. When carried out at low temperatures the reaction proceeds quantitatively in the direction of hexahydrobenzene formation without by-products due to side reactions. During the progress of the work opportunity was also taken to study the effect of certain possible gaseous impurities and, in addition, the effect of modifying the nature of the catalytic agent by the presence of other elements.

In a discussion of hydrogenation and dehydrogenation processes[1] Rideal and Taylor had suggested that the hydrogenation of benzene was doubtless an equilibrium process, the equilibrium constant for which

$$K = \frac{(C_6H_6)\ (H_2)^3}{(C_6H_{12})}$$

could probably be obtained at temperatures below 270° C, the temperature below which side reactions are unimportant. An application of the Nernst approximation formula to the reaction by Dr. R. N. Pease of this laboratory served to show that the equilibrium data as given by the formula were in close agreement with Sabatier's observations as to the temperatures of complete hydrogenation. Thus, the heat of reaction, Q, of the process is obtainable from the heats of formation of benzene and hexahydrobenzene:

$$C_6H_6 + 3H_2 = C_6H_{12} + Q.$$

[1] "Catalysis in Theory and Practice," page 207 (1919).

**The Nernst approximation formula:**

$$\log K = -\frac{Q}{4.571\,T} + 3(1.75)\log T + 3(1.6)$$

**gives the following values at the several temperatures under consideration:**

| T°C | 0 | 27 | 200 | 227 | 527 |
|---|---|---|---|---|---|
| log Kp | —16.91 | —13.85 | —1.21 | —0.03 | 8.17 |

**It is therefore apparent that the lower limit of temperature should give complete hydrogenation, whereas at temperatures just above 227° reversal of the process should have begun. Attempt has been made to follow quantitatively such an equilibrium change.**

## Experimental

*Apparatus.*—**The apparatus used is illustrated by Fig. 1. In the early experiments the source of hydrogen used was a Kipp generator containing zinc and sulphuric acid. The gas was passed, for purposes of purification, through concentrated sulphuric acid, then silver nitrate solution, over hot copper and**

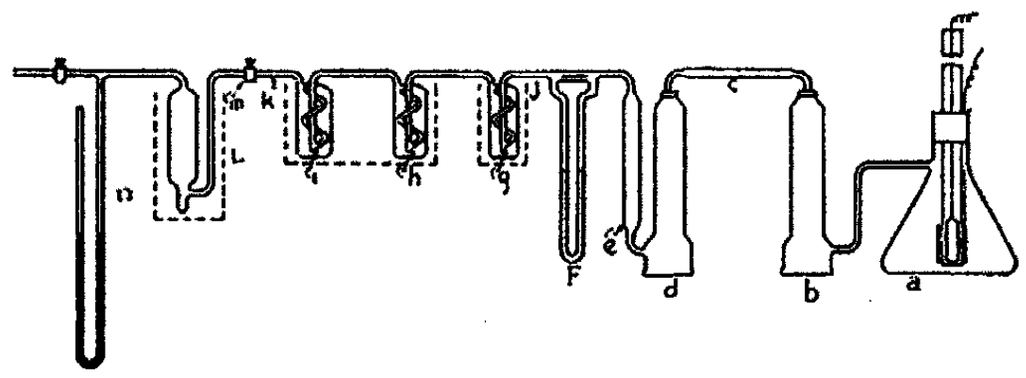



Fig. 1

**drying agents. In later experiments the hydrogen was generated in an electrolytic cell (a) containing a solution of potassium hydroxide and electrodes consisting of nickel sheet and wire. In this case the gas was first passed through a soda-lime tower (b) to eliminate any carbon dioxide, then through**

a quartz tube (c) containing palladized asbestos and heated to a dull red to convert any oxygen present to water, next through another soda lime tower (d) and finally through a glass tube (e) containing phosphorus pentoxide. No difference in the experimental results, which might be attributed to the different sources of hydrogen, has been noted. Since it was necessary to have the same rate of gas flow in all the experiments, a flow meter (f) was interposed in the path of the hydrogen. From the flow meter, the gas was passed into a spiral wash bottle (g) containing pure dry benzene. This bottle was surrounded by a water bath kept at a temperature from 10 to 20 degrees higher than that at which it was desired to saturate the hydrogen with benzene vapor. The hydrogen was next passed through two wash bottles (hi), similar to the first, containing benzene and placed in a thermostat which was maintained at the desired saturation temperature and was kept constant to 0.1° C. With this arrangement and, knowing the atmospheric pressure, the specific gravity of the liquid in the generator, and the head of liquid in the generator both when hydrogen was passing through the benzene and when through the by-pass it was possible, with the aid of the vapor pressure data on benzene at various temperatures, to calculate the ratio of benzene to hydrogen in the gas stream after it emerged from the wash bottles in the constant temperature bath. Care was used to keep the glass tube (k), beyond this point, at such a temperature that the benzene vapor would not condense. The gas mixture was finally passed into the reaction chamber (l) containing the catalyst and which was maintained at a temperature constant to 0.5° C by means of a gas heated air bath or an electrically heated stove. The catalyst consisted of finely divided nickel spread on a porous support. This was prepared by causing small pieces of diatomite brick (mesh 4–16) to soak up a solution composed of nickel nitrate with a little nitric acid until the weight of the added nickel was equivalent to 11.11 percent of the weight of the brick. The mass was dried and heated until fumes of oxides of nitrogen could no longer be detected, and then placed

in the reaction chamber and reduced *in situ*. The reduction began at 110–120° C but it was necessary to raise the temperature to 275–300° to transform the oxide completely to the metal.

*Procedure.*—In making a run, a given mixture of benzene vapor and hydrogen was passed through the catalyst chamber, which was maintained at a definite temperature, until the chamber was filled. The stopcock (m) was then closed, the open end of the apparatus sealed very rapidly, and the rate of diminution in pressure noted by means of the manometer (n) until the reaction was complete. Of course, with this apparatus, it was necessary to work at temperatures at which the reaction was comparatively slow. The length of time necessary for passage of the gases, to insure complete filling of the reaction chamber, was determined experimentally. The hydrogen and benzene vapor were passed through the reaction system for a length of time obviously in excess of that needed for filling, say for 2 hours (gas stream 20 cc per minute and capacity of vessel 50–75 cc); the total diminution in pressure was then noted after the apparatus was closed and the reaction allowed to go to completion. With succeeding runs the gases were passed for successively shorter lengths of time, until the minimum time of passage necessary to give the end-point, reached in the case of the 2 hour passage, was obtained.

Owing to variation in the activity of the catalyst, it was necessary to exercise great care in carrying out experiments where comparisons were to be made. By observing one catalyst over a long period of time it was found that, in general, starting with a fresh catalyst, there was an increase of activity at first which extended to a certain point, after which for a considerable period there was diminution to a second point, beyond which there were fluctuations following no fixed course. However, it was possible, by using great care in keeping parallel conditions in matters such as sweeping off the catalyst with hydrogen after experiments, to obtain six or even seven runs in succession which checked fairly well. This is shown by the following figures which were obtained by sealing up identical

mixtures of hydrogen and benzene vapor and observing the rate of the diminution of pressure when the reaction was allowed to proceed at 100° C.

| No. of Run | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| D of P, 1st 5 minutes, in cm | 28.7 | 27.5 | 28.2 | 29.8 |
| D of P, 1st 10 minutes in cm | 46.8 | 45.9 | 46.8 | 48.4 |
| **No. of Run** | **5** | **6** | **7** | **8** |
| D of P, 1st 5 minutes in cm | 28.1 | 31.7 | 28.4 | 27.4 |
| D of P, 1st 10 minutes in cm | 46.4 | 50.0 | 46.9 | 46.0 |

When experiments at 100° C were made successively and the products of the reaction were not removed by sweeping out with hydrogen after each, there was a gradual slowing up from run to run. This is shown by the following figures:

| Order in which runs were made | % of reaction complete in 5 minutes | % in 10 minutes | % in 15 minutes | % in 20 minutes | % in 49 minutes |
|---|---|---|---|---|---|
| 1 | 11 | 20 | 30 | 38 | 80 |
| 2 | 12 | 22 | 29 | 37 | 76 |
| 3 | 7 | 18 | 29 | 33 | 68 |
| 4 | 5 | 17 | 26 | — | — |

This effect was noticeable only at comparatively low temperatures and disappeared at higher temperatures. In the neighborhood of 180° C the reaction could be continued for hours with complete conversion of the benzene and hydrogen to hexahydrobenzene, with no sign of diminished activity.

While the final diminution in pressure, caused by allowing a given mixture of hydrogen and benzene to react to completion, was a reproducible quantity, it was found that the reduction in pressure was far in excess of that possible if only the quantity of benzene and hydrogen in the gas space had re-

acted. For example, when the hydrogen was passed through the benzene at 25° C at a pressure slightly in excess of atmospheric, say 762 mm, it could be calculated that the resulting mixture contained its components in the ratio by volume of 93.3/762 of benzene to 668.7/762 of hydrogen. For convenience let us assume that the total free space of the catalyst chamber amounted to 100 cc. This would be filled by 12.24 cc of benzene vapor and 87.75 cc of hydrogen and, allowing this to react according to the equation representing the formation of hexahydrobenzene, the volume at completion of the reaction should be 63.27/100 of the original volume or, at constant volume, we should have 63.27/100 of the original pressure, that is, about 482 mm. Actually, when a run with such a mixture was made, the final pressure was only some 120 mm. Evidently the reaction not only took place between the amounts of hydrogen and benzene in the free space, but large quantities of the reactants must have been adsorbed by the catalyst, support and walls of the chamber, and these also took part in the reaction. This, however, does not explain the total deviation from the theoretical diminution in pressure as the following considerations show. A saturation of hydrogen with benzene at 25° C would give 93.3 mm of benzene vapor and 668.7 mm of hydrogen. Assuming, however, sufficient benzene on the catalyst surface to react with all the hydrogen present, it is obvious that 668.7/3 or 222.9 mm represent the pressure of hexahydrobenzene which should have been produced. Actually, the diminution in pressure was even greater than this, since experimental observation recorded a final pressure in such a case of 120 mm. It is evident therefore that, in addition to the diminution in pressure due to volume change in the reaction, the pressure drop also arose from adsorption of the reaction product, hexahydrobenzene. That it was not due to adsorption of the reactants, after the closing of the reaction vessel, is almost certain in view of the rapidity with which adsorption equilibria have been shown to establish themselves in all cases of adsorption by metallic catalysts studied in this laboratory. That the excess pressure

was not accounted for by adsorption of hydrogen and benzene from the free space in the apparatus on the catalyst after the apparatus was closed, is further confirmed by the fact that the same end-point, as regards pressure, was reached when the reactants were initially passed over the catalyst for widely varying periods of time.

| | | | |
|---|---|---|---|
| Time of passage in hours | 3 | 0.5 | 0.25 |
| Final reduction of pressure in cm | 65 | 65.6 | 64.7 |

During the passage of the gases preliminary to a run, the catalyst could become saturated at the temperature with hydrogen and benzene, but not with hexahydrobenzene since, although being formed slowly all the time, it was continuously swept off by the other gases. Further evidence that benzene was soaked up by the catalyst well in excess of the amount needed to react with all the hydrogen was given by an experiment in which hydrogen, saturated with benzene vapor at 22° C, was passed through the catalyst chamber for $1^1/_2$ hours. The apparatus was then sealed and the reaction allowed to proceed at 100° C. The following results were obtained:

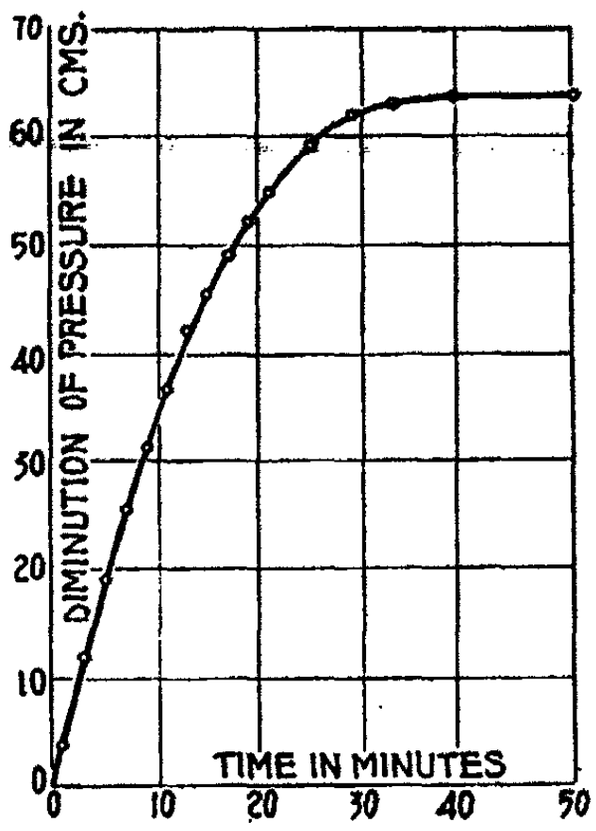
(T is time in minutes; D of P is diminution of pressure in cm)

| T | 1 | 3 | 5 | 7 | 9 | 11 |
|---|---|---|---|---|---|---|
| D of P | 2.7 | 17.8 | 31.2 | 42.5 | 50.3 | 56.1 |
| T | 12 | 13 | 15 | 17 | 19 | 25 |
| D of P | 57.8 | 59.2 | 60.7 | 61.2 | 61.6 | 61.6 |

After the end-point (61.6 cm) had been reached, the apparatus was opened and hydrogen run in rapidly until the pressure was again atmospheric and the bulb was again sealed. There was further reduction in pressure as follows:

| T | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| D of P | 5.8 | 9.3 | 10.7 | 10.9 | 11.2 |

This further reduction is a measure of the surplus benzene in the reaction vessel. Not knowing the actual rate of the hydrogen flow or the volume of the free space in the catalyst chamber, it was not possible to use these figures actually to calculate the amount of benzene present in the chamber, but qualitatively the demonstration is decisive.



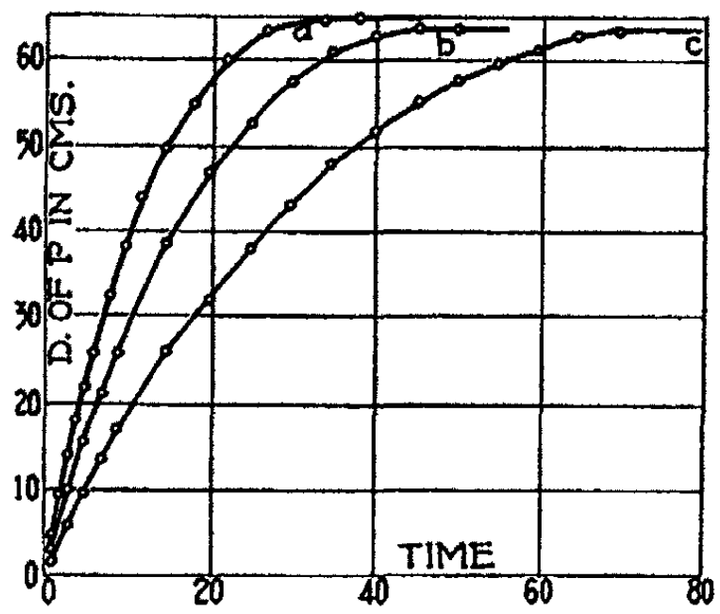

Curve No. 1
Catalyst at 100°

These facts concerning the abnormal limit of the reaction, as measured in this way, lead to the conclusion that the excess diminution in pressure was largely due to strong adsorption of hexahydrobenzene on the catalyst as it was formed. It is qualitative evidence that the hexahydrobenzene is at least as strongly adsorbed by the nickel catalyst and support as benzene. Any results, from one of the experiments recorded in changes of pressure with time, must be a measure, then, of several effects. The one predominating factor is the actual reduction in volume due to the reaction which, at the temperature chosen for study, is slow in comparison with the rate of adsorption of reactants and products.

Using the above method of experiment and plotting diminution of pressure against time, smooth curves were obtained. For example, Curve No. 1 illustrates the results of a run in which hydrogen, saturated with benzene at 25° C, was passed over the catalyst at 100° C. The apparatus was then closed and the reaction allowed to proceed.

**Influence of Temperature on the Reaction**

No attempts were made using the above static method (static in contrast to flow method described later) to determine the minimum temperature at which the reaction could be induced. Some data on this point, however, were obtained by the flow method. Sabatier gives 70° C as the temperature at which reduction becomes marked. We found that, with a catalyst carefully prepared from nickel oxide by reducing at as low a temperature as possible, we were able to bring about hydrogenation at lower temperatures. For instance, at 60° C a mixture of the reactants in one case gave a conversion of about 68 percent of the theoretical in a single passage. The minimum temperature required is, however, a function of the activity of the nickel catalyst, and the yield is dependent on this and the rate at which the gases are passed over the catalyst. In general, reduction of the nickel oxide at a minimum temperature gives a catalyst of greater activity than one reduced from the oxide at high temperatures.




Curves No. 2

a = 100°
b = 90°
c = 80°

In endeavoring to determine the influence of temperature on the reaction, using the static method, identical mixtures of benzene vapor and hydrogen were passed for equal periods of time over the catalyst when maintained at different temperatures. The apparatus was then closed and the diminution of pressure with time noted. Due to the frequent variations in the activity of the catalyst, it was necessary in these experiments to make sure that the catalyst was holding constant

over a number of runs at different temperatures. To do this a reference temperature of 100° C was chosen and, before and after each run at some other temperature, a run at 100° C was made. If the two runs at 100° checked, the run at the other temperature was held to be capable of fair comparison with the 100° runs, and also with other runs which had occurred between similar 100° runs. If the experiments at 100° did not check, the results at the other temperature were discarded and the experiment repeated. Results obtained in this way at 80°, 90°, and 100° C are shown on Curves No. 2.

The striking feature of the experiments that we have carried out with benzene-hydrogen mixtures at temperatures below 100° C is the initial linearity of the decrease in pressure with time. The figures for dP/dT at 80° and 90° are given below.

80° C

| Time in minutes | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| D of P in cm | 1.6 | 3.9 | 5.9 | 7.6 | 9.6 | 11.7 |
| dP/dT | 1.6 | 1.9 | 1.9 | 1.9 | 1.9 | 1.9 |

| Time in minutes | 7 | 8 | 9 | 10 | 15 |
|---|---|---|---|---|---|
| D of P in cm | 13.6 | 15.3 | 17.1 | 18.6 | 26.1 |
| dP/dT | 1.9 | 1.9 | 1.9 | 1.8 | 1.7 |

90° C

| Time | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| D of P | 3 | 6.3 | 10.1 | 12.7 | 15.6 | 17.4 |
| dP/dT | 3 | 3.1 | 3.3 | 3.2 | 3.1 | 2.9 |

| Time | 7 | 8 | 9 | 10 | 15 |
|---|---|---|---|---|---|
| D of P | 21.1 | 23.6 | 25.9 | 28.2 | 38.7 |
| dP/dT | 3.0 | 2.9 | 2.8 | 2.8 | 2.5 |

It will be noted that the linearity extends, in each case, over a period covering about the same fraction of the total pressure change. This stage of the reaction would be reached at higher temperatures, 100° C or above, very soon after the start; and for this reason, in addition to the fact that the experimental error is greatest at the beginning, experiments made with a very active catalyst might not show the region of linearity at all. This turns out to be the fact. The experiments at 100° C with an active catalyst show only a small linear range or none at all, while those made using a relatively inactive catalyst continue to exhibit the region of linearity over approximately one-third of the total pressure change.

This observation constitutes a most important factor in regard to conclusions as to the mechanism of the reaction. It is obvious that such an experimental fact is quite inconsistent with a reaction mechanism based upon the stoichiometric equation, which would demand a rate of reaction directly proportional to the cube of the hydrogen concentration and to the partial pressure of the benzene vapor. The most cursory mathematical analysis shows that such a mechanism is quite irreconcilable with the experimental measurements. Indeed these results in their initial period are most readily explainable on the assumption that the rate of reaction over such a period is practically independent of the hydrogen pressure. Now this conclusion is in good agreement with the experimental studies of Taylor and Burns on the adsorption of hydrogen by a nickel catalyst, in which it has been shown that the concentration of hydrogen on the surface of a nickel catalyst at 25° C is practically independent of the hydrogen pressure between the limits of 260 mm and 760 mm. At higher temperatures it is to be anticipated that the region would be more restricted. If the hydrogenation occurs at the surface of the catalyst it should therefore be, at the outset, when hydrogen pressures are relatively high, independent of the hydrogen pressures in the gas phase. Similarly the relatively sudden deviation from linearity at lower partial pressures of the gas phase is qualitatively, at least, in agree-

ment with the rapid drop in adsorption of hydrogen by nickel at 25° C when the hydrogen pressure falls below 250 mm, as also experimentally verified by Taylor and Burns. In the kinetic study the rôle played by the benzene vapor is a complicating factor, of a minor order, however, owing to the low partial pressures used and also as a result of the high concentration of benzene on the nickel catalyst surface. This is, as has already been pointed out, considerably more than sufficient to bring about the reaction of all the hydrogen in our reaction system. Since the reduction in partial pressure of benzene would tend to reduce the concentration of that substance at the nickel surface, the qualitative effect would be to cause a diminution of $dP/dT$ with progress of the reaction. Finally, as the experimental results already cited have shown, the reaction product, hexahydrobenzene, is markedly adsorbed under reaction conditions. Therefore a certain effect due to the covering of the nickel catalyst might also be anticipated, the tendency of which would be to overcome the constancy of the pressure change with time, and which would become the more pronounced the further the reaction proceeded and the lower the reaction temperature.

The general conclusion from these reaction velocity experiments may therefore be stated as follows: (*a*) The reaction does not occur at all according to the stoichiometric equation. (*b*) It does occur in a manner which indicates reaction only at the catalyst surface, and at rates governed by the ratio of distribution of the several reactants and product between the gas phase and the nickel surface, which distribution ratios are specific to the catalytic material chosen. Evidence supporting this view-point as far as the influence of benzene vapor is concerned will now be considered.

In most of the experiments the hydrogen was saturated with benzene at 25° C, at which temperature benzene has a saturation pressure of 93.3 mm. Changing the proportions of hydrogen and benzene should have an effect on the reaction velocity unless the concentration of benzene on the catalyst is independent of the partial pressure of benzene in the space

around it, through the pressure range at the temperature of the experiment. To get information concerning this, hydrogen, saturated with benzene vapor at 35° C where the saturation pressure is 149.66 mm, was allowed to react in the closed system. The results obtained were compared with the runs at 25° C (benzene temperature) and it was found that the different mixtures gave the same reaction velocity, as measured this way, within the experimental error. This is shown in the following table where the first ten minutes of two pairs of runs are given. Experiments 24 and 29 were allowed to go to completion and there was no appreciable difference between the two during the remainder of the runs. The results would lead one to believe that the velocity of the reaction was independent of the concentration of benzene in the free space around the catalyst, and that the concentration of the benzene on the catalyst was at least not directly proportional to the partial pressure of the vapor in the free space. If this were not so, marked differences in the figures obtained in the two sets of experiments would be expected.

Catalyst at 100°

| Run No. | Saturation temperature of benzene | Diminution of pressure after | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1 min. | 3 min. | 5 min. | 7 min. | 9 min. | 10 min. |
| 24 | 35° | 4.6 | 13.4 | 21.7 | 29.6 | 35.9 | 38.8 |
| 25 | 25° | 4.8 | 13.9 | 21.8 | 29.0 | 35.5 | 38.3 |
| 26 | 35° | 4.7 | 14.1 | 22.4 | 29.8 | 36.1 | 38.3 |
| 29 | 25° | 4.8 | 14.1 | 21.8 | 29.3 | 35.7 | 38.3 |

### Effect of Carbon Monoxide in the Reaction Mixture

Carbon monoxide to the extent of 2.3–2.4 percent of the volume of hydrogen present was added to the reaction mixture, and the whole sealed up in the catalyst chamber and allowed to react. The following results were obtained. The catalyst temperature was 100° in all the experiments.

**Run No. 36 was made with CO present, 35, 36, 37, 38 without CO**

| Run No. | D of P in cm after | | | | |
|---|---|---|---|---|---|
| | 1 min. | 3 min. | 5 min. | 10 min. | 15 min. |
| 35 | 5.7 | 17.6 | 27.4 | 45.5 | 56.3 |
| 36 | 2.1 | 6.3 | 10.0 | 17.5 | 23.7 |
| 37 | 3.7 | 11.5 | 18.8 | 33.1 | — |
| 38 | 7.4 | 19.9 | 30.1 | 48.5 | 58.9 |

| Run No. | D of P in cm after | | | | |
|---|---|---|---|---|---|
| | 20 min. | 25 min. | 30 min. | 50 min. | 100 min. |
| 35 | 62.1 | 64.0 | — | — | — |
| 36 | 29.0 | 34.0 | 38.7 | 51.6 | 64.0 |
| 37 | — | — | — | — | — |
| 38 | 63.3 | — | — | — | — |

The depressing effect of the CO can be observed in No. 36. On cleaning off the catalyst by passing hydrogen over it for 15 minutes at 300° and then making a run with benzene and hydrogen alone, the velocity was still below normal (No. 37). However, when the cleaning procedure was repeated and another run made with hydrogen and benzene, the reactivity was greater (No. 38) than in the experiments made before carbon monoxide was added (No. 35). Thus it would appear as if the carbon monoxide, although a poison as long as present on the catalyst, had the effect of leaving its surface in a rejuvenated condition. The ordinary benzene-hydrogen runs following No. 38 showed a gradual return to a slower speed, the 8th consecutive one after No. 38, that is No. 46 given below in part, checked very well with No. 35.

| Time, minutes | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| D of P in cm | 5.7 | 12.2 | 17.6 | 22.6 | 27.4 |
| **Time, minutes** | **6** | **7** | **8** | **9** | **10** |
| D of P in cm | 31.8 | 36.1 | 39.0 | 42.9 | 45.6 |

The carbon monoxide run gave even a slightly greater total diminution in pressure than the normal runs. This would lead one to believe that, in whatever state the carbon monoxide existed in the reaction chamber, its volume was very small. Further, even if it were adsorbed on the surface of the catalyst, its presence did not seem to interfere markedly with the adsorption of the reactants and the resultant. The relatively large amounts of catalyst used in these experiments by the static method may account for the small influence of carbon monoxide on these several factors. Indication showed that the influence of carbon monoxide in small amounts (2%) on the rate of hydrogenation was less marked at temperatures above 100°. In large quantities, however (around 50%), the gas completely stopped the reaction at 180° when the flow method was used. Usually, immediately after the experiments with carbon monoxide, the apparatus was swept out with hydrogen without allowing the apparatus to cool appreciably. In fact, as a rule, on completing a run the temperature was raised rapidly to 300° while hydrogen was passed over the catalyst. In these cases no deposition of nickel on the warm parts of the apparatus was ever noted. However, on one occasion, the apparatus was not swept out immediately after the run with carbon monoxide, but was allowed to cool to room temperature and stood for some time. On starting up again a black deposit formed on the interior of some of the glass tubing which was heated only to 60°. Some of this black deposit was tested qualitatively for nickel and was found to be that metal, evidently from nickel carbonyl. When reaction temperatures of 100° and upwards were used, no difficulties of this type were met.

### Effect of Water Vapor on the Velocity

In order to ascertain if water vapor had any effect on the velocity of the reaction, a reaction mixture was prepared by first saturating the hydrogen with benzene at 25° and then adding a small amount of water vapor (about 2% of the volume of the hydrogen). This was allowed to fill the catalyst

chamber which was then closed, maintained at 100° and the diminution of pressure noted. Reference runs, using only hydrogen and benzene, were made before and after the water vapor experiments. Of these only the one carried out immediately before the water vapor run is noted below.

Without water vapor

| Time | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| D of P in cm | 5.7 | 11.6 | 16.7 | 21.5 | 26.3 |
| Time | 6 | 7 | 8 | 9 | 10 |
| D of P in cm | 30.4 | 33.9 | 37.4 | 40.7 | 43.3 |

With water vapor

| Time | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| D of P | 6.0 | 11.2 | 15.9 | 20.4 | 24.6 |
| Time | 6 | 7 | 8 | 9 | 10 |
| D of P | 28.2 | 31.9 | 34.4 | 37.7 | 40.5 |

It will be noted that the depressing effect is small and not nearly so marked as in the case of the carbon monoxide poisoning.

### Comparison of a Nickel Catalyst with a Copper-Nickel Catalyst

A catalyst composed of 90% nickel and 10% copper was prepared and attempts were made to compare its efficiency with that of the ordinary nickel catalyst in bringing about the hydrogenation of benzene. It was found, however, that, due to the varying activity of each, it was impossible to get any certain basis for comparison. Our results showed that the efficiency of both catalysts was of the same general order. It was found possible to make one nickel-copper catalyst that

produced a greater velocity of reaction than a given nickel catalyst; it was also possible to prepare one, precisely in the same manner as the first, that was less active. Examples of runs with two copper-nickel catalysts are given below. The temperature in each case was 100° C.

| Run No. | Time | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| 1 | D of P | 5.9 | 11.8 | 17.1 | 22.3 | 27.4 |
| Run No. | Time | 6 | 7 | 8 | 9 | 10 |
| 1 | D of P | 32.0 | 36.3 | 39.8 | 42.3 | 44.8 |

| Run No. | Time | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| 2 | D of P | 9.0 | 16.5 | 23.7 | 29.5 | 34.5 |
| Run No. | Time | 6 | 7 | 8 | 9 | 10 |
| 2 | D of P | 38.9 | 42.8 | 43.9 | 45.6 | 47.1 |

## Equilibrium Study

The apparatus used in the flow-method work for equilibrium measurements is illustrated in Fig. 2. The method of generating, purifying, and drying the hydrogen was the same as in the first experimental work. From the last drying tube,

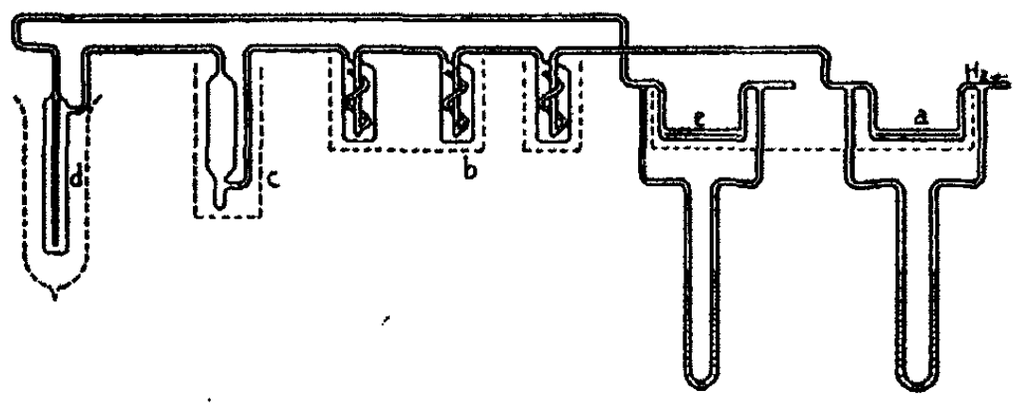


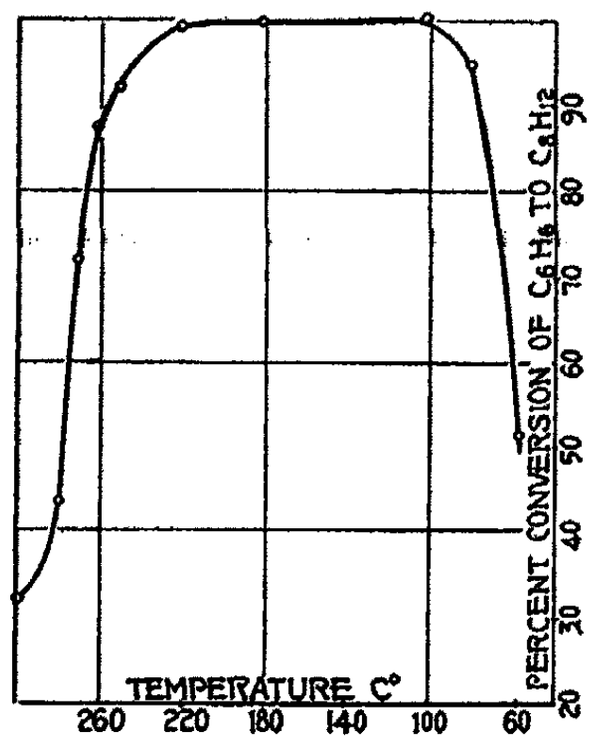

Fig. 2

the gas was passed through a flow meter (a), carefully calibrated in position, both by aspirating water from a measuring flask, and by means of an ammeter used in connection with the electrolytic cell in which the hydrogen was generated. The

capillary of the flow meter was submerged in a constant temperature bath. From this flow meter the gas passed through the same arrangement of benzene-filled, spiral wash bottles (b) as used in the first method. The resulting mixture of hydrogen and benzene vapor then passed into the catalyst chamber (c), the temperature of which was controlled by an electrically heated stove. The exit tube of the reaction chamber connected with a larger, vertical glass tube (d) which was placed in a Dewar flask containing solid carbon dioxide. The products issuing from the reaction chamber passed through this cold space and the unconverted benzene and the hexahydrobenzene were condensed out. The temperature of —78° C is sufficiently low effectively to remove all the benzene and hexahydrobenzene vapors. The hydrogen passed from the cold tube through another flow meter (e) which was calibrated like the first and maintained at the same temperature by keeping it in the same constant temperature bath. It was possible then to calculate the amount of reduction taking place during the passage of the reaction mixture by measuring the quantity of hydrogen entering the reaction vessel and the quantity emerging from it. Due to a rather large amount of free space in the apparatus, and also because of the quantity of catalytic material used which had to be saturated with the respective gases, it was necessary to have the runs continue over quite a period of time to obtain constant readings on the flow meters. This was particularly true when changing from one hydrogen-benzene concentration to another. As a rule, when using a hydrogen flow of about 25 or 30 cc per minute, one-half to an hour would elapse before constant readings were obtained. When constancy was reached, readings were taken at five minute intervals over a period which averaged at least an hour. The plan of procedure was to make experiments with three different benzene-hydrogen mixtures. Each of these was passed over the catalyst at ten different temperatures, and at different speeds.

Below 150° C the results obtained were extremely variable from run to run although during a given experiment con-

stancy of readings was easily obtained. Above 150°, however, the difficulties encountered at lower temperatures disappeared and fair reproducibility was attained. At low temperatures the amount of exit hydrogen indicated incomplete reaction but from 100° onwards, until temperatures beyond 200° were reached, hydrogenation of the benzene was complete. The curve No. 3 given indicates the mean results of a series of experiments at different temperatures on a 90–10% hydrogen-benzene mixture, and at a rate of passage of 30 cc per minute. The flat maximum indicates the region of complete reaction. The range of this flat maximum is, however, obviously dependent on the rate of gas passage. Beyond 220° C there is a rapid decrease in the amount of hexahydrobenzene formed due to the shifting of the equilibrium towards the side of the benzene and hydrogen. The rate of decrease seems to change abruptly in the neighborhood of 300°. This is shown by all curves constructed from data from several different experiments. This may be due to the appearance of side reactions at this point, although decomposition of benzene in such a way as to yield gaseous products would tend to straighten the curve in the opposite direction.




Curve No. 3

The interesting part of the curve (3) is the region between 220° and 280°. Since the flat maximum section indicates a conversion of 100%, and since there are no grounds to suspect that the temperature coefficient changes its sign after this point, it is obvious that the region 220–280° should furnish

data for equilibrium calculations. Such calculations were made using the stoichiometric equation for the reaction:

$$C_6H_6 + 3H_2 = C_6H_{12}$$

$$\frac{C_{C_6H_{12}}}{C_{C_6H_6} \cdot C^3_{H_2}} = K$$

but no constant was obtained. On the other hand, the figures inserted in an equilibrium equation where only unit concentration of the hydrogen appeared gave rather good constants. The following figures were obtained when different mixtures of benzene and hydrogen were passed over the catalyst at 250°, and the results calculated in partial pressures.

| % Hydrogen | % Benzene | Constant with $C^3_{H_2}$ | Constant with $C_{H_2}$ |
|---|---|---|---|
| 85 | 15 | 29.94 | 15.64 |
| 87.8 | 12.2 | 23.01 | 15.23 |
| 89.4 | 10.6 | 21.41 | 15.37 |

The following were obtained at 260° C.

| % Hydrogen | % Benzene | Constant with $C^3_{H_2}$ | Constant with $C_{H_2}$ |
|---|---|---|---|
| 84.34 | 15.65 | 15.36 | 8.32 |
| 87.65 | 12.35 | 12.43 | 8.31 |

A third figure was obtained at 260° with 91.9% hydrogen and 9.9% benzene which was 8.29. However, since it represents an average of three rather widely differing results, too much emphasis should not be placed on its agreement with the others.

The following were obtained at 280° C

| % Hydrogen | % Benzene | Constant with $C^3_{H_2}$ | Constant with $C_{H_2}$ |
|---|---|---|---|
| 84.4 | 15.6 | 1.244 | .811 |
| 87.7 | 12.3 | 1.223 | .890 |
| 90.2 | 9.8 | 1.120 | .880 |

A set of runs, using the same mixture of benzene and hydrogen but different rates of flow over the catalyst, gave the following results for the constant with a single hydrogen concentration.

| Gas flow, cc per minute | K with $C_{H_2}$ |
|---|---|
| 24.94 | .881 |
| 29.38 | .873 |
| 31.57 | .890 |

These last simply indicate that the reaction had gone as far as possible at the highest rate of flow (31.57 cc per minute) and that no change could be brought about by leaving the reactants on the catalyst for a longer time.

Although the experimental error in the above work is quite large, it favors the significance of the results that nothing like such concordance could be obtained when the cube of the hydrogen concentration was used in the equilibrium equation. It will be noticed, in addition, that there is a distinct drift in the figures for the cube of the hydrogen concentration, the constant decreasing with decrease of benzene concentration, but this does not occur in the results for the single hydrogen concentration. In the figures at 280° with the cube of the hydrogen concentration, the average deviation from the mean is not much larger than with the constant where the single concentration was used, but a distinct drift does appear. When a zero order in respect to hydrogen concentration is assumed, a slight drift in the other direction is indicated. It is not possible from the experiments cited to state whether this is real or not. To ascertain this an extension of experiments to wider variations of hydrogen concentrations would be necessary, or alternatively, a study of hydrogen adsorption isotherms at these temperatures.

The results obtained confirm, however, the reaction velocity experiments in that equations involving the cube of the hydrogen concentration in the gas phase will obviously not satisfy the experimental results. They are further proof that the reaction is occurring at the catalyst surface, at which

presumably an equilibrium is set up governed by the concentrations of the reacting species at the surface, which concentrations may, as previously pointed out, be largely independent of the concentrations in the gas phase. The experiments cited demonstrate the inherent difficulties in the determination of equilibria in catalysed reactions in which one or more of the reacting species is strongly adsorbed on the surface of the catalytic agent. We believe that difficulties of this kind are the cause of anomalies recently observed by Rideal[1] in the determination of the equilibrium position in the dehydrogenation of ethyl alcohol in the presence of metal catalysts. Only when low partial pressures prevailed were concordant equilibrium values obtained. At such pressures the distribution of the reacting species between the catalyst surface and gas phase is more nearly a linear function of the partial pressure.

## Summary

1. An attempt has been made to gain some insight, by kinetic measurements, into the mechanism of the catalytic reduction of benzene to hexahydrobenzene. The results indicate that the reaction does not occur at all according to the stoichiometric equation, as calculated from gas concentrations, but at rates governed by the distribution of the reacting materials between the catalyst and the gas phase.

2. The trend of the reaction with change of temperature has been studied, and equilibrium values at the higher temperatures have been calculated. The results on the latter show that apparent equilibria in the gas phase, as measured in this way, do not necessarily coincide with those which would be expected on the basis of the ordinary equation representing the reaction.

3. Information has been obtained regarding the poisoning effect of water vapor, carbon monoxide, and hexahydrobenzene on the reaction. Water vapor in small amounts, up to 2% of the hydrogen volume used in the reaction mixture, had only a slight depressing effect on the reaction velocity.

[1] Rideal: Proc. Roy. Soc., 99A, 153 (1921).

Carbon monoxide in small amounts, about 2% of the hydrogen volume, had a very marked poisoning effect, particularly at low temperatures of 100° or under. As the reaction temperature was raised the poisoning was less noticeable. In large quantities, however, around 50% of carbon monoxide, the reaction was completely stopped at 180°. Hexahydrobenzene, at low temperature, 100° or less, had a depressing effect on the reaction velocity. This effect disappeared at higher temperatures, in the neighborhood of 180°.

4. The observations show that it is necessary to use great care in making comparative measurements on account of the variability of the nickel catalyst. It was found that different catalysts, although prepared exactly in the same manner, might have quite different activities, and that the activity of a given catalyst changed markedly with time and use. The observations also show that quantitative measurements on a reaction of this kind are difficult due to the fact that the actual reactant concentrations, on which the velocity of the reaction depends, are those on the catalyst surface; and these concentrations may be independent of, or bear a varying relation to, the reactant concentrations in the gas phase.

5 From experiments at 80° and 90° C it is shown that the temperature coefficient of the reaction measured is approximately 3.1/1.9 or 1.65 per 10 degree rise. This is evidently the temperature coefficient of a chemical reaction as opposed to that of a diffusion process.

*Princeton University*

# THE SCATTERING OF LIGHT BY DUST-FREE LIQUIDS—CHANGES WITH TEMPERATURE[1]

BY W. H. MARTIN AND S. LEHRMAN

All the experimental work recently done on light-scattering in homogeneous media[2] appears to favor the Einstein-Smoluchowski theory of density fluctuations as being in best agreement with the observed results in all kinds of media.

Einstein's result is:[3]

$$\frac{Ir^2}{EV} = \frac{RT\pi^2\beta\,(\mu^2-1)^2\,(\mu^2+2)^2}{18N\lambda^4} \qquad (1)$$

where

I is the illumination of a plane normal to the scattered beam, at a distance $r$ from the volume of liquid V causing the scattering, and in a direction at right angles to the direction of the exciting beam.

E is the illumination of a plane normal to the exciting beam supposed parallel and unpolarized.

R is the gas constant and T the temperature, RT being expressed in ergs.

N is the Avogadro number.

$\beta$ is the compressibility and $\mu$ the refractive index of the scattering medium.

$\lambda$ is the wave-length of the exciting light.

In one important respect, it is true, the theory fails: namely that, according to the theory in its original form, the light scattered in a direction at right angles to that of the exciting beam should be completely plane-polarized. Exper-

[1] Owing to lack of space many details of the experimental method have been omitted from this paper. These will be given in a paper which will appear later.

[2] For bibliography see Trans. Roy. Soc. Canada, **16**, III, 276 (1922); also Jour. Opt. Soc. Amer., **6**, 105 (1922).

[3] Ann. Phys., **33**, 1275 (1910).

iment has shown that this expectation is not realized even in the case of gases, and that for most liquids the scattered light is very far from being completely polarized.

Cabannes[1] has shown how equation (1) may be modified to take account of this imperfection of polarization, with the result that, when the right-hand side of the equation is multiplied by the factor

$$\frac{6(1+\rho)}{6-7\rho} \qquad (2)$$

the expression is brought into better agreement with the observed results. $\rho$ is commonly called the depolarization factor of the scattered light and is the ratio of the weak component to the strong component polarized at right angles to it. Factor (2) becomes very important in the case of liquids.

Equation (1) then indicates that considerable changes in intensity in the scattered light may be expected with change of temperature, since T, $\beta$ and $\mu$ are functions of temperature. Factor (2) has also been found, as will be seen later in the paper, to vary greatly with temperature.

It has long been known that liquids near the critical temperature, where $\beta$ approaches infinity, exhibit a very considerable opalescence which is approximately plane-polarized. The following experiments were undertaken to bridge over the existing gap between liquids at ordinary temperatures and at their critical temperatures.

## Experimental Method

The liquid is contained in a large pyrex cross with sealed-in flat glass end-plates[2] the large one 4 cm in diameter. The liquid is rendered dust-free by the method of distillation in vacuo described in former papers. Parallel light from a tungsten arc (pointolite) lamp is the exciting light. The scattered light is observed through a double image Wollaston prism carefully oriented to give the vertically and horizontally po-

[1] Jour. Phys., [6] **1**, 129 (1920).

[2] Jour. Phys. Chem., **26**, 75 (1922).

larized components of the scattered light. The resulting images are then equalized by rotating a Nicol and the reading of this Nicol gives the relative intensities of the two components. This is essentially the same method as that used by Lord Rayleigh in measuring $\rho$ for gases.[1]

The $\tan^2 \theta$ law was not assumed for the Nicol. Instead it was calibrated by a photographic method to be described in a later paper, making due allowance for the small amount of stray light,—about 0.8 percent of the strong image—, which covers the whole field.

### Depolarization Factor of Benzene near its Freezing Point

This part of the work was done with considerable care. The pyrex cross was immersed in a glass vessel painted dead black except for the windows and kept at a temperature constant to one-tenth degree by water circulating rapidly through it from a large thermostat. The double image of the track of the light was photographed six or eight times on adjacent parts of the same plate, the Nicol being moved 0.2° between successive exposures. By an interpolation the correct setting of the Nicol for equality is obtained. The results of several series of photographs were averaged to reduce the error resulting from inequalities in the various parts of a plate.

Professor L. V. King suggested that the depolarization factor might vary near the freezing point of the liquid. Benzene was chosen as a suitable liquid since its freezing point, 5°, is easily reached. It was quite easy to keep the benzene undercooled for several hours at 0°.

| Temperature | Depolarization factor |
|---|---|
| 0° | 0.488 |
| 5 | 0.483 |
| 10 | 0.481 |
| 20 | 0.490 |

Average 0.485

[1] Proc. Roy. Soc., **97A**, 435 (1920).

It is apparent that within the error of the experiment there is no variation of $\rho$ as the temperature is lowered through the freezing point. At first the polarization appeared to vary around 5°, but it was found that some condensation of moisture on the outside of the cold glass vessel was affecting the result. The authors believe the above result to be correct to within 2 percent for the value of $\rho$ for benzene near room temperature. The incident light was parallel, the Nicol was carefully calibrated for its reading here (42.3° on the arbitrary scale) and the cross-shaped container excludes stray light well. Raman[1] has published a result for benzene which is considerably lower than this and for that reason the result published by the authors first in 1920 for benzene has been repeated by the entirely different method described here. The presence of dust or impurities in the benzene would probably give a low value of $\rho$. The sample used in the above experiment had a M.P. 5.0°. It was purified from Baker's C.P. thiophene-free benzene by fractional distillation followed by recrystallization and careful draining. The difference between the results cannot be attributed to the kind of light used, as the authors have found that for benzene the value of $\rho$ is constant within 2 percent for $\lambda$ 5461 and 4358. These photographs on the dependence of $\rho$ on the wave length of the light were made with a glass mercury-vapour lamp and are being continued with a quartz mercury lamp which will shorten greatly the time of exposure.

### Depolarization Factor and Intensity of Scattered Light for Benzene and other Liquids at High Temperatures

For temperatures approaching the critical the cross-shaped container has not sufficient strength to withstand the vapour-pressures of the liquids. Thick glass bulbs were therefore used of 4 cm outside diameter and of glass 1.5 mm thick. A second bulb and stem allows for expansion of the liquid with rising temperature.

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[1] Phil. Mag., 45, 625 (1923).

For safety, and for control of temperature, the bulb is placed in the centre of a five-way steam-fitters iron cross with thick plate-glass windows. The cross was electrically heated so that the temperature could be controlled to about 2° at 250° and better at lower temperatures.

Several times after heating the liquids showed a changed value of $\rho$ or of intensity of scattering on cooling to room

| Temperature | Depolarization factor | Relative intensity | Intensity calculated from Einstein formula |
|---|---|---|---|
| *Benzene.* | | | |
| 20° | 0.485 | 1.00 | 1.00 |
| 100 | 0.394 | 1.33 | 1.32 |
| 200 | 0.154 | 2.40 | — |
| 250 | 0.061 | 6.0 | — |
| 260 | 0.045 | 10.7 | — |
| 270 | 0.025 | 19.4 | — |
| 280 | 0.015 | 62.0 | — |
| 288 (critical) | | | |
| *Heptane.* (Kahlbaum's - aus petroleum. B.P. 97.5–99°.) | | | |
| 20° | 0.127 | 1.00 | 1.00 |
| 100 | 0.100 | 1.30 | 1.76 |
| 200 | 0.038 | 3.97 | — |
| 225 | 0.026 | 6.8 | — |
| 240 | 0.020 | 10.1 | — |
| 250 | 0.017 | 13.4 | — |
| 260 | 0.0165 | 16.8 | — |
| Critical | | (very high and uncertain) | |
| 270 | 0.0155 | 28.1 | — |
| *Naphthalene.* B.P. 218° | | | |
| 80° | 0.71 | 1.00 | — |
| 200 | 0.635 | 1.04 | — |
| 300 | 0.41 | 1.30 | — |
| Naphthalene begins to discolor at higher temperatures. | | | |

temperature. Some benzene which exhibited this peculiarity behaved normally after careful recrystallization. A sample of heptane in soda glass went bad on heating whereas a sample of the same heptane in a pyrex bulb was good. In no case is any result of this kind included in the preceding table.

Photometric measurements of the intensity of the scattered light were made by viewing the beam through the other arm of the cross. Measurements on both polarization and intensity were made visually to save time. The method of temperature control was hardly accurate enough to warrant the use of the photographic method. In the neighborhood of the critical temperature the measurements of intensity are least accurate since here temperature has such a great effect on the result.

The intensities for each liquid are taken only as relative to that for the same liquid at 20°. We hesitate to bring these to any common basis because round bulbs make such a comparison difficult, the bulb concentrating the beam by varying amounts depending on the size of the bulb and on the contained liquid. Naphthalene however scatters about 3.9, and heptane about 0.40 times as much light as does benzene at room temperature.

It is clear from the table that the following generalizations may be made.

(1) The intensity of the scattering increases with temperature; becomes very great near the critical temperature; and in the case of heptane, the only substance followed through the critical point, falls off again rapidly above the critical temperature. It is clear that the long known critical opalescence is but an extreme value of the scattering now observed at lower temperatures.

(2) The depolarization factor falls off rapidly towards the critical temperature and approaches a value of $\rho$ which is somewhat, though little, greater than zero.

Since this work was well under way Raman[1] has published data on scattering in liquid ether up to its critical temperature. His results are in keeping with these generalizations.

### Comparison of Results with Einstein Theory

The lack of compressibility data on liquids at high temperatures makes the results impossible of comparison with the

[1] Proc. Roy. Soc., **102A**, 151 (1922).

theoretical in most cases. The comparison has been made where data permit and the results are given above. In calculating the variation of $(\mu^2 - 1)^2 (\mu^2 + 2)^2$ with temperature $\frac{\mu^2 - 1}{\mu^2 + 2}$ has been taken as proportional to the density.

## Relation of Results to Theories of Crystalline Structure in Liquids

Some experiments on X-ray diffraction patterns obtained with liquids have led to hypotheses of some sort of crystalline structure in ordinary liquids. Professor L. V. King read a paper before The American Physical Society in December, 1923 in which he considered that Einstein's points of density concentration might be incipient crystals. He suggested then that if this theory be satisfactory the tendency of these crystals to enlarge and grow permanent should increase near the freezing point, with a probable resulting change in the depolarization factor. Such is not the case. The curve of the depolarization factor with temperature is a smooth curve through the freezing point.

Mr. Lehrman has been enabled to carry out this research by reason of a bursary awarded by the Advisory Research Council of Canada.

## Summary

(1) The effect of change of temperature on the light scattered by three liquids has been studied.

(2) The intensity of the scattering increases with temperature and passes through a very great value at the critical temperature, falling off again rapidly above the critical temperature.

(3) The scattered light becomes more nearly plane-polarized towards the critical temperature and in the immediate neighborhood of the critical temperature is almost but not quite completely plane-polarized.

*Chemical Laboratory*
*University of Toronto*
*March, 1923*

# DIALYSIS OF SMALL VOLUMES OF LIQUID: THE LILY-PAD DIALYZER

BY R. W. WOOD

In a recent study of the changes produced in fluorescent organic solutions it has been necessary to arrange an apparatus for the dialysis of very small volumes of solutions. The following type, which may be called for convenience the lily-pad dialyzer, enables one to operate with as small an amount as a single drop. If it is desired to retain only the colloid in its original concentration, which has always been the case in my own work, we proceed as follows. A small plate of glass is arranged so that it can be rotated at moderate speed in its own plane: I use an old "turn-table" such as is used for ringing microscopical preparations with cement.

A few drops of collodion, considerably thinned with ether, are poured on the centre of the plate, and the plate set in slow rotation: With a small camel's hair brush or a match stick, the edge of the collodion pool is touched, and the brush moved slowly away from the centre, the speed of rotation being immediately increased, as soon as the collodion is drawn into a perfect circular disc, the brush is lifted. The whole operation should take place in a few seconds, and if properly carried out we have a very thin disc of collodion with a thickened rim. After drying the film a few drops of water are placed on the plate and brought into contact with the edge of the disc. Usually the disc will immediately start to separate from the plate; if not it can be started with a needle point. As soon as the water has crawled between the disc and the plate, the latter is lowered at an angle of 45° into a bowl of water. The disc will float off with a perfectly dry upper surface. The solution to be dialyzed is now piled up in a globule, drop by drop on the centre of the disc, where it floats, supported by the disc, like a frog on a lily-pad: a disc of 4 cm diameter will support two cc of solution.

The thickness of the film at the center need be only a few wave-lengths of light (soap-bubble colors seen), and the dialysis under these conditions is quite rapid. I find a good deal of difference in the rate at which dialysis proceeds, discs made by diluting the collodion with ether only function very slowly while those made by diluting with ether and alcohol work more rapidly. A few drops of uranine (sodium salt of fluorescein) placed on the disc in a large jar of still water should throw down a slender bright green stem in a few minutes. This makes the lily-pad complete. A 5% solution of argyrol, containing sufficient uranine to cause a bright green fluorescence, is completely freed of the fluorescein in an hour or two. If it is desired to avoid over-dilution of the substance passing through the dialyzer, the lily-pad can be dipped up in a watch crystal, and as much of the water as is necessary can be removed from under it with a small pipette. We can, if necessary, dialyze from a single drop into a drop of pure water by lifting the film from the water on a glass or wire ring rendered sticky with shellac, and placing the drops on opposite sides of the disc, mounting the preparation in an atmosphere saturated with moisture to prevent evaporation. The film can also be prepared by pouring somewhat thinner collodion on the plate and allowing it to spread out of its own accord. If the dialysis proceeds too slowly, it can often be made more rapid by adding a few drops of water to say 25 cc of the thinned collodion.

*East Hampton, N. Y.*
*June 22, 1922*

# THE PHYSICO-CHEMICAL PROPERTIES OF STRONG AND WEAK FLOURS. IV. THE INFLUENCE OF THE ASH OF FLOURS UPON THE VISCOSITY OF FLOUR-IN-WATER SUSPENSIONS*

QC 237

BY ROSS AIKEN GORTNER AND PAUL FRANCIS SHARP**

In the preceding paper[1] of this series the use of a viscosity method for determining the state of hydration of the flour colloids as influenced by the addition of various amounts of different acids is described. Wood and Hardy,[2] Upson and Calvin,[3] Gortner and Doherty,[4] Stockman,[5] and Sharp and Gortner[6] have all shown that the imbibition of wheat gluten in the presence of acids is markedly influenced by the addition of salts. It therefore seemed desirable to ascertain what effect the presence of salts would have on the measurements of imbibition by the viscosity method.

The same flours, B-780 and B-783, used in our earlier work[1,6] were employed in the present study. In each experi-

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[1] Gortner, R. A., and Sharp, P. F.: "The Physico-chemical Properties of Strong and Weak Flours. III." Jour. Phys. Chem., **27**, 481(1923).

[2] T. B. Wood, and W. B. Hardy: Proc. Roy. Soc., **81B**, 38–43 (1908).

[3] F. W. Upson, and J. W. Calvin: "The Colloidal Swelling of Wheat Gluten in Relation to Milling and Baking." Nebr. Agr. Exp. Sta. Res. Bull., No. 8 (1916).

[4] R. A. Gortner, and E. H. Doherty: Jour. Agr. Research, **13**, 389–418 (1918).

[5] W. L. Stockman: "Some Factors Related to the Quality of Wheat and Strength of Flour." No. Dak. Agr. Exp. Sta. Bull., No. 139 (1920).

[6] P. F. Sharp, and R. A. Gortner: "Physico-chemical Studies of Strong and Weak Flours. II." Jour. Phys. Chem., **26**, 101–136 (1922).

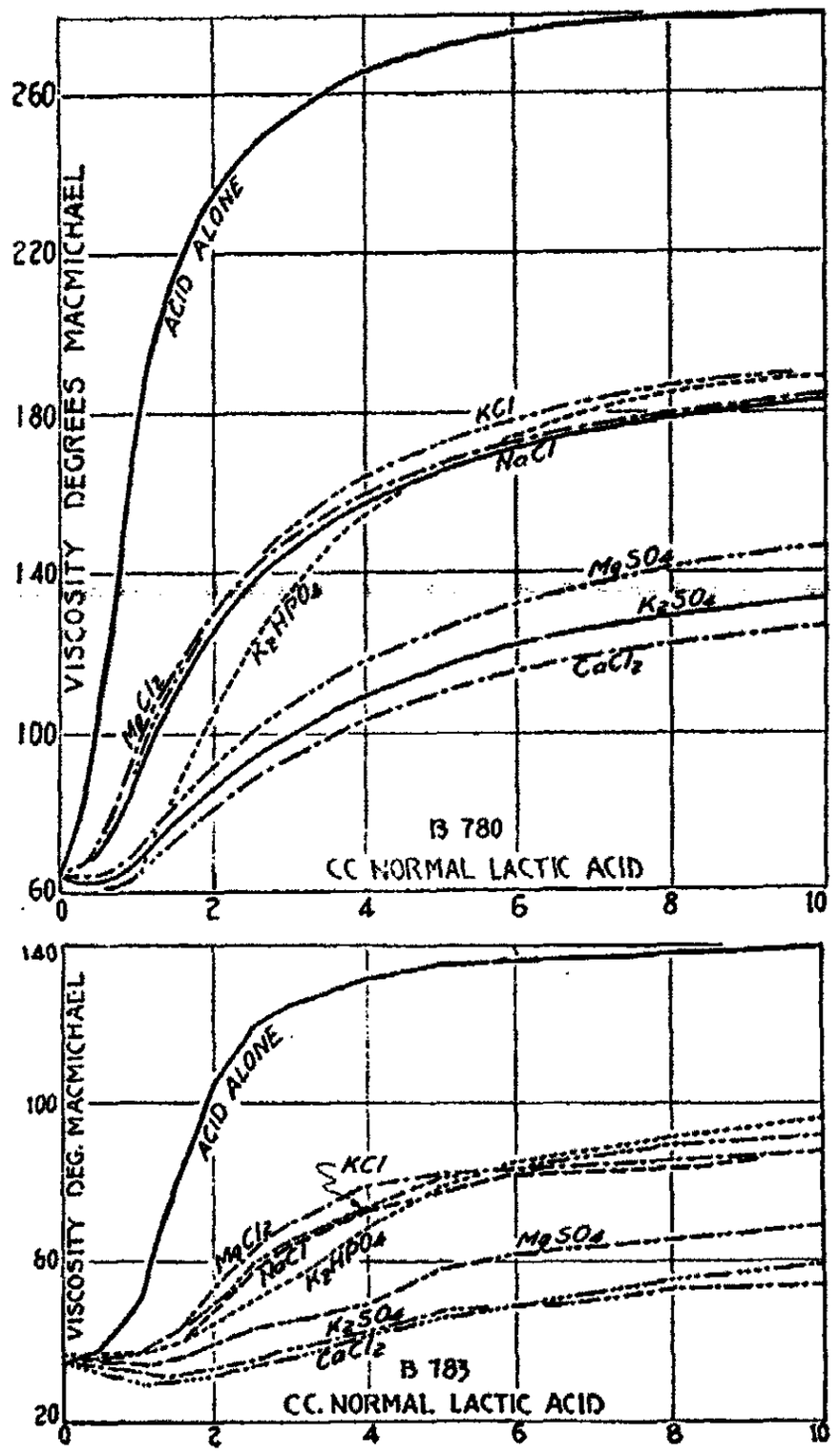



Fig. 1

Viscosity of 100 cc of 20% flour-in-water suspensions of B-780 and B-783 made 0.01 normal with respect to various salts and with the subsequent addition of various amounts of lactic acid

ment the equivalent of 25 grams of flour on the moisture-free basis were treated with enough water and salt solution to make 100 grams of 0.01 N salt solution and the viscosity changes caused by the addition of various amounts of normal lactic acid were determined according to the viscosity method previously described.[1] In the case of $K_2HPO_4$ the normality used was 0.005. The results obtained are expressed graphically in Figure 1.

It will be noted that the salts fall into two groups with respect to their inhibiting effect on imbibition. There appears to be no relationship between the valency of the ion and the groups into which the salts fall. It will be noted that the grouping is the same in the case of the two flours and that the relative effect on viscosity is also about the same.

Bailey and Collatz[7] by measuring the conductivity of water extracts of wheat flour have shown the presence of appreciable amounts of soluble electrolytes. They found that the conductivity of such extracts was directly related to the ash content of the flour. We accordingly initiated experiments to ascertain what rôle the electrolytes present in the original flour were playing in the determination of imbibition by the viscosity method.

The method which was adopted for removing the electrolytes was to make the equivalent of 18 grams of flour on the moisture free basis up to a total volume of 1 liter with distilled water and extract the soluble ash with occasional shaking for one hour. At the end of this time the material was centrifuged, the supernatant liquid containing the dissolved electrolytes was discarded, the residue made up to a total volume of 100 cc and the imbibition effects produced by various amounts of different acids were determined.

In order to ascertain to what extent this treatment removed the electrolytes, two flours, Nos. 1004 and 1008, were selected because of their different ash contents. First, the specific conductivity of an extract obtained by making 18

[7] C. H. Bailey and F. A. Collatz: Jour. Ind. Eng. Chem., 13, 319-321 (1921).

grams of flour up to a total volume of 100 cc with distilled water and digesting one hour was determined. Second, 18 grams of flour were digested with 1 litre of distilled water for one hour, the supernatant liquid removed by centrifuging, the flour residue made up to a total volume of 100 cc, digested 15 minutes, centrifuged and the conductivity of the supernatant liquid determined. Third, 18 gram portions of flour were digested with two successive 1 litre portions of distilled water, the residue was then made up to a total volume of 100 cc and the conductivity of this final extract determined. The results obtained are given in Table I together with the values for maximum viscosity obtained by treating the flour residues from the above extractions with lactic acid.

TABLE I

Showing the extent to which the soluble electrolytes are removed from flour by extraction with various amounts of water together with the effect of such removal on the maximum point on the viscosity curve (degrees MacMichael) produced by the addition of various amounts of normal lactic acid. The first row of figures refer to flour No. 1004 with 0.92% ash and the second row to flour No. 1008 with 0.52% ash.

| Specific conductance at 30° C of residue made up to 100 cc | | | Highest viscosity reached with lactic acid at 25° C | | |
|---|---|---|---|---|---|
| Direct extraction with 100 cc of water | After 1 extraction with 1 litre of water | After 2 extractions with 1 litre of water | Without previous extraction | After 1 extraction with 1 litre of water | After 2 extractions with 1 litre of water |
| $\kappa$ | $\kappa$ | $\kappa$ | M° | M° | M° |
| 0.00172 | 0.000110 | 0.0000339 | 75 | 329 | 324 |
| 0.00109 | 0.0000712 | 0.0000281 | 393 | 502 | 498 |

Extraction with 1 litre of water increases viscosity to a marked extent, especially in the case of the flour 1004 which has the higher ash content. This shows that the electrolytes actually present in the flour are exerting an inhibiting effect on the viscosity produced by the addition of acids. Extraction with a second litre of water apparently does not increase the viscosity further. Although a decrease in electrolytes is

produced as is shown by the conductivity data. Because of these results, it was believed that extraction with 1 litre of water, as described, decreased the electrolyte content to an

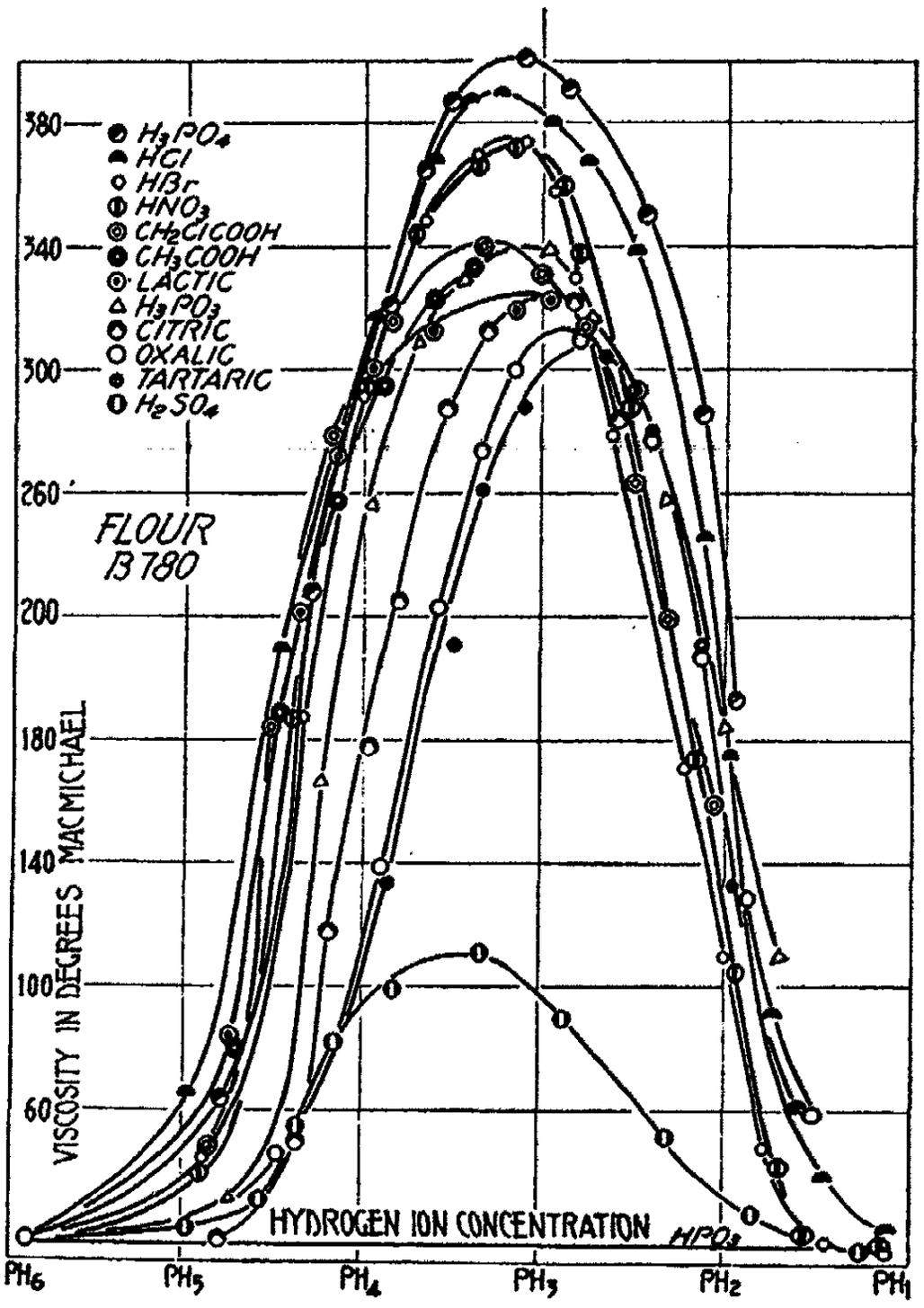



Fig. 2

Viscosity of extracted flours, 18 grams of extracted B-780 made up to 100 cc and treated with different amounts of various acids

easily reproducible level where subsequent extraction had but little effect. Later work has shown that a further increase in viscosity may be obtained by repeated extraction.

The effect of different concentrations of various acids on the imbibition of extracted flours as shown by the viscosity method was determined, using flours B-780 and B-783. With these flours it was necessary to reduce the weight of flour from 25 to 18 grams because of the high viscosity of the suspensions. The speed of the motor of the MacMichael viscosimeter was regulated for this series of experiments so that a 60

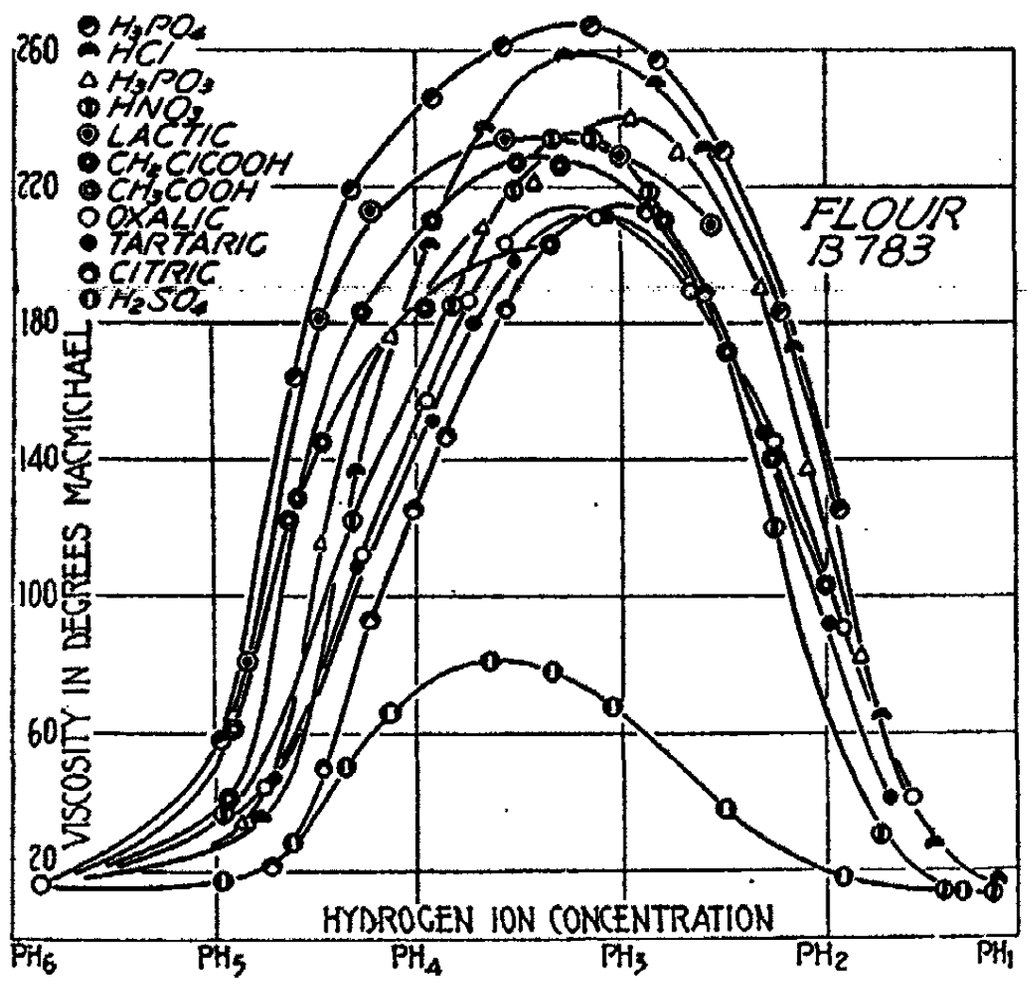



Fig. 3

Viscosity of extracted flour, 18 grams of extracted B-783 made up to 100 cc and treated with different amounts of various acids

percent sucrose solution having an absolute viscosity at 25° C of 43.86 centipoise gave a reading as nearly as possible of 87.7 degrees MacMichael. The results obtained plotted against the pH of the mixtures as determined electrometrically are given in Figures 2 and 3. These curves should be compared with those shown in Figures 3 and 4 of the preceding paper.[8]

[8] R. A. Gortner and P. F. Sharp: Jour. Phys. Chem., 27, 481 (1923).

With the extracted flours a much smaller amount of acid produced a marked increase in imbibition as compared with the non-extracted flours, indicating that the electrolytes which were removed had appreciable buffer action. The extracted flours in every instance show much greater imbibitional effects than did the non-extracted flours. The action of the different acids on the extracted flours is more nearly the same, although

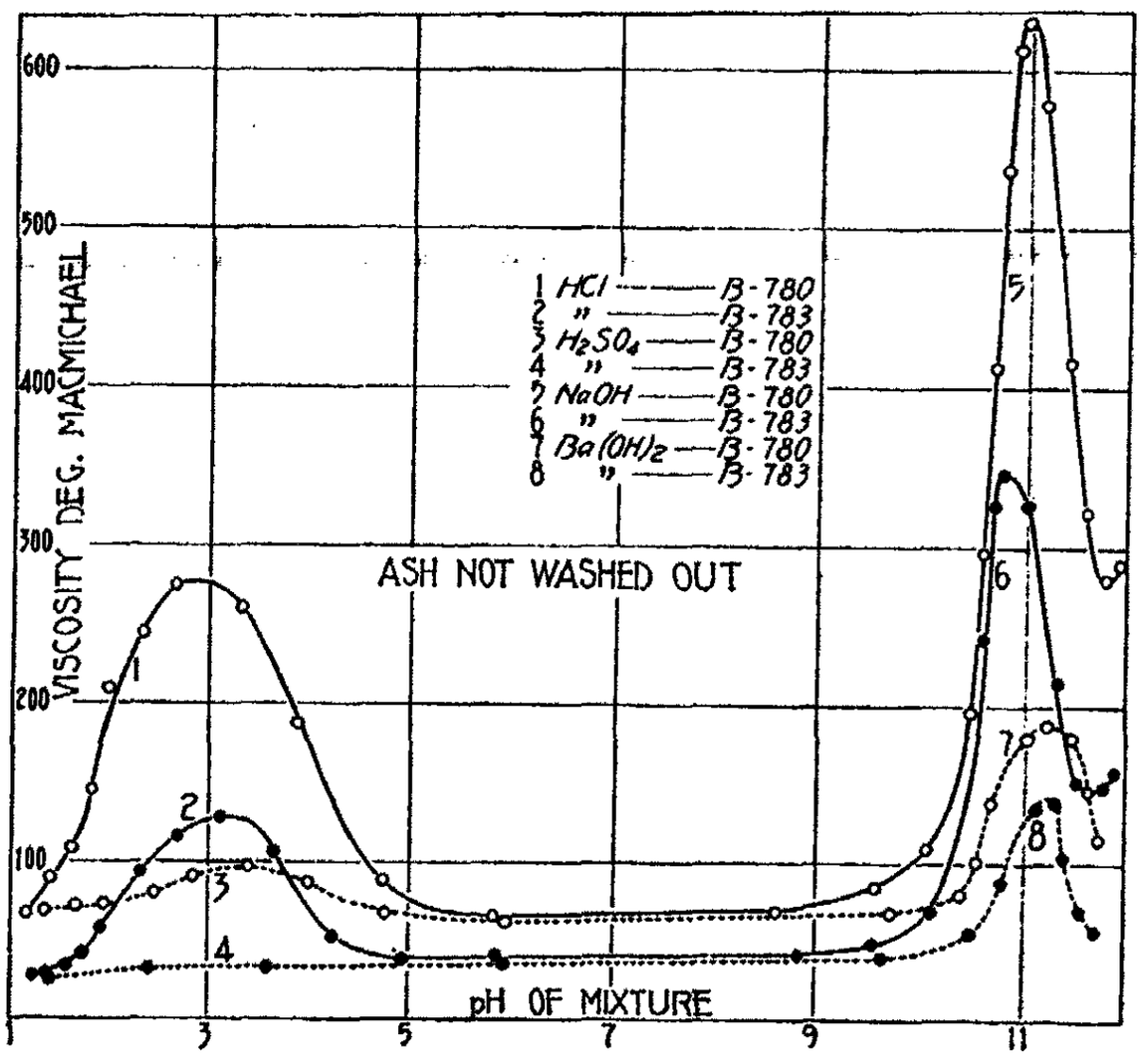



Fig. 4

Relation of viscosity and hydrogen ion concentration with unextracted flour

the differences are still much greater than the experimental error. Whether the small amounts of electrolytes remaining in the mixtures after extraction with water are sufficient to prevent all monobasic acids from reaching the same high point, or whether there is a lyotropic series of the monobasic acids and both the anion and cation are influencing the results can only be ascertained by further study.

It should be noted that the differences between a strong gluten (B-780) and a weak gluten (B-783) do not disappear when the soluble materials in the flour are removed, but that the relative differences in the hydration capacity of the glutens still persist.

Sulfuric acid produces increased imbibition with flour B-783 which was not the case when the soluble ash was present. It is interesting to note that the sulfuric acid curve lies very much below the curves for the monobasic acids. This is in accord with the experiments of Loeb[9] on gelatin and casein.

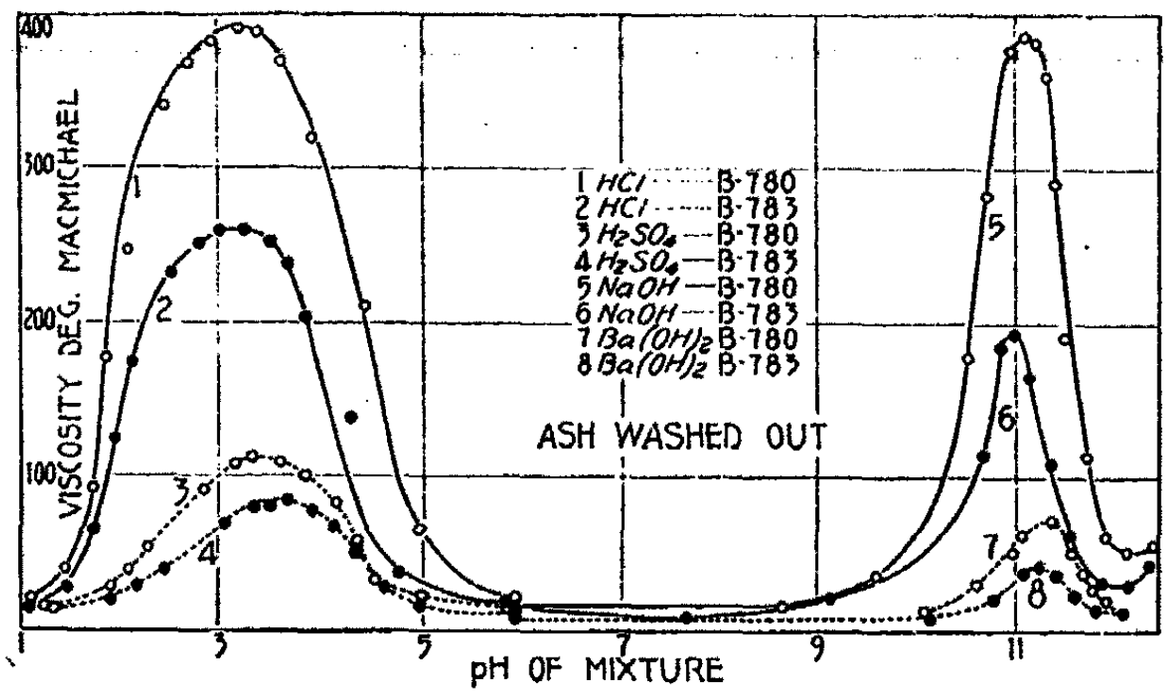



Fig. 5

Relation of viscosity and hydrogen ion concentration with extracted flour

If, however, the reason for this behavior is solely that suggested by Loeb, i. e., that it is due to the fact that sulfuric acid is a dibasic acid, we might expect the maximum point on the sulfuric acid curve to reach approximately one-half of the value reached by the monobasic acids. As a matter of fact sulfuric acid gives a viscosity of from one-third to one-quarter of the value given by monobasic acids.

The acids all reach their maximum imbibition at about the same hydrogen ion concentration. This optimum hydrogen

[9] J. Loeb: "Proteins and the Theory of Colloidal Behavior," (1922).

ion concentration is apparently the same regardless of whether or not the ash has been extracted from the flour.

The effect of sodium and barium hydroxides on the viscosity of these two flours was investigated both with and without the removal of the soluble electrolytes. The results are expressed graphically in Figures 4 and 5 which also include results obtained with hydrochloric and sulfuric acids for comparison.

The difference in the effects of mono- and dibasic acids and alkalis has been noted by other workers. The point of special interest in these graphs is that the curves indicate that the salts present in the original flours have a greater inhibiting effect on imbibition in the presence of acids than they have in the presence of alkalis. The maximum viscosity in the presence of alkalis occurs at about a pH of 11.0.

The untreated flours show a greater maximum viscosity in alkalis than do the flours from which the salts have been removed. The maximum viscosity reached by B-780 in sodium hydroxide surpassed any viscosity which we have been able to secure with the use of acids.

Here again in the alkalis there is a marked difference between the maximum viscosity attained by strong and weak flours, indicating that the colloidal condition of the protein is markedly different. It may be that the imbibition in alkalis will prove a more valuable method of studying flour strength than will imbibition in acids. One of us (G) hopes in the near future, to initiate experiments to test this point.

It is believed that when acids are used the determination of the viscosity with the soluble ash removed, as indicated, represents more nearly the true imbibitional powers of the proteins present in the flour. This is essentially a study of gluten, hence those variables in its environment (such as electrolytes) which influence the hydration of the gluten colloids should be removed, or rendered uniform. The ash content of flours even of the higher grades is so variable as to cause a corresponding variation in the imbibitional properties of the gluten, unless the soluble ash components are removed before comparisons of the physical state of the gluten are made.

**Summary**

1. Certain inorganic salts were found to depress the viscosity produced by lactic acid in flour-in-water suspensions. This is in accord with the well-known depressing effects of inorganic salts on the hydration of protein sols. The salts tested, however, were found to fall roughly into two groups: $MgCl_2 < NaCl < K_2HPO_4$ and $MgSO_4 < K_2SO_4 < CaCl_2$; the last group showing the greater inhibiting effects. The depressing effect apparently is not solely regulated by either the anion or the cation, neither does the valence of the anion or cation appear to be the sole determining factor. Both strong and weak flours gave the same relative grouping of the salt effects.

2. A marked increase in the viscosity of flour-in-water suspensions was produced when the soluble electrolytes present in the natural flours were removed by leaching with water, and the resulting "ash free" residue treated with various amounts of different acids. The different monobasic acids produced more nearly the same maximum viscosity than was the case when the soluble ash was present.

3. The optimum hydrogen ion concentration for maximum imbibition is practically the same with the different acids and was found to be at a pH of approximately 3.0. This is also the optimum pH for maximum viscosity when no attempt has been made to remove soluble electrolytes.

4. The maximum imbibition obtained with sodium and barium hydroxides was found to occur at a pH of approximately 11.0.

5. The electrolytes present in the original flour exert much greater inhibiting effect on imbibition in the presence of acids than on imbibition in the presence of alkalis.

6. The true imbibitional properties of the gluten proteins in acid solutions can best be studied by the viscosity of suspensions of flour-in-water from which the soluble ash has been previously removed by leaching.

# FLUOSILICIC ACID[1]

## THE MAXIMUM CONCENTRATION OF THE ACID AT ROOM TEMPERATURES

BY C. A. JACOBSON

2.1016

Fluosilicic acid and its salts are becoming increasingly important in the industries and yet the chemistry of this acid has not been worked out as well as it might be.

After a perusal of the literature on this subject, several problems presented themselves for consideration. First: Is it possible to obtain a 100% $H_2SiF_6$ at ordinary temperatures? If not, what concentration of the acid may be attained, and how stable is it? Second: Does this acid ever occur in the vapor phase as intimated by Baur[2] or is it present solely in solution like $H_2CO_3$? Third: Is it possible to improve upon the present method of determining this acid in the presence of other acids?

For the solution of the first problem a glass apparatus of the form shown in Fig. 1 was constructed, each bulb having a capacity of one litre. These bulbs were connected by a tube 25 mm inside diameter which was large enough to allow a fairly rapid passage of vapor from one bulb to the other.

The strong fluosilicic acid to be further concentrated in this apparatus was prepared in the following manner: One part of the purest obtainable fluorspar and two parts of precipitated silica were treated with six to eight parts of concentrated $H_2SO_4$ and the resulting vapors passed through absorption tubes packed with glass wool, in order to retain any HF that might get over, and then conducted into water in a five litre balloon flask. The end of the glass tube which con-

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[1] This and the two following investigations were carried out at Johns Hopkins University in co-operation with Associate Professor B. F. Lovelace and supported by the Graflin research fund of that institution. The author is indebted to Doctor Lovelace for many helpful suggestions throughout the work.

[2] Ber. deutsch. chem. Ges., 36, 4209 (1903).

ducted the vapors to the water ended under mercury held in a small cup at the bottom of the flask.

The determination of the resulting fluosilicic acid was made by a modification of the method of Katz[1] which will be taken up later.

It was assumed that the following reaction between water and silicon tetrafluoride occurred:

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + H_4SiO_4, \qquad (1)$$

and that the reaction

$$SiF_4 + 3H_2O = H_2SiO_3 + 4HF, \qquad (2)$$

suggested by Hudleston and Bassett[2] was of negligible importance. A further discussion of this will appear in the next paper. However, if HF had been formed to any appreciable extent it would have been transformed into $H_2SiF_6$ as shown in equations three, four, and five.

$$2SiF_4 + 4HF = 2H_2SiF_6, \qquad (3)$$

$$4HF + SiO_2 = SiF_4 + 2H_2O, \qquad (4)$$

which becomes $H_2SiF_6$ by equation (1), or

$$12HF + 3SiO_2 = 2H_2SiF_6 + H_4SiO_4 + 2H_2O. \qquad (5)$$

As evidence in support of the above reasoning, it might be mentioned that Baur (loc. cit.) found no free HF in a 30% solution of $H_2SiF_6$. In view of the above considerations as well as for the reason that a trace of HF could have been detected in the two-phase titration method employed, glass vessels were used in this work, and with entirely satisfactory results.

The concentration of $H_2SiF_6$ in the absorption flask was found to be about 4% after the first run. The silica was allowed to settle, and the clear supernatant liquid siphoned off

[1] Chem. Zeit., **28**, 356 (1904).

[2] Jour. Chem. Soc., **119**, 403 (1921).

and then used over again for the absorption of more $SiF_4$. By successive runs in this manner the concentration of fluosilicic acid was stepped up to about 25%. From this point on the concentration was increased by means of distillation under diminished pressure, which was accomplished at room temperature by means of the double distillation flask method, where a tiny stream of air was admitted into the distilling liquid. This method yielded a concentration of 40–45% $H_2SiF_6$.

Bulb A, Fig. 1, served as the distillation flask and B as the receiver. The apparatus was evacuated by the tube and

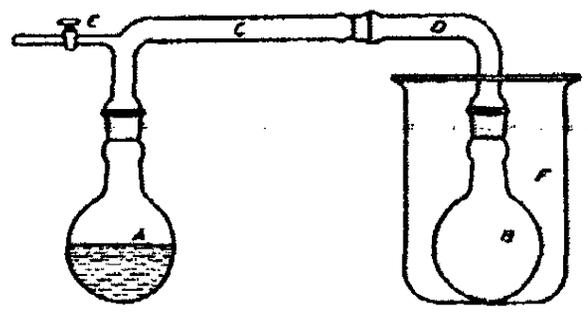


Fig. 1

stopcock on the left. The ends of C and D were ground into the mouths of the bulbs so that a vacuum could be maintained.

Three hundred cc of a 41.41% $H_2SiF_6$ solution in water were introduced into the left hand bulb, A, and the tube and receiver connected up as shown. The apparatus was exhausted to about 8 mm with an oil vacuum pump. The receiver B was packed in crushed ice and salt in a large battery jar, surrounded with hair packing and allowed to stand. Bulb A was kept at room temperature (20–22°). The ice and salt mixture was renewed morning and evening for three days. At the end of this time, 15.5 cc of distillate were found in the receiver, which showed a concentration of 1.17% $H_2SiF_6$.

Another 16 cc of liquid was distilled over in the same manner, showing a concentration of 1.58% $H_2SiF_6$. The solution in A was not tested after these two distillations, but the apparatus again set up with 200 cc conc. sulfuric acid in B, and the distillation continued for six days. At the end of this period 10 cc of the $H_2SiF_6$ solution in A were withdrawn, diluted and titrated, showing its concentration to be 53.6%.

At this point the volume of the distilling liquid had diminished considerably, and more of the same acid, though less concentrated, was added. The distillation was continued in the same manner until the concentration of the distillate was 1.53%, and the acid in A, 54.46% $H_2SiF_6$. After this the successive distillations, carried out, are recorded in Table I.

TABLE I

| Time | Cc distilled | % $H_2SiF_6$ in B | % $H_2SiF_6$ in A |
|---|---|---|---|
| 4 days | 7.5 | 3.54 | 56.31 |
| 6 days | 6.5 | 4.09 | 58.95 |
| 7 days | 5.0 | 11.09 | 60.77 |
| 8 days | 3.0 | 24.20 | 60.54 |
| 6 days | 2.0 | 41.52 | 60.92 |
| 15 days | 8.0 | 49.61 | 60.85 |

## Conclusions

Fluosilicic acid is generally put upon the market in concentrations ranging between ten and twenty-five percent, and has rarely been made over thirty percent.

It is seen from the above table that 60.92% is the maximum concentration of $H_2SiF_6$ obtained at room temperature, (20–22°), and that this concentration could be maintained for a long period of time, perhaps indefinitely.

It will be observed that the acid in the distillate increases regularly, as the concentration of the acid in the distilling flask increases. The reason for this may be found in the fact that water in the form of vapor was removed from time to time by the vacuum pump. The concentration of the distillate continued to increase over a period of 36 days, which suggests that if the process had been continued the distilling and distilled liquids would finally have assumed the same concentration of $H_2SiF_6$.

# NEW BOOKS

**The Reign of Rubber.** *By William C. Geer. 21 × 14 cm; pp. 344. New York: The Century Co., 1922. Price: $3.00.*—This is a popular book on rubber by an expert and therefore very welcome. The chapters are entitled: the evolution of an industry; problems of a pioneer; fundamental methods and machinery; the rubber man's cook-book; raw rubber; reclaiming waste; the chemistry of rubber mixtures; the bicycle tire; the pneumatic automobile tire; transportation by truck; water-proof footwear and clothing; broadening of the field of sport; power and light; communication; fighting fire; in the service of health; belting, packing, and hose; rubber in the home; gas masks; balloons; the future of rubber.

Rubber is obtained from the milky sap or latex of certain tropical trees in which it occurs much as butter fat does in milk, though in much higher concentration. It is usually precipitated from the latex by addition of dilute acetic acid, and is rolled into sheet form. When manufactured, it has zinc oxide, carbon black, sulphur, and other things added to it and it is then heated to produce the reaction between rubber and sulphur which is known as vulcanizing and which keeps rubber from becoming sticky in warm weather and brittle in cold weather. The early uses of rubber were for rubber boots and waterproofs. This is still a very considerable business for seventy-five million pairs of rubber boots, overshoes, and rubbers were made in the United States alone during 1919, p. 171.

This sinks into insignificance however in comparison with the tire business. The first pneumatic bicycle tire was invented by Dunlop in 1888 and the pneumatic automobile tires came into use in the nineties. The world registration of cars at the beginning of 1922 was twelve and a half million which, at three tires per car per year, is about thirty-seven million tires per year as against a productive capacity of fifty-five million, p. 333. Mr. Geer predicts a consumption of sixty-six million tires per year in 1928. As Mr. Geer points out, p. 133, there are other things in the tire beside rubber. In a cord tire thirty-five by five there are more than 5700 miles of fiber if placed end to end; but we are not told whether there is any ratio between miles of service and miles of fiber.

The vulcanized rubber core of the baseball is the thing that makes home runs possible, p. 189, and the substitution of the rubber-thread golf ball for the solid gutta percha ball has brought joy to the hearts of all golfers. In 1921 over seven million golf balls were made and sold in this country. On p. 200 Mr. Geer gives some good information to golfers. "Golf balls do not break; they are cut. The edges of mashies and other irons are sharp; and when this edge strikes the surface of the cover with the force of a heavy blow, the cover cuts. Some of the golf players in this country believe that their game would be much better if they used the same brand of ball favored by the accurate, heavy-hitting professional players. The most powerful one is the harder ball, for it contains thread so wound that it has the maximum return force. Being hard, this type of ball is readily cut when topped with an iron club. . . .The golf ball with the most resistant cover is usually the one that is the softest wound, for the ball inside the cover yields even under the force of a cutting blow."

Mr. Geer raises the question how long a golf ball should last and answers it by saying that most of them last until they are lost, which is true but not helpful. Another interesting but purely academic statement is that the life of tennis balls would be much less if they were filled with carbon dioxide instead of air.

"The hand-ball of the gymnasium is a beatifully constructed spherical ball of strong, lively rubber. There are also the squash balls. Polo employs a rubber ball and hockey a rubber puck. In foot-ball there is the rubber bladder inside the leather case; the players are protected by rubber nose-pieces and ear guards. The basket-ball is a sphere of carefully softened and shaped leather inside of which is a rubber bladder blown up to tension. Even in billiards the cushions upon which the player depends for the return at his chosen angles are a most carefully worked out rubber composition of high resiliency and of great permanence. Here is no particular question of durability, for the action of billiards is not one of an abrasive or wearing character, but there is a question of permanency and resiliency. The moment the billiard cushion becomes even slightly dead, the skilled player can determine the fact, and the accuracy of the game is reduced. In the realm of sport the use of rubber products is essential to most games. They surely would be dead and lifeless without it," p. 204.

All electric light and power lines are insulated with rubber, p. 216. "Manifold are the uses of electricity, and with them rubber insulation. The ignition system of automobiles, the hot days cooled by the swiftly rotating fan, the electrical adding-machine in factory, office, and store, vacuum cleaners, the breakfast toaster, form a host of conveniences. We feel civilized by means of electrical power. Without it how bare would our lives become! And without rubber, we should lose the use of most electrical appliances."

Hard rubber is used in telephones and in automobile battery cells, while an intermediate product is used in typewriter platens, p. 231. "The rubber platen is to the typewriter what the pneumatic tire is to the automobile. It receives the blow of steel, softens the shock to just the right degree, and yet is hard and uniform enough to permit a true impression. Typewriter platens are made of a peculiar sort of rubber composition, capable of vulcanizing neither into hard rubber nor soft rubber, but into an intermediate grade. The rubber compound can contain only substances capable of the finest state of subdivision; no particles of grit must show through the surface to blur a letter. The platens are vulcanized to a tested hardness. If they are too soft, the impression of the letters upon the paper will be blurred; and if they are too hard, the paper is liable to be cut or the type injured. Through compounding and vulcanizing, the maker must obtain an exact degree of hardness."

"Rubber stamp-making is a little industry by itself in every city in this country. The operators who make the stamps prepare molds by the use of what they call a matrix compound—a quick-setting mixture of mineral powders into which, while soft, the impression of the steel type is forced. An unvulcanized rubber compound of the size and thickness desired is then laid in sheet form upon this matrix when it is set and dry. Pressed in a steam or electrically heated mold, the rubber is forced into the lettering in the matrix and vulcanized. After vulcanizing the set of rubber type is removed, and the stamp is trimmed and mounted upon a sponge rubber backing on a wooden block with a handle. Rubber stamps are numerous; in fact, they are as indispensable to the business activ-

ities of the world as the telephone, for they are tremendous time savers. Small as the stamps are, it has been estimated that the rubber stamp manufacturers of the United States employ fifteen million dollars in capital to produce an annual output evaluated at about five million dollars," p. 234.

"The fires of Rome were not easy to put out. While the flames curled out of the windows, the small boys might have seen men stretching hose made of the intestines of oxen. For a fire-engine, a few men sat heavily on a skin filled with water, and so forced a tiny stream upon a second-story blaze. So says the architect Apollodorus who wrote in the time of the Emperor Trajan, about 100 A.D. These means accomplished little, but they expressed an attempt to control fire," p. 235.

"Like that of most developments, the history of hose-making is one of constant change, but the problem now seems to be settled. Rubber-lined fire-hose in reality consists of two parts, a cotton jacket and a rubber lining, the strength of the hose and its flexibility being supplied by the jacket. This jacket is circularly woven, a process that means it is built upon a loom by which a number of cotton threads are unwound from spools and are woven into the hose parallel to its length. This constitutes what is known as the warp and serves the purpose of keeping the strength-giving part of the hose in position; for the filling is, in point of fact, a heavy, strong cotton thread that is spirally and closely wound in one continuous length from end to end. The loom is so made that the warp of lengthwise threads are woven in and out among the spirals of filling. Thus there is built a seamless, heavy, strong cotton tube with no rubber in it.

"The rubber lining is made of a high-grade rubber composition—in fact, the highest grade that the rubber manufacturer is capable of producing for this purpose. A great deal of experimentation has been done in the development of the composition. Because it is too soft, pure rubber cannot be used. The compound used must be stiff; it must be strong in tensile strength, indicating the highest quality; and it must resist aging to the maximum degree, for hose stands in locations convenient for use, not best for storage. It must also have those properties that permit it to adhere to the cotton. Since fire-hose must be in perfect condition when the call comes, every part of it must be designed, constructed, and finished accordingly," p. 242.

"Out of the many articles made in the rubber industry, there are few subjected to such careful supervision, testing, and accuracy of workmanship as fire-fighting hose. Each length is submitted to a hydrostatic test. During this test, it must not leak, nor must the threads break; it must not contract in length or diameter; it must not rise from the level of the test table. Circular-woven hose has a tendency under pressure to untwist, with all kinds of peculiar movements. The manufacturer is required so to make it that these movements will be reduced to a minimum. Imagine the consternation, if not fatality, to the fireman if, when water pressure of 125 pounds came hurling through a hose, the nozzle in his hand should untwist and the hose writhe. He would be thrown off his feet, possibly off a building. Consequently, fire-hose must be as permanent and free from movement as it is humanly possible with the best of machinery to make it. Fire-hose, too, must be as light as is consistent with strength. A fifty-foot length of single-jacket fire-hose weighs about forty pounds; and the double-jacket hose; such as is used with the high pressure of some cities, weighs

about seventy pounds. Even this is no small weight for firemen to drag over the ground and up ladders," p. 244.

Ashurst makes the remark that Esmarch introduced his rubber tube and inaugurated an era of absolutely bloodless surgery, p. 252. "While we must not give rubber the full credit for changes in operative surgery, yet it came to be one of those important tools which contributed to the technique of the surgeon. . . .Most surgeons are so impressed with the impossibility of sterilizing bare hands that they wear gloves in operations. . . .Because rubber is impervious, today we find the operative surgeon using thin seamless rubber gloves. . . .Surgeon's gloves are the finest article of the kind made. By this dipping process they come to the hospital seamless, with wrists usually reinforced by rubber tape or cord. Since the vulcanization was performed by sulphur chloride, they are entirely free from any hard substances inside the rubber. This not only serves to limit the danger from puncture, but naturally renders true the sense of touch. There are smooth, although some have been made with a finely pebbled surface. For special purposes, many of them are made with long sleeves.

"During the course of an operation there are a number of other articles that play important parts. Although I have concentrated upon gloves, there are solutions of specially prepared sterile rubber which may be applied over the cutaneous surface and thus prevent the spread of infection. The commonly used protectives developed by Lister included not only silk protectives, paraffin paper and so on, but rubber membranes and gutta-percha tissue," p. 259.

The chapter on rubber in the home begins, p. 282: "A comparison between the American bath-room and the English one, reveals some interesting differences. In England one may not find a rubber hot-water bottle hanging behind the door, but he is likely to find a stone or metal one under the wash basin. Of late years, the English bath-room has achieved a rubber sponge, sometimes a solid rubber shaving dish, and a rubber bath-plug to keep the water from running out of the bath-tub. In American homes, however, rubber has worked its way into a large variety of convenient uses. The hot-water bottle is one of the basic necessities. Then there are fountain syringes, rubber bathmats, rubber soap-dishes, rubber aprons, rubber sponges, women's bathing caps, the tooth-brush with its hard rubber to keep the bristles from coming out, hand brushes, nail brushes, shower attachments, and, in the spring when colds are prevalent, the rubber bulb and tube connected to the nasal spray outfit. We surely depend upon rubber in the American bath-room and medicine cabinet. The American loves his bath-room, whether it has tub or shower. But he does not want the water to run all the time. It leaks too much from bib and faucet as it is. By a soft rubber disk pressing against metal when the wheel is turned, the water is shut off. If our plumbers would use high-grade rubber mixtures for these disks, there would be less trouble in the household; too many of them contain no rubber at all, being merely paper, which soaks up water and wears out rapidly."

Another of the necessary uses of rubber in modern days is in the home canning of fruits and vegetables, p. 291. "The canning industry has become extensive. The figures amaze one. The National Canners' Association reports that in 1919 there were packed in the United States more than 1,385,000,000 cans of vegetables, more than 634,000,000 cans of fruits, and more than 716,000,000 cans of fish and oysters. These make a total of more than 2,736,000,000 cans

put up in one year. And the home is not heard from in these records. Without entering into the principles of hot canning, we should note one fact as fundamental; the cans must so be sealed as to prevent any ingress of air. Among the many substances used for this purpose, the chief of them is rubber; even the tin can usually has a little rubber seal between the sides and the base. Because it is odorless and tasteless, because it is resistant to the action of fruit acids, because bacteria cannot grow in it, rubber has become one of the most necessary links in this chain of important operations, the end of which is the preservation of food in palatable, healthful, usable condition. Before canning, all the fruits and vegetables are picked over in the factory, just as our cooks do in the kitchen. Girls with carefully sterilized and manicured hands sit before a long table upon which slowly moves a sanitary rubber conveyor belt, usually white in color, which carries the fruit to be sorted."

In the final chapter, p. 335. the author says: "About 70 percent of the rubber consumed has been in tires. If we consider tires to consume even 80 percent, the total demand for raw rubber in 1928 will be 550,000 long tons. Yet a serious question confronts us: can there be produced in the world crude rubber enough to supply this tremendous demand? There was planted in the Far East, at the end of December, 1921, a matter of 3,321,000 acres. This was in British Malaya, the Dutch Indies, Ceylon, South India, British North Borneo, French Indo-China, Burma, and other countries. Still the area in square miles of the Dutch East Indies is 735,000; of the Federated Malay States, 27,506; of the Island of Ceylon, 25,332. We neglect here, too, any consideration of the enormous areas in South America and Africa that are yet jungle and where rubber trees may be planted and grown, providing man will be enterprising enough to go into those territories, open them up, and provide means of transportation and labor. The question seems to be one of cultivation of virgin land for raw rubber production."

While this is a very interesting book, there are some points which should be changed. In the latex everybody but the author considers that the rubber is present in a liquid form, p. 99. The author does not seem to know that the question of creaming, pp. 77, 101, is primarily one of the size of the globules and not of the nature of the protective colloid. Even in a popular book, the discussion of vulcanization, p. 108, should have been better and it is extremely improbable that what Mr. Geer calls gray sulphur, p. 110, is really an allotropic modification.

The publisher is responsible for the worst feature about the book, the casual way in which the illustrations are sprayed around. Drying rubber comes in under compounding, p. 49, about sixteen pages from where it belongs. Frictioning cloth appears under accelerators, p. 52. The rubber plantation faces p. 64 on the discovery of rubber, at least eleven pages ahead of time. Zinc oxide and carbon black appear under vulcanization, four pages ahead of the text. Rubber shoes come under golf balls, p. 193; hot-water bottles under wire insulation, p. 208; and golf balls under electric wiring, p. 212.

*Wilder D. Bancroft*

**The Origin of Spectra.** *By Paul D. Foote and F. L. Mohler. 23 × 15 cm; pp. 250. New York: The Chemical Catalog Co., 1922. Price: $4.50.—*

This is one of the scientific monographs of the American Chemical Society Series. "Although several accounts of the quantum theory of spectra from the mathematical standpoint have appeared in the past year, the experimental aspect of the problem has been greatly subordinated. In this book the authors have endeavored to present the subject from the experimental side. However, in order to do this, it was found necessary to discuss briefly the theoretical developments. In this regard, the important assumptions involved are enumerated, and only the essential steps in the mathematical analysis are presented."

The chapters are entitled: the quantum theory of spectroscopy; energy diagrams; ionization and resonance potentials for the elements; line absorption spectra of atoms; line emission spectra of atoms; thermal excitation; thermochemical relations; X-ray spectra; photoelectric effect in vapors; determinations of $h$ involving line spectra.

Spectral lines which arise in ionized atoms are called enhanced or spark spectra. Formerly they could be produced in the laboratory only by high voltage condenser discharge—whence the terminology spark spectra. The enhanced spark spectrum of an alkali earth resembles in all detail the arc spectrum of the alkali of next lower atomic number. This relation may be extended to other pairs of elements. If we remove the valence electron from sodium the configuration is similar to that of neon. Hence the spark spectrum of sodium should resemble the arc spectrum of neon, and similarly for the other pairs of elements in these two groups. Such is observed, qualitatively, to be the case. Quantitative evidence is not at hand since the series relations are yet unknown for the spark spectra of the alkalies and are not known at all completely for the rare gases; but both are alike in their complexity of structure. From these and a few other facts Kossel and Sommerfeld proposed a general displacement law for spectra. The displacement law states that the spark spectrum of any *simply ionized element resembles the arc spectrum of the elements of next lower* atomic number. If an element loses two electrons, its spectrum should be similar to the arc spectrum of the element of second lower atomic number. There is some indication of this second type of enhanced spectra in the spark spectra of carbon and of silicon; but nothing definite has yet been established. The spectrum of a negatively charged atom, one which has attached an extra electron, should resemble the arc spectrum of the element of next higher atomic number. It therefore appears that the behavior of the elements as regards their spectra is analogous to that in radioactive transformations where the emission of an alpha particle gives rise to an element two steps to the left in the periodic table and the emission of a beta particle, an element one step to the right.

"When electrons are accelerated through gas or vapors there are, especially for monatomic gases having a small electron affinity and the metallic vapors, well-defined critical velocities at which a large transfer of energy takes place between electrons and atoms. For velocities below this minimum critical value the collision is elastic, the electron rebounding from the atom with usually an alteration in its direction of path but with the same kinetic energy. In general two types of inelastic collision occur, one in which an outer electron of the atom undergoes an interorbital transition, and the other in which an outer electron is completely removed. In the latter case the atom is 'simply' ionized, having a total net charge $+e$. The potential through which an electron must fall in

order to accumulate just sufficient velocity to produce the first type of inelastic collision has been termed by Tate and Foote the resonance potential. The corresponding value for a collision resulting in ionization is known as the ionization potential. In general there may be several ionization potentials corresponding to the removal of 1, 2, 3, etc. electrons, but only simple ionization will be considered in the present section. Experimental evidence has shown that the loss in kinetic energy of the impacting electron during a collision of the 'resonance' type is equal to the resonance potential, whether the initial energy be exactly equal to or greater than that corresponding to the resonance potential. Whether or not this be true in the case of ionization remains to be demonstrated, for it is possible that the ejected electron may leave the atom with any velocity whatever, depending upon the nature of the impact," p. 60.

The authors are able to calculate with considerable accuracy the four critical potentials of hydrogen; but this does not make them absolutely happy, p. 75. "In spite of this apparent agreement between theory and experiment it is doubtful that the above table represents the correct analysis of the data, the difficulty being in the accounting for the presence of the quantity of monatomic hydrogen necessary to give such a pronounced indication of a resonance potential at 10.4 volts. In experiments where a hot cathode is employed there will be only a slight amount of thermal dissociation even for a wire operated at 2500° C. There is possibly sufficient dissociation, however, to account for the weak ionization observed at 13.3 volts. Using pressures of about 0.1 to 0.2 mm Hg in a discharge tube where the collisions occur over a space of 1 cm, it is found that about half of the electrons lose 10.4 volts velocity at this resonance potential. Now if ½% of the gas at any instant had been dissociated by the hot wire, a very liberal estimate, only one collision in one hundred would have taken place with an atom. Hence one would conclude that half of the electrons collided some 100 times elastically in this small distance before encountering an atom responsible for the energy loss of 10.4 volts, a conclusion at variance with probability considerations. Thus it appears likely that the observed resonance potential of 10.4 volts, as well as 12.0 volts, is due to the molecule.

"We have made experiments using a potassium hydride and potassium surface as a photo-electric source of electrons, instead of a hot cathode. Precisely the same results were obtained, with the exception of ionization at 13.3 volts, in regard to which no conclusion could be drawn, as the sensitivity was not sufficient to detect this critical potential. It is doubtful whether monatomic hydrogen could have been present in such an apparatus, operated cold.

"The possibility of dissociation by electron impact below the resonance potential is still an open question, but even so, this could scarcely account for a sufficient amount of atomic hydrogen to explain our result.

"The agreement between the observed value of 16.0 volts for the ionization of the molecule and that predicted by Bohr's theory again must be of no significance. If ionization of the molecule results in a neutral atom and an ionized atom, the ionization potential should be 13.5 + 3.6 = 17.1 volts, on the basis of Langmuir's determination of the work of dissociation. This disagreement with experiment suggests the possibility that a molecular ion is formed at this low voltage. In support of such an argument we have found that the secondary spectrum of hydrogen predominates over the Balmer series below

20 volts, and the secondary spectrum is usually ascribed to vibrations of the molecule or molecular ion."

"The phenomena of resonance radiation must not be confused with the fluorescence of metallic vapors. Fluorescent spectra are best observed with much greater densities and with intense illumination. The emitted radiation is very complicated and depends upon the wave-length of the exciting source. The stimulus may have an entirely different wave-length from any line in the emission spectrum of the pure vapor. As briefly described in the latter part of this chapter, fluorescence may be generally ascribed to unstable, polyatomic, molecular formations," p. 90.

"Sodium vapor at fairly high density shows thousands of fine absorption lines which Wood believes are the complement of the fluorescent spectrum excited by white light. Light may be absorbed by sodium vapor from a nearly monochromatic source in which there is no frequency corresponding to any line of the principal or other series of sodium. *Hence the presence of the absorbing molecules cannot be attributed to the preliminary activation of the atoms by* the source of radiation. Strong monochromatic illumination of sodium vapor by a red or green line, *not* present in the arc spectrum of sodium, gives re-emission of that line and a series of lines at intervals of about 37 A on each side of the exciting line. These spectra are almost the exact counterpart of the phenomena *obtained with iodine. The theory* that they likewise are due to a diatomic molecule is supported by this similarity, but the presence of the molecules again cannot be attributed to activation of the atoms by light which they are not capable of absorbing. Likewise with mercury fluorescence it is found that the most effective illumination is not light near λ2537 but of a higher frequency, again in no relation to the series lines of the mercury atom. We accordingly see that molecular compounds may be formed *without* excitation of the atoms by light of a series converging at 1 *s* or 1 *S*. It appears necessary to assume that the vapors contain molecular formations whether or not they are illuminated. Wood states that the fluorescence of mercury appears only in case of vapor freshly liberated from the fluid metal. Fluorescence cannot be excited in a bulb of cooling (hence condensing) mercury vapor, containing an excess of mercury at the same temperature at which it is brilliant in case the temperature is rising, accordingly where evaporation is taking place. Apparently then molecular compounds such as $Na_2$, $Hg_2$ may be evaporated from the liquid surface. Now if Franck and Grotrian's explanation of the structure of these compounds is correct, that is, if $Hg_2$ consists of an excited and a normal atom, simply boiling mercury briskly should produce an emission of $1\,S - 2p_2$, λ2537. Decomposition of the metastable compound $Hg_2$ should release an atom having an electron in the $2p_2$ ring which on returning to normal emits this fundamental line. A six hour exposure to a vessel of boiling mercury, by Dr. Meggers and the authors, failed to show a trace of this line. The experiment, however, is worthy of further thought.

"The entire subject of the behavior of excited atoms is a new field of research which promises interesting development. No doubt the chemist of the future will deal familiarly with such compounds as the helides, argides and so on," p. 107.

"If a metal is vaporized in a bunsen flame, an emission spectrum is produced. Usually this consists of the first pair $1\,s - 2\,p$ of the principal series of

the alkalis and 1 $S - 2\ p_1$ and sometimes 1 $S - 2\ P$ for the metals of Group II. Observations on the alkalis are a matter of common experience. The slightest trace of sodium vapor in the bunsen gives rise to the D-lines. Using a very simple device of McLennan and Thomson in which a small furnace surrounding the bunsen maintains the heat necessary to vaporize the metal at a slow and constant rate, the flame spectra of the elements of Group II are readily observed.

"In general we may conclude that the fundamentally important lines, from the standpoint of atomic theory, are those which appear in the low temperature flame. These same lines determine the values of the resonance potentials, as discussed in Chapter III. They appear in the arc below ionization; they are prominent absorption lines of the normal vapor and are readily reversed. They are the 'long' lines and the *'raies ultimes'* as discussed in the latter part of Chapter V. They are the result of the ejection of an electron to an orbit of next higher energy level than the normal state of the unexcited atom.

"These lines by no means appear in the flame because they normally are the most intense lines of the arc spectrum and hence by contrast only *seem* to be excited alone. In fact they are *not* the bright lines of the arc; especially is this true of the metals of Group II. Furthermore one may photograph a *low*-temperature sodium flame until the plate is 'burned up' at the D-line and only a slight trace of other lines can be detected. We may conclude that in general the ratio of intensities of these fundamental lines to other lines is extraordinarily high in the flame. We have in the bunsen another method of producing single-line or two line spectra.

"When a salt is injected in the flame we obtain again the simple single-line spectrum of the metal. Under certain conditions, however, other lines appear faintly, for example lines of the subordinate series. This is readily explained by the fact that dissociation of the salt, such as NaCl, by the flame, gives rise to $Na^+$ and $Cl^-$. If the sodium ion captures an electron, it is thereby able to emit any line of the arc spectrum. Zahn estimated that each sodium atom in a bunsen flame fed with NaCl emits on the average 2000 quanta of D-radiation per second. It is readily believable with the minute partial pressures of sodium or chlorine in a flame (order of magnitude $10^{-6}$ mm Hg and less) that the probability of a sodium atom capturing a chlorine atom and forming NaCl to be again dissociated is comparatively small. In other words the number of times a reaction of the form

$$NaCl \longrightarrow Na^+ + Cl^-,$$

occurs, which may involve a subsequent reaction

$$Na^+ + E^- = Na,$$

and the emission of all arc lines is small compared to the number of times the reversible reaction

$$Na' \longrightarrow Na$$

takes place with the emission of the D-lines. Hence while the dissociation of NaCl does give rise to all arc lines, the formation of Na', having the short life $\tau = 10^{-8}$ seconds is so much more frequent that the intensity of these fundamental lines is extraordinarily high relative to the other arc lines. The main service of the salt is accordingly in furnishing a carrier for the metal and the *immediate* spectroscopic consequence of the dissociation is incidental," p. 165.

*Wilder D. Bancroft*

**Glue and Gelatin.** *By Jerome Alexander. 23 × 16 cm.: pp. 236. New York: The Chemical Catalog Company, 1923. Price: $3.00.*—This volume is one of the technological series of monographs issued by the American Chemical Society. In the preface the author says: "The manufacture of glue and gelatin is important not only because of the magnitude of the industry itself, but also because these products are essential to the production of many others, thus making it a key-industry. Furthermore glue and gelatin are typical jelly-forming colloids and they have been used in numberless experiments on and investigations into the nature and behavior of colloids. As a consequence there is an embarrassing wealth of publications from which to draw material for a monograph. For the same reason, a discussion of the behavior of glue and gelatin involves the consideration of many moot points in colloid chemistry, and gives the subject an interest rather broader than the title would indicate."

The chapters are entitled: introduction; position of gelatin among the proteins; chemistry, physical chemistry, and colloidal chemistry of gelatin and glue; the structure of gelatin solutions and gelatin jellies; the influence of various factors on the swelling of gelatin; the viscosity of glue and gelatin solutions; collagen or ossein; the effect of tanning substances on glue and gelatin; chemical examination of glue and gelatin; technology of glue and gelatin; the testing and grading of glue and gelatin; uses of glue and gelatin; fish-glue and isinglass; test methods of the National Association of Glue and Gelatin Manufacturers.

Glue is defined, p. 11, as "an organic colloidal substance of varying appearance, chemical constitution, and physical properties, obtained upon drying the solutions resulting from boiling with water properly prepared animal matter such as skin and bone. The jellies which form on chilling soups, stews, boiled chicken, and the like, represent very impure glue solutions."

"Since the essential meaning of glue is that which draws or sticks together, while gelatin means essentially that which gelatinizes, it is but natural that, in popular parlance, the use of these words have, by similitude, been extended to many substances which are not glue or gelatin at all. Thus solutions of gums, dextrins, converted starches, etc., are often called glues, the modifying adjective 'vegetable' being generally used. Silicate of soda is sometimes termed 'mineral glue,' solutions of rubber, pitch and the like are called 'marine glue,' and those of casein are called 'casein glue.' Several varieties of sea weed, including *Gelidium corneum* or agar-agar, form, when cleaned and dried, a cord-like product having enormous gelatinizing power, which appears in commerce under various names, such as vegetable or Japanese gelatin, vegetable or Japanese isinglass, Chinese moss, gelose, etc. Our well-known fruit jellies, when pure, contain no gelatin, their gelatinization being due to a jelly-forming carbohydrate known as pectin," p. 13.

"Many of our most important discoveries have come as the result of some keen mind noting an incidental or accidental result. Though we may doubt the correctness of Charles Lamb's story as to the origin of roast pig, discovery of British gum and dextrin is said to have followed the observation that some starch, which had been roasted or torrified during a fire in a Manchester warehouse, yielded a sticky, gummy solution when wet with water. In all probability the discovery of glue grew out of the fact that stews, especially those containing bones or skins, yield a sticky solution and gelatinize when cold. It is

to Egypt that we must look for the oldest record of the use of glue, the discovery of which evidently antedates the Exodus," p. 13.

Wolfgang Ostwald believes that beyond a certain critical point the swelling of gelatin passes over into solution, the spatial continuity of the two phases relative to each other being then destroyed. "Based upon ultramicroscopic evidence the writer agrees with Ostwald's view. When the Brownian motion of particles becomes sufficiently violent to carry them beyond each other's range of molecular attraction, then the dispersion due to swelling begins to pass over into solution. With the proteins there seems to be no sharp line between swelling and solution, for slight thermal changes or mechanical action may produce sufficient dispersion of part of the swollen protein to produce a colloidal solution, which may later aggregate once more to a gel with larger motionless particles. Indeed with some, if not all salts, colloidal dispersion precedes true solution. Thus Alexander and Bullowa observed that sodium citrate, on going into solution, gave off streams of actively moving ultramicrons.

"Solution, then, results when the intramolecular adsorption of the solvent is powerful enough to force molecules or molecular groups beyond a certain critical distance from each other. The greater the degree of dispersion of the particles, the more rapid the Brownian motion and the nearer the approach to true or molecular solution; and this is conditioned by temperature, pressure, protective substances, coagulators, etc. As dispersed particles aggregate, the Brownian motion decreases sharply, groups about 1.1$\mu$ being nearly motionless. The closer particles are the less water they tend to adsorb. Therefore dilute jellies, when dried, take up more water than do concentrated jellies. Heating to 40° annihilates these differences for the time being, as the complexes are then broken down. The molecular groups constituting gelatin are so large and possess such a powerful idio-attraction, that it is not easy to separate them. Furthermore the degree of separation, that is, the size of the gelatin 'molecule,' seems to depend upon circumstances, as may be seen by considering work on the molecular weight of gelatin," p. 45.

On p. 51 the author says that "gelatin always contains considerable gelatoses and even some gelatones which are products of its own hydrolysis, but practically no one reports what percent these are or even gives the jelly strength, or optical rotation (mutarotation) from which a rough idea as to their percentage might be figured out. It is safe to assert that no one has ever prepared and experimented with 'chemically pure gelatin,' assuming that such a thing could be made. From the evidence at present available it seems that gelatin is not a definite chemical entity." Alexander points out, p. 53, that if gelatin is not a definite chemical entity, it is not justifiable to speak of "gelatin chloride" and "sodium gelatinate." On p. 66 he states that "the Donnan equilibrium and its consequences, which Loeb relies upon to prove the formation of definite chemical compounds, is just as well explainable on the basis of a kinetically balanced adsorption as on the basis of chemical compounds which hydrolyze." Fischer's experiments show that the order of acids in increasing the swelling of gelatin, p. 90, is as follows:

$$HCl > HNO_3 > CH_3CO_2H > H_2SO_4 > H_3BO_3$$

The position of acetic acid between nitric and sulphuric acids shows that the

hydrogen ion concentration is not the sole factor in determining swelling. Mechanical agitation decreases the viscosity of gelatin solutions, just as it does with many other colloids, p. 105. It is hard to see how this can occur in a true solution.

Wood found, p. 122, that "the combination of gelatin and tannin is not of constant composition, nor a purely physical one, since it does not obey the solution laws, which require the concentration in the solution and the tannin in the gelatin to maintain a constant ratio." Alexander points out that the so-called tannate of gelatin is a typical adsorption compound and that the precipitation of gelatin by tannin follows the adsorption isotherm.

"The precipitation of gelatin by tannin is also a typical instance of the precipitation of one colloid by another of opposite charge. Aqueous solutions of tannin are positively charged (negatively conducted), whereas gelatin is amphoteric, and as Ricevuto has shown is not precipitated by tannin unless in the negative condition (positively conducted). Carefully dialyzed gelatin is not precipitated by tannin, nor is hide tanned by tannin unless it is on the acid side. When dry the gelatin-tannin compound forms a yellowish-brown, brittle mass which melts in boiling water to a tenacious sticky mass like bird-lime. In this state it may be drawn out or spun into fibers fine as a spider's web, which have a metallic luster like silver slightly tinged with gold. When soaked in alum solution they acquire a blue tinge like polished steel. The gelatin-tannin compound is tasteless and does not yield tannin to alcohol, ether, or acetone. Prolonged boiling with water, especially in the presence of magnesia, decomposes it, probably because of the hydrolytic cleavage of the gelatin," p. 122.

"Gelatin is totally insoluble in absolute alcohol, ether, chloroform, benzene, carbon disulphide, and fixed and volatile oils. It is practically insoluble in ice-cold ten percent alcohol and precipitates as a white, coherent, elastic mass if an excess of alcohol is added to its aqueous solution. The precipitate swells in cold water and may be redissolved as before," p. 137.

"The 'crackle' of new banknotes is produced by sizing them with a solution of high-grade (test about 150), light-colored glue to which alum has been added. For tub-sizing writing paper, to give a smooth surface which will hold the ink, a light-colored glue is essential; the stronger it is the more dilute it can be used. About 2–4 percent of alum is used with the glue, and the sizing increases the strength of the paper materially. Glue can also be used to size paper in the beater. E. Heiser reports that precipitation methods were unsatisfactory, but upon adding sufficient talc, the glue was adsorbed and held by the paper. In making wall paper, the glue solution serves to 'free out' or deflocculate the clay and color with which it is mixed, as well as to bind it to the paper. Any sweet, free-flowing, foam-free glue may be used, grades testing about 60 being most employed. In sizing barrels, it is essential that the glue should not melt even in hot weather, while its jelly is being dried out inside the barrel. In the turpentine belt, a concentrated solution of cheap glue is used, but where care and attention prevail, the best and most economical results are had with high-grade glues, the melting point of the jelly being sometimes raised by the addition of chemicals. Gelatin is largely used to stiffen straw hats, but many factories get good results with light-colored glues of medium strength," p. 207.

"Good edible gelatin (formerly called 'patent isinglass') is now produced in large quantity and at so low a price that it has replaced isinglass practically

entirely in making jellies, confectionery, etc. Fish sounds, especially mixed with tongues, are used as food, and fried cod sounds are said to taste like fried oysters.

"The advent of prohibition in the United States has curtailed one of the main uses of isinglass, for it has long been used as a fining or clarifying agent for cider, wines, beers, etc. It acts both mechanically and as a colloidal adsorbent, removing tannins and turbidity-producing particles. For white wine the isinglass is swollen in water and then beaten with wine and a little tartaric or sulphurous acid and strained through linen before adding to the wine. One ounce of isinglass usually serves to clarify 200 to 500 gallons of wine in 8 to 10 days. For a barrel (36 gallons) of beer about $^1/_8$ ounce of isinglass is cut or softened in cold water containing a little acetic or sulphurous acid, and without dissolving is poured in and allowed to settle slowly through the barrel, carrying with it the 'cloud.' One pound of isinglass will clarify 100 to 500 barrels of beer. Gelatin is now used also, to replace isinglass as a fining material.

"The formulae and recipes found in old books show that isinglass was once largely used as an adhesive, even for postage stamps, envelopes and gummed paper. For these purposes it is now obsolete, being replaced by dextrin, gums, glues, etc. It is still used in leather belting cements, jewelers' cements, and in special adhesives such as those used in covering iron rolls in textile mills.

"White gives the following recipe for making court plaster with isinglass as the adhesive: 10 grams of isinglass are dissolved in 120 grams of water, and one-half of this solution is painted out on about 38 square centimeters of taffeta silk stretched on a frame. When this layer is dry, a second one is applied, consisting of the other half of the isinglass solution, to which has been added 1 gram of glycerin and 40 grams of alcohol. Finally the other face of the taffeta is painted out with tincture of benzoin," p. 223. *Wilder D. Bancroft*

**A Comprehensive Treatise on Inorganic and Theoretical Chemistry.** *By J. W. Mellor. Vol. III. 25 × 17 cm; pp. x + 927. London: Longmans, Green and Co., 1923. Price: $20.00.*—The third of these remarkable volumes has now appeared with astonishing, apparently autocatalytic, speed. This one deals with copper, silver, gold, and the alkaline earths. The author believes, p. 3, that the early bronze was made by combining copper and tin; but he leaves it very vague as to where the tin was found. On p. 69 we read that "copper is attacked so readily by various reagents that the old alchemists called it *meretrix metallorum*—the harlot among metals." This will be a shock to the Copper Producers Association if they ever hear of it. Six pages, pp. 73–79, are given to the corrosion of copper; but the observations are very confused. The reviewer was interested in the conclusion by Acworth and Armstrong, p. 93, that the successive stages in the reduction of nitric acid are nitrogen peroxide, nitrous acid, nitrous oxide, hyponitrous acid, hydroxylamine, and ammonia. This is purely a formal conclusion with practically no evidence to support it. In view of what we now know about the reduction of nitrobenzene to aniline, it is certain that this rather elementary prediction is not accurate.

The rather elaborate discussion, p. 173, of the color of cupric chloride solutions brings out clearly how unsatisfactory is our knowledge of this subject. The same remark might be made about the basic sulphates of copper, p. 264, and one can no longer feel any confidence in the work of LeBlanc and A. A. Noyes,

p. 162, deducing the existence of the complex $H_3Cu_2Cl_4$ from the freezing-point measurements. The reviewer was glad to see references to his theory of electroplating, p. 13, to flame reactions, p. 49, and to the possibility of copper oxide being blue, p. 144. The author is not modern in his characterization of the potential of the calomel electrode, p. 55, as negative.

From the fact that there is no common word for gold among the descendants of the Aryan peoples, the author concludes that the interest in, and perhaps the knowledge of, this metal developed after the linguistic separation. We have some form of *aurum* in the Latin languages and in old German, and some form of the word gold is found among the Esthonians and Lapps as well as in the Teutonic languages, while the various Hindu and Uranian languages use a term derived from the Sanskrit. A similar situation arises with silver where we have the two distinct words, *argentum* and silver.

There seems to be some confusion as to the color of silver vapor by transmitted light—Stas calling it blue, p. 321, and Lockyer and Roberts-Austen calling it red, p. 332. It may be that Stas was talking about chemiluminescence and the others about a silver fog. The 2-3 law of Gladstone and Tribe is mentioned, p. 318, and the correction by Langley referred to. Germann's work is cited, p. 435, showing that silver iodide does not adsorb iodine to the extent claimed by Carey Lea. Brown's work on silver peroxy-nitrate is mentioned, p. 483, and Turrentine's work on silver anodes in hydrazoic acid, p. 351. The reviewer's summary of the phenomena of the latent image seems to have been taken at face value, p. 414.

The author shows a proper scepticism as to the existence of the compound $Ag_4O$, p. 371. "This review shows that the evidence for the existence of alleged silver suboxide, $Ag_4O$, is very unsatisfactory. Where the reactions have been examined sceptically, the conclusion is drawn that the suboxide is non-existent, and where they have been examined sympathetically, it is concluded that silver suboxide is a true chemical individual and its properties are described. It seems as if man cannot always balance evidence with a purely logical and unbiased mind. Logic and temperament each plays its own part in forming his opinions or belief."

When speaking of the solution of gold chloride, p. 586, we are told that Roger Bacon, in urging this terrestrial hippocrene to the attention of Pope Nicholas IV related that "an old man, when ploughing a field in Sicily, one day found some of the yellow potable liquid in a golden phial, and, supposing it to be dew, drank up the liquor. He was thereupon transformed into a hale, robust, and highly accomplished youth. The youth was thereafter received into the service of the Sicilian king, where he served some eighty years." As an introduction to colloidal gold, the author takes up the flocculation and deflocculation of colloidal solutions, p. 536, and pretty nearly writes a short treatise on colloidal chemistry.

On p. 644 the author tells us that "calcium is used as a reducing agent in the preparation of metals and alloys from their oxygen and halogen compounds; as a reagent in the purification of the inert gases; as a scavenger for non-ferrous metals and alloys; as a scavenger, decarburizer, and desulphurizer for ferrous alloys; as a dehydrating agent in the treatment of oils and alcohols, etc.; as a means of fixing atmospheric nitrogen; as a source of pure calcium carbide by direct reaction with pure carbon; as a stiffening filling for hollow metal structural mem-

bers; as a constituent of a light aluminum alloy having useful properties; and as a hardening component in certain lead-base antifriction alloys. Calcium alloys have been proposed for bearing metals. Lime or limestone is used in the preparation of mortars, cements, sand-lime bricks, glass, glazes, bleaching powder, calcium carbide, calcium cyanamide, calcium nitrate, etc.; the purification of water, the manufacture of soda, the purification of coal gas; the manufacture of insecticides and sprays, the manufacture of sugar, the distillation of wood, the manufacture of paper; paints; and in tanning."

Up to about 1880, the expansion of plaster in setting was utilized in Persia as a means of executing criminals, p. 773. "The criminals were placed in hollow stone columns and surrounded with wet plaster of Paris. At first a little inconvenience was suffered, they would then show signs of distress and scream loudly; finally paralysis and death supervened. This would no doubt occur as the expansion of the plaster compressed the thorax and abdomen." In Europe a cheerful disregard for the welfare of others led to the discovery of Bordeaux mixture, p. 262. "The discovery of its value had been accidental. It had been the practice in the vineyards in the neighborhood of Bordeaux to sprinkle those vines which were near a road with verdigris in order to give them the appearance of having been poisoned, and so prevent depredations. A mixture of lime and copper sulphate was soon substituted for the verdigris, being cheaper, and, when the downy mildew of America (*Peronospora viticola*) made its appearance in Europe, it was noticed (1882) that those vines which had received the copper dressing were those which kept their leaves longest, and were least affected by the disease."

The physical character of calcium carbonate has some influence on the speed of dissociation, for limestone is completely decomposed after many hours heating at 900°, while marble, under similar conditions suffers very little change, although at 1030° it is decomposed completely, p. 656. As T. Bergmann pointed out in 1774, "workmen reject lime which is too much burned—dead-burned lime—as being useless, because it does not fall into powder when slaked. Lime which has been less burned falls into powder at the instant of slaking, and is then in a form suitable for making into mortar. Limestone containing clay is particularly liable to dead-burning, presumably because a more or less inert calcium silicate or alumino-silicate is formed which is not free to take part in slaking. Herzfeld found that eight percent of silica suffices for the dead-burning of lime at 1000°; alumina is less active than silica and required a higher temperature to produce dead-burning," p. 657.

"Alabaster and mammillated gypsum are used as ornamental stones. Gypsum is used in the preparation of plaster of Paris—which is sold under various special trade names, for wall plaster, etc.—and of various cements—Keene's cement, Martin's cement, parian cement, etc. Finely-ground gypsum is sold as *mineral white*, or *terra alba*, and is used as filling for paper; in finishing cotton goods; in adulterating paints and various other substances; in manufacturing crayons; etc. Gypsum is used by some breweries for hardening the water—*brewer's gypsum*—on the assumption that hard water gives better results—due, it is said, to the greater solvent action of such water on the albuminous matters in the malt. Gypsum is used in making some polishing powders; as a fertilizer for restoring sulphates to certain soils—e. g., the hop districts of Kent and Sussex.

It is also used as a retarder for the setting of Portland cement. Strontianite and celestine are the main sources of strontium compounds which are mainly used in pyrotechny, and in the beet-sugar industry. The uses of barytes are mainly dependent on the fact that it is a heavy white mineral, cheap, and chemically inert. Precipitated barium sulphate is the *blanc fixe*, and *permanent white* of commerce. The finest qualities are finely ground and used in the preparation of white paints; it is also used as an adulterant for white-lead in paint. Ground barytes—it may be water-floated, or air-elutriated—is admixed with white lead and zinc oxide, and used in place of white-lead for making paint. The powdered barytes is also tinted with dyes and likewise used as a pigment—e. g., the para-red paints have 90 percent of barium sulphate. Barytes is used in filling wall papers, glazed paper, rubber goods, linoleum oil-cloth, flannel, shoddy cloth, etc. It has several minor uses—e. g., it is employed as a fluxing agent in certain operations. Barytes and witherite are the main sources of the barium compounds," p. 802.

"The limestones are more or less impure forms of calcium carbonate; and they occur in many diverse forms—calcareous sinter or tufa or *travertine;* the *tophus* of Pliny, and the *lapis tiburtinus* of Pliny and Vitruvius. At Mammoth Hot Springs (Yellowstone National Park) the snow-white deposits from the geysers and hot springs form massive terraces of travertine, as calcium carbonate, held in solution by carbonated water, is deposited through the escape of the carbon dioxide from solution in water. The formation of stalactites and stalagmites in caves, and the work of the so-called petrifying springs, is due to the same cause. The carbon dioxide may also be abstracted from the water by vegetable organisms—bacteria, algae, mosses, and aquatic plants like the chara, etc., which, according to J. Walther, and E. J. Garwood, are active agents in the formation of limestones. A. Payen discussed the occurrence of calcium carbonate in plants. G. Steinmann has shown that the albumen present in the organic parts of aquatic animals, may, by fermentation, form ammonium carbonate which would precipitate calcium carbonate from calcareous waters. Calcium carbonate may also be precipitated from river waters charged with calcium carbonate as they enter the sea; and C. Lyell noted that this is taking place in the delta of the Rhône, and S. Sanford, and T. W. Vaughan, along the coast of Florida. Limestone is made up of shells and corals, and the organic remains may be conspicuous or they may be quite obliterated. Chalk is derived from marine ooze. Pearls are largely composed of calcium carbonate deposited by the oyster about an invading parasite," p. 814. *Wilder D. Bancroft*

**Ultraviolet Radiation.** *By M. Luckiesh. 23 × 16 cm; pp. xi + 258. New York: D. Van Nostrand Company, 1922. Price: $3.50.*—In the preface, the author says that "it is the primary aim of this book to present authentic data of such scope as to be useful to those who are interested in ultraviolet radiation. Theory has purposely been subordinated to experimental facts because the latter are not affected by the inevitable changes in theory."

The chapters are entitled: introduction; solar radiation; transparency of gases; transparency of liquids; transparency of solids; transparency of glasses; reflection of ultraviolet radiation; ultraviolet radiation in common illuminants;

experimental sources; detection and measurement; effects upon living matter; various photochemical effects.

The author divides ultraviolet radiation into three groups: the extreme region with wave-lengths less than 200$\mu\mu$; the middle region with wave-lengths 200-300$\mu\mu$; and the near region with wave-lengths 300-390$\mu\mu$. The book is a treasure-house of facts; but, partly because of this, one must dig out of it the facts that one wants. The author criticizes very properly the rather sloppy work that has been done in the past in photochemistry in the ultraviolet; p. 7. "It is unfortunate that more accurate data have not been given in many investigations especially pertaining to the wave-lengths of radiant energy employed. Too often such indefinite terms as 'ultraviolet light,' 'actinic rays,' 'blue light,' etc., have been used in describing results. In other words, the spectral limits and the spectral distribution of energy have not been determined. Many of the effects of radiation upon plant life, in industrial chemistry, in therapeutics, and in other fields are still uncertain because of the lack of specifications as to spectral limits and energy distribution."

While agreeing to all this, one cannot become enthusiastic over the author's constructive suggestions which are merely to buy a quartz spectrograph and "to ascertain the spectral limits and energy distribution of the illuminant used." That is not good enough. As the author himself admits, there is often "no question regarding the spectral limits of the radiation of chief interest but there may be doubt as to the presence of other radiation. For example, effects are sometimes attributed to ultraviolet radiation when visible radiation is present. What effect may the latter have had?"

If we are going to study the photochemical effect of ultraviolet radiation scientifically, we must have means of isolating more or less definite regions of ultraviolet radiation, for instance 200–250$\mu\mu$, 250–300$\mu\mu$, 300–350$\mu\mu$, and 350–390$\mu\mu$; but how are we to do it? We must either use screens or different illuminants or a combination of both. Screens are objectionable because the best cut down the intensity of the transmitted light considerably. Even at that there is no clear-cut statement in the book as to what to use, though one could probably dig it out from different places in the text. If one is to use different illuminants, the question at once arises as to the relation, if any, between the spectrum produced by the silent discharge through acetone, for instance, and the absorption spectrum of acetone. It is very likely that this has not been worked out and yet it is an absolute prerequisite to any satisfactory photochemical work in the ultraviolet. A book like this should call attention to such gaps in our knowledge if they really exist.

Of course it must be admitted that criticism like this, though natural, is really quite unreasonable. If Mr. Luckiesh had taken the time to go carefully into all the things that various people would have liked to have found in the book, he never would have got round to writing the book. We must therefore be thankful for an admirable compilation with plenty of literature references, one which will save each of us some work, though not as much as we hoped.

*Wilder D. Bancroft*

**Outlines of Theoretical Chemistry.** *By Frederick H. Getman. Third edition. 22 × 15 cm; pp. xi + 625. New York: John Wiley and Sons, 1922.*

*Price: $3.75.*—The first two editions were reviewed nine and four years ago, respectively (**18,** 183; **23,** 142), and now we have the third edition thoroughly revised and enlarged. The student is told about space lattices in crystals, which is a good thing, though the reviewer doubts whether many people will get a clear idea of the difference between a face-centered cubic and a body-centered cubic. The chapter on photochemistry is well done though the reviewer would have welcomed a more extended treatment of chemiluminescence in relation to its bearing on colored flames. The chapter on colloids is exceptionally good as might be guessed from the sub-heads: crystalloids and colloids; disperse systems; nomenclature; the ultramicroscope; ultrafiltration; classification of dispersoids; the Brownian movements; Perrin's experiments; the law of molecular displacement; recent investigations of the Brownian movement; density of colloidal solutions; viscosity of colloidal solutions; surface tension of colloidal solutions; osmotic pressure of colloidal solutions; molecular weights of colloids; electroendosmosis; cataphoresis; electrical conductance of colloidal solutions; precipitation of colloids by electrolytes; precipitation of suspensoids; precipitation and valence; precipitation of emulsoids; action of heat on emulsoids; protective colloids; mutual precipitation; emulsions; characteristics of gels; physical properties of gels; hydration and dehydration of gels; velocity of imbibition; heat of imbibition; imbibition in solutions; adsorption; adsorption of gases; adsorption in solutions; the adsorption isotherm; surface energy of colloids; surface concentration; the theory of von Weimarn; preparation of colloidal solutions; crystallization methods, solution of methods.

Under indicators, p. 452, it would probably have been a good thing to have put in a diagram showing a few typical, pH-titration curves and certainly some statement as to pH range for the standard indicators, making clear which indicators can be used for which base or acid and why. The books by Clark and Prideaux are written so as to be of practically no use to anybody who needs such books. Getman makes something the same mistake. We use indicators as a means to determine total acidity and not to enable us to determine the dissociation constant of an acid. One would never guess this from the text.

*Wilder D. Bancroft*

**Gesammelte Abhandlungen.** *By F. Kehrmann. Vol. I. 25 × 17 cm; pp. 207. Leipzig: George Thieme, 1922. Price: $1.70.*—The author, who is professor at Lausanne, is publishing his collected papers in order to give a clearer idea of what he has done. This pamphlet contains his investigations on complex inorganic acids and on steric interference. Usually a man's papers are reprinted for a historical purpose, to show how the subject had developed in his hands and not in the least to give a clearer idea of our present knowledge. If this was the real object, it would have been more satisfactory if the author had written a series of monographs on the different phases. That might have been well worth while.

By complex inorganic acids the author means, of course, the phosphotungstates, etc. To a layman reading these articles for the first time, the striking thing is that apparently no effort was ever made to show that the products analyzed were even approximately pure. At the time these papers were written, people did not know how to do that; but a word on the subject now would not have

been out of place, especially as another avowed object of the publication was to enable people to see the gaps which should be filled up.

In the monoximes of 4-chlorotoluquinone, p. 154, the author was dealing with two forms which reached equilibrium in the melt; but there are no footnotes to show this and to call attention to the fact that the temperature of the true triple point is not known now. The whole subject is left just where it was in 1900 and does not even represent what the author should have known at that time. *Wilder D. Bancroft.*

**The Principles of Radiography.** *By J. A. Crowther. 22 × 15 cm; pp. vi + 138. New York: D. Van Nostrand Company, 1922. Price: $2.00.*—"In this little volume I have tried to give an intelligible, though non-mathematical, account of the physical principles involved in the production of a radiogram, and in the construction and use of the apparatus employed for the purpose. The book contains little or nothing that an experienced X-ray worker will not have had to discover for himself during the course of his work. The discovery of physical principles with the aid of an elaborate X-ray installation is, however, apt to be an expensive as well as a tedious process, and the ordinary text-books of Physics are not primarily concerned with the needs of the radiographers."

The subject is presented under the headings: electrical phenomena; the electric current; the induction of currents; electricity in gases; X-rays; the X-ray tube; the production of high-tension currents; the X-ray installation; making the radiogram; localisation of foreign bodies.

As a sample of the treatment we will quote part of the account of the Coolidge tube, p. 79. "A new form of tube has been devised by Coolidge which entirely overcomes the difficulties due to alterations in the pressure of the residual gas. In this tube the gas is completely removed from the tube and from the metal electrodes by a prolonged process of heating and exhausting. In fact, the tube is so completely evacuated that it is quite impossible to pass a discharge across it in the usual way. In the ordinary type of tube the current is conveyed from one electrode to the other by the action of the molecules of the residual gas. In the Coolidge tube the number of these is so small that no appreciable current can be transmitted by their means. To overcome this difficulty the cathode is made of a closely wound spiral of tungsten wire which can be raised to a white heat by means of an electric current from an insulated battery of storage cells. A metal when heated is found to emit negative electrons, or thermions as they are often called, which are identical with those constituting the cathode stream in an ordinary discharge tube. The quantity of these thermions emitted by the spiral increases rapidly with the temperature, and can be increased or diminished at will by raising or lowering the temperature of the spiral. If now the tube is excited in the usual way while the spiral is glowing, the thermions set free from the latter will be projected by the electric field across the tube, the velocity which they require being proportional to the square root of the potential difference between the electrodes. It is found that the thermions can be focussed into a narrow beam by surrounding the spiral with a metal tube. The beam can then be made to impinge on an anticathode in the usual way."

"At the moment, while the Coolidge tube has been adopted by many of the leading radiographers, its use is by no means general, and many radiographers

have stated that the radiograms obtained with the Coolidge tube are lacking in the fine detail shown by those obtained with an ordinary tube. This is due to the fact that X-radiation is emitted not only from the focus, but to a quite appreciable extent by the whole of the tungsten anticathode, and even by part of the molybdenum support," p. 81. *Wilder D. Bancroft*

**Soap-Making Manual.** *By E. G. Thomssen. 15 × 12 cm; pp. viii + 243 New York: D. Van Nostrand Co., 1922. Price: $4.00.*—"The material contained in this work appeared several years ago in the American Perfumer and Essential Oil Review. Owing to the numerous requests received, it has been decided to now place these articles in book form before those interested," p. III.

The subject is divided into seven chapters: raw materials used in soap making; construction and equipment of a soap plant; classification of soap making methods; classification of soaps; glycerine recovery; synthetical methods; standard methods for the sampling and analysis of commercial fats and oils.

The physical chemist will hardly agree with the author in his statement on the first page that "the detergent properties of soap are due to the fact that it acts as an alkali regulator, that is, when water comes in contact with soap, it undergoes what is called hydrolytic dissociation." The book suggests a number of interesting problems. The question of lather in shaving soap is one; the theory of the open and closed soap is another. On p. 40 is the statement that it is impossible to grain soft soaps; but the difficulty does not seem insurmountable except as a question of cost.

The soaps formed from naphthenic acids seem to be interesting, p. 24. "They resemble the soaps made from cocoanut oil and palm kernel oil, in that they are difficult to salt out and dissociate very slightly with water. The latter property makes them valuable in textile industries when a mild soap is required as a detergent, e. g., in the silk industry. These soaps also possess a high solvent power for mineral oils and emulsify very readily..... That naphthenic acids are a valuable soap material is now recognized; but the soap is not manufactured to any extent at the present time except in Russia."

*Wilder D. Bancroft*

**An Introduction to Theoretical and Applied Colloid Chemistry.** *By Wolfgang Ostwald. Translated by Martin H. Fischer. Second edition. 24 × 16 cm; pp. xiii + 266. New York: John Wiley and Sons, 1922. Price: $2.50.*—In the preface to the second American and eighth German edition, the author says: "The editions preceding this have been exhausted in successively shorter periods—the last in a little more than six months. Such friendly reception touches my sense of responsibility. A thing so widely read needs to be tested and thought about. If the volume is to be more than a momentary cross-sectional view of colloid chemistry, if it is to continue in the eyes of a scientific world an introduction to the subject, repeated revision will be necessary. For this reason this edition has been gone over carefully, been improved and enlarged. I have previously emphasized the limits that must be set for enlargement and yet this volume contains some thirty additional pages. It seemed unnecessary to increase the number of demonstration experiments for I have collected many such in a laboratory manual." *Wilder D. Bancroft*

# THE BEHAVIOR OF CUPROUS OXIDE PHOTO-VOLTAIC CELLS

BY ALLEN D. GARRISON[1]

## Introduction

The terms "Becquerel effect" and "photo-voltaic effect" have been used to distinguish between the light-sensitive systems of the electrode-electrolyte type and the well known "Hallwachs effect" or "photo-electric effect." Cells having one or more light-sensitive electrodes of the former type are able to convert radiant energy into electrical energy and have been called "photo-voltaic cells."

Photo-voltaic cells may be divided for convenience into two general classes: (I) those having the light-sensitive material in the electrodes, in which the electrodes enter into the chemical reaction of the cell and (II) those having the light-sensitive material in the electrolyte, in which the electrodes may be inert. Since the experiments of Becquerel a large number of photo-voltaic cells have been described. Hans Kochan[2] has given a summary of the literature on the subject up to the year 1905. The most complete experimental data on the first class of cells have been recently obtained by Goldmann and Brodsky,[3] and Samsonow[4] using cells consisting of oxidized copper electrodes in various electrolytes. A theoretical explanation of their results was offered by Goldmann[5] based upon the theories of the photo-electric effect. Baur,[6] Titlestad,[7] and Samsonow[8] have studied the cell consisting of inert electrodes of platinum and an electrolyte con-

[1] National Research Fellow in Chemistry.
[2] Kochan: Jahrb. der Rad. und Elect., **2**, 186 (1905).
[3] Goldmann and Brodsky: Ann. Phys., [4] **44**, 849 (1914).
[4] Samsonow: Zeit. wiss. Phot., **18**, 141 (1918).
[5] Goldmann: Ann. Phys., [4] **44**, 901 (1914).
[6] Baur: Zeit. phys. Chem., **66**, 683 (1908); **72**, 323 (1910).
[7] Titlestad: Ibid., **72**, 257 (1910).
[8] Samsonow: Zeit. wiss. Phot., **9**, 12 (1910); **11**, 35 (1912).

taining uranyl and uranous salts, which is the best known example of the second class of cells.

It has been found that the behavior of the cells of the first class is more complicated than it appeared to be from the results previously obtained. The theories advanced have also been found inadequate. It is the purpose of this report first, to present the experimental results which have been obtained using cells of the first class having oxidized copper electrodes and second, to offer an explanation of their behavior.

## Experimental Results

A copper electrode which has been coated with a film of cuprous oxide and placed in a neutral solution of some salt such as an alkali chloride, sulphate or nitrate, has the property of altering its potential relative to the electrolyte on illumination.

A cell consisting of two such electrodes in an electrolyte will set up an e.m.f. and produce a current if one electrode is illuminated while the other is kept in the dark. This is a photo-voltaic cell of the first class since the electrodes contain the light-sensitive material and enter into the chemical action of the cell. Goldmann and Brodsky (loc. cit.) found that the behavior of the cell was independent of the nature of the electrolyte with the exception of certain active ions.

It was previously thought that the cuprous oxide electrode always becomes positive when illumined but it has been found that the direction of the current is dependent on the manner in which the oxide coating is prepared and may be changed by certain changes in the electrolyte and by a variation in the intensity or color of the light. The cuprous oxide electrodes used by Goldmann and others were prepared by the oxidation of copper in a flame. The following method has been devised which produces a more uniform and dense coating of oxide having different properties.

The polished copper electrodes were placed in a solution of cupric chloride in which a cuprous chloride coating was

quickly formed on the copper. This was hydrolyzed in water to the cuprous oxide. By repeating this process several times a very dense and uniform coating was produced. With such dense cuprous oxide films in a neutral electrolyte the effect of illumination was found to be in the opposite direction, that is the electrode becomes negative to the solution. By varying the treatment electrodes of both kinds have been made in this way, their properties depending on the condition of the oxide coating.

Electrodes which on illumination become more positive with respect to the electrolyte will be spoken of as having a "positive light effect" and those which become more negative as having a "negative light effect." The term "photo-potential" will be used to express the change in potential of the light-sensitive electrode or the change in voltage of the photo-voltaic cell on illumination when no current flows. Where photo-potentials are compared, the same intensity of white light was used for illumination unless otherwise stated.

Many cuprous oxide electrodes have been found which ultimately have a positive light effect under prolonged illumination although at first they have a large negative light effect. The maximum of the negative effect is attained more rapidly than that of the positive effect so that electrodes which have intermediate properties have first a negative light effect followed by a recoil in the positive direction which may or may not cross the value of the original potential, that is the initial light effect is negative; the final effect may be either negative or positive. The tendency to a negative effect appears to increase as the density of the oxide film over the copper is increased, at the same time the extent of the positive recoil is diminished.

The following experimental facts have been established in addition to those given by the authors cited above:

1. A cuprous oxide electrode which when illuminated becomes positive with respect to a neutral solution may be made to become negative by increasing the density of the oxide coating.

Goldmann and Brodsky (loc. cit.) concluded from their experiments that the positive light effect was not influenced by varying the thickness of the oxide coating. They, however, produced all their coatings by oxidation in the flame and it has been found that this method while producing varying thicknesses of cuprous oxide does not give a dense and uniform layer. If the copper is first coated with cuprous chloride by dipping in cupric chloride solution, then hydrolyzed to the oxide in water a very uniform oxide coating is produced. After a single treatment the electrode ordinarily behaved as though it had been oxidized in a flame, but after several treatments, by applying thin layers of chloride and by slow hydrolysis of each coating in cold water a dense, red, coherent deposit was produced which had a large negative light effect. Electrodes have been made in this way which had a negative photo-potential of 0.30 volt in the light of a 500 candle power lamp at a distance of 25 cm. These are the largest light effects which have ever been obtained. The positive photo-potentials are small compared to these values rarely exceeding 0.05 volt.

2. A cuprous oxide coating is slowly formed on copper when it is left standing in a neutral solution for a long time in contact with air or oxygen and as a result electrodes which have only a positive effect at first slowly develop the negative effect on contact with oxygen.

A polished copper electrode was placed in a neutral $K_2SO_4$ solution and left standing in contact with it for a long time. Its potential with respect to a normal calomel electrode was recorded at intervals and also the effect of light on the potential. The electrode was approximately —0.093 volt with respect to the calomel electrode at the start and illumination of the electrode produced no marked change in this value. After standing for several days the copper was found to have become coated with a thin, irregular, cuprous oxide layer and its potential slightly increased. This electrode had a slight positive light effect. After standing for a week or so the potential had increased slightly and the effect of illum-

ination was found to be first a small negative effect followed by a larger positive effect. These changes were found to be brought about in a shorter time by causing a discharge of oxygen at the copper electrode by electrolysis. The final state of the electrode is one in which the copper is entirely covered by a dense red crust of oxide, its potential relative to the calomel electrode having become approximately —0.027 volt and its light effect strongly negative. Without electrolysis it requires several weeks to reach this condition. Cuprous oxide electrodes which were prepared in other ways and had positive light effects were found to develop also a negative effect on standing where oxygen was available.

3. When the hydrogen ion concentration is not too high in the electrolyte the illumination of a cuprous oxide electrode causes just enough chemical action to alter the potential of the electrode and no further action takes place until a current flows through the cell. Chemical changes which go on when current passes, produce a current in the opposite direction when the light is removed.

Two cuprous oxide electrodes were prepared of approximately 10 cm.$^2$ area and placed in a normal KCl solution. Electrodes which were to be exposed to light in the photo-voltaic cells were coated on the back with paraffin or some other inert insulator so that only the portion of the electrode which was uniformly illuminated was in contact with the electrolyte. This was necessary in order to reduce local currents in the electrode to a minimum. This photo-voltaic cell having identical electrodes produced no e.m.f. in the dark. It was arranged so that one electrode could be illuminated from a 500 candle power tungsten lamp while the other electrode was kept in the dark. The electrodes were first connected through a low resistance galvanometer. When light was allowed to fall on one electrode a current passed in a direction which indicated that the exposed electrode had become positive with respect to the electrolyte. If this current was permitted to pass for several minutes and the light then turned off, the current dropped to zero and reversed its direction

indicating that the exposed electrode had now become negative to the one which had not been exposed. The extent of this reversal depended on the duration of the illumination. However, when a potentiometer was substituted for the galvanometer and the e.m.f. of the cell in light balanced so that no current passed, the tendency to reverse after illumination was entirely destroyed. No perceptible action took place on illumination other than the change in potential of the electrode. When the light was turned on or off the electrode changed its potential at a moderate rate and was found to come into equilibrium in 15 to 30 seconds.

4. A high concentration of hydrogen ions in solution causes a destruction of cuprous oxide with the formation of copper and cupric ions and a higher concentration is required in the dark than is required in light.

It is a well known fact that the addition of a dilute acid to cuprous oxide decomposes it with the formation of copper and cupric ions in equivalent amounts as follows:

$$Cu_2O + 2H^+ \longrightarrow Cu + Cu^{++} + H_2O$$

Two electrodes were coated with $Cu_2O$ and placed in distilled water. One was exposed to intense white light and the other shaded. The liquid was kept well stirred while very dilute sulphuric acid was added slowly a drop at a time. When the concentration of the hydrogen ions had reached a certain value the coating on the electrode which was illuminated was decomposed, while the other remained unattacked. It required the addition of a few more drops of acid to destroy the coating on the electrode in the dark. If the electrodes were already in a solution which contained cupric ions a higher concentration of hydrogen ions was required to cause the decomposition. This fact may be deduced from the above reaction by the application of the mass law but its real significance may be seen when the reaction is considered from the electrochemical standpoint.

5. The current produced by the light flows in such a direction that the cuprous oxide coating at the exposed electrode is destroyed.

A cuprous oxide electrode was placed in a neutral $K_2SO_4$ solution where the oxide was stable. The electrode was illuminated strongly on one side while the other side was left shaded. This was a photo-voltaic cell producing a current through the electrode itself. The current was found to destroy gradually the cuprous oxide on the illuminated side.

6. A cuprous oxide electrode which has a negative light effect in a neutral electrolyte such as a solution of $K_2SO_4$ or KCl, may be made to have a positive effect by increasing the concentration of the hydrogen ions in solution. The negative effect may also be developed in an electrode which has only the positive effect by decreasing the concentration of the hydrogen ions in the solution.

TABLE I

The Effect of $H^+$ Ion Concentration

| Current | KOH |
|---|---|
| +3.0 | 0.0 cc. |
| +4.0 | 0.1 |
| −0.5 | 0.2 |
| −1.0 | 0.3 |
| −3.0 | 1.0 |
| −4.0 | 2.0 |
| −4.0 | 3.0 |
| −4.0 | 4.0 |
| −2.5 | 7.5 |
| −0.5 | 10.0 |
| | HCl |
| −0.5 | 2.0 |
| +1.0 | 5.0 |
| +1 | |
| +3.0 (neutral) | 5.25 |
| +3.5 (acid) | 5.5 |
| Coating destroyed | 5.6 |

TABLE II

The Effect of $H^+$ Ion Concentration

| Current | $H_2SO_4$ |
|---|---|
| −10.0 | 0.0 cc. |
| − 5.0 | 0.5 |
| − 3.0 | 0.75 |
| − 2.5 | 1.0 |
| − 2.0 | 1.5 |
| − 1.0 | 2.0 |
| − 0.5 | 2.5 |
| + 4.0 | 2.6 |
| + 4.5 | 2.7 |
| + 5.0 (neutral) | 2.8 |
| + 5.0 (acid) | 2.9 |
| Coating destroyed | 3.0 |

Two similar cuprous oxide electrodes were placed in a normal KCl solution and connected through a galvanometer of high resistance. It was arranged so that one electrode could be quickly illuminated or shaded at will. Table I

contains the data obtained with this arrangement. In the first column will be found the deflections of the galvanometer when one electrode was illuminated the sign indicating the direction of the change in potential of that electrode. In the second column will be found first the relative amount of KOH solution added and second the amount of HCl added. In Table II are the results of adding $H_2SO_4$ to a cell whose electrolyte at the start consisted of $K_2SO_4$ containing 1.6 grams of KOH per 100 cc. These results are similar to those obtained with other electrodes.

The law holds only for electrodes having a fairly dense cuprous oxide deposit. Electrodes having a very thin deposit do not always develop a negative light effect on the addition of alkali. Also, electrodes having dense and uniform coatings as has been stated before already have a large negative light effect in neutral solutions. In this case the effect is not increased by the addition of alkali. Thus an electrode which had a maximum negative photo-potential of 0.16 volt in neutral normal $K_2SO_4$ solution retained this photo-potential even after the solution had been made strongly alkaline with KOH.

The same peculiar behavior was found on varying the concentration of the cupric ions in the solution.

7. In the case of electrodes having very dense $Cu_2O$ coatings, those having large negative light effects, an increase in cupric ion concentration in solution reduces the negative effect but does not produce a positive effect. In the case of electrodes having positive effects the addition of cupric ions to the solution causes the appearance of a negative effect.

A photo-voltaic cell was prepared having two electrodes of dense cuprous oxide in normal $K_2SO_4$ solution. The photo-potential of this cell was —0.20 volt. Increasing amounts of solid $CuSO_4$ were added to the cell and the initial negative photo-potential was found to diminish to values which appeared from these preliminary experiments to be proportional to the logarithm of the cupric ion concentration, that is the potential dropped less rapidly than the concentration rose.

Table III contains the results of experiments on a photo-voltaic cell having electrodes with less dense cuprous oxide coatings. The electrodes were connected through a galvanometer and in column one will be found the initial current produced on illumination after concentrated $CuSO_4$ solution had been added as recorded in the second column.

TABLE III

The Influence of $Cu^{++}$ Ion Concentration

| Current Scale divisions | $CuSO_4$ added cc |
|---|---|
| +6.0 | 0.0 |
| +3.5 | 0.5 |
| +1.5 | 1.0 |
| +0.5 | 1.5 |
| 1st. −1.0 then 0 + .2 slowly | 2.2 |
| 1st. −2.0 then 0 + .1 slowly | 3.0 |
| −3.0 | 4.0 |
| −4.0 | 5.0 |
| −4.5 | 6.0 |

The behavior of this electrode is typical of all electrodes when their condition is such that they are near the change from a positive to a negative effect. The initial effect of light is a quick change in the negative direction. If the illumination be kept constant, however, the negative potential is not maintained but approaches again the original dark value sometimes crossing this value and developing a steady positive photo-potential. This phenomenon must not be confused with the reversal of the e.m.f. *after* illumination which was shown to be the result of chemical action of the current *during* illumination.

8. The initial maximum negative photo-potential is approximately proportional to the intensity of the light for low intensities but beyond a certain intensity is constant and no longer increases with the intensity. The initial negative photo-potential attained on constant illumination is not maintained but after the maximum is reached the photo-potential diminishes to an extent which depends on the intensity.

An electrode having a dense cuprous oxide coating was placed in a 0.1 formal $K_2SO_4$ solution and its potential was compared with that of a 0.1 formal calomel electrode by the use of a potentiometer. Its maximum changes in potential relative to the calomel electrode and also the potential after some fixed time had elapsed were observed while the electrode was being illumined with a known intensity of white light.

The intensity of the light was measured with a thermopile and galvanometer, the thermopile being placed as close as possible to the light-sensitive electrode of the photo-voltaic cell. One way of varying the intensity without varying the distribution of energy in the spectrum of the light was to place the light at different distances from the cell and thermopile. A more convenient method was to place a large lens in the path of the light at a distance from the source less than the focal length of the lens. This produced a diverging cone of light and the cell and thermopile were placed in the center of this cone. By a relatively small variation in the distance from the lens to the light source a large variation in the angle of the cone was obtained and a resultant large change in the intensity of the light at the point desired, without any appreciable change in the distribution of the energy. The intensities of the light expressed in the deflections of the galvanometer and the corresponding changes in the e.m.f. of the photo-voltaic cell were recorded at the same time. Table IV contains the experimental results which were obtained with an electrode having a large negative light effect. The results are typical of such electrodes the nature of the effect being always the same although the values of the photo-potentials vary from one electrode to another. The light intensities are given in the first column. In the second column are the maximum values of the photo-potentials which were reached in a few seconds after the light was turned on. Five minutes after the maximum was reached the potential relative to that at the start was recorded in column four. The positive recoil thus obtained increased indefinitely with the intensity.

Up to the value of the intensity marked 100.0 in column

one it may be seen from column three that the maximum photo-potential was almost proportional to the intensity but beyond this point it became independent of the intensity. Electrodes having less dense oxide coatings were found to have relatively less negative effects and larger positive recoils. In those electrodes which had only one thin coating of oxide the positive effect was the only one noticed.

TABLE IV

The Influence of Intensity on the Negative Effect

| Intensity (L) | Maximum Photo-potential ($dv$) | $(dv)/L$ | ($dv$) After 5 min. |
|---|---|---|---|
| 6.2 | −0.0131 | 0.0021 | −0.012 |
| 7.0 | −0.0140 | 0.0020 | −0.013 |
| 8.0 | −0.0146 | 0.0017 | −0.0135 |
| 10.0 | −0.0188 | 0.0019 | −0.016 |
| 16.5 | −0.0367 | 0.0022 | −0.032 |
| 40.0 | −0.082 | 0.0020 | −0.032 |
| 52.0 | −0.105 | 0.0020 | −0.035 |
| 71.0 | −0.119 | 0.0017 | −0.029 |
| 77.0 | −0.121 | 0.0017 | −0.019 |
| 93.0 | −0.152 | 0.0016 | −0.012 |
| 100.0 | −0.157 | 0.0016 | −0.007 |
| 183.0 | −0.206 | 0.0011 | −0.005 |
| 260.0 | −0.200 | 0.0007 | +0.001 |
| 339.0 | −0.202 | 0.0005 | +0.005 |
| 490.0 | −0.205 | 0.0004 | +0.010 |

9. With increasing intensity of illumination the positive effect increases approximately as the logarithm of the intensity. The maximum positive photo-potential remains constant with constant illumination.

In Table V are the results of experiments in which varying intensities of light were used with an electrode having a single coating of cuprous oxide and consequently having only the positive effect. In the first column are the light intensities and in the second column the corresponding values of the positive photo-potentials. Unlike the negative light effects the positive photo-potentials increase more slowly when the

light is turned on to a constant value which is maintained as long as the intensity remains constant and no current flows. In the third and fourth columns are the values of the photo-potentials divided by the corresponding intensities and logarithms of the intensities, respectively.

TABLE V

The Influence of Intensity on the Positive Effect

| Intensity (L) | Photo-potential ($dv$) | $(dv)/L$ | $(dv)/\log L$ |
|---|---|---|---|
| 52.0 | +0.024 volts | $4.7\times10^{-4}$ | 0.0140 |
| 56.5 | +0.025 | 4.5 | 0.0146 |
| 75.0 | +0.029 | 4.27 | 0.0175 |
| 80.0 | +0.030 | 3.7 | 0.0158 |
| 157.0 | +0.052 | 3.3 | 0.0231 |
| 395.0 | +0.056 | 1.3 | 0.0212 |
| 477.0 | +0.057 | 1.2 | 0.0213 |

From this it may be seen that the relation is nearly the logarithmic one. Although he did not arrive at this relation Goldmann (loc. cit.) found that direct proportionality did not hold for electrodes oxidized in the flame and that the photo-potential did not increase as rapidly as the intensity.

10. In the case of electrodes having both a positive and a negative effect, it has been found by using a monochromatic illuminator that light of long wave-length produced the negative effect, that light of short wave-length produced the positive effect and that the light of intermediate wave-lengths produced both effects, the negative effect appearing first as has been described. It was also found that an increase in the concentration of the hydrogen ions in the solution shifted the intermediate position toward the longer wave-lengths, and that a decrease shifted the position toward the shorter wave-lengths. However, the data are at present incomplete on this phase of the problem chiefly due to the fact that the intensity of the radiation throughout the spectrum of the illuminator was not uniform, the maximum intensity being in the infra red and the shorter waves having relatively small

energy. In view of the complicated changes introduced by variations in intensity the effects thus far obtained cannot be attributed entirely to variations in wave-length. For this reason the experiments on this point will be reported when they are in a more satisfactory condition.

## Theoretical Part

It is difficult to explain the complicated behavior of the cuprous oxide cells by application of the theory of electron emission as has been attempted by Goldmann. It cannot be clearly seen from this theory how the light may cause either a positive or a negative effect or both determined by the condition of the oxide or the concentration of the hydrogen ions or the cupric ions in solution. There is also additional experimental evidence that the values of the absolute electrode potentials used by Goldmann were not the most probable ones.[1]

Consequently the problem will be attacked in this report from the photo-chemical rather than the photo-electric standpoint. By the application of the established laws of electro-chemical equilibrium to the cuprous oxide electrode it is possible to isolate a single light-sensitive reaction and to explain all the known characteristics of the photo-voltaic cells by attributing certain properties to this single photo-chemical equilibrium. If this theory proves itself to be the most probable explanation of the photo-voltaic cells it becomes of interest to those who are studying thermal and photo-chemical reaction velocities or photo-phenomena in general since it offers a new and direct method of measuring the effects of light.

For simplifying the explanation of electrode behavior it has been found convenient to classify equilibria in a more precise manner than is usually done in electro-chemical text-books. Reactions are described as reversible, irreversible, polarizable or nonpolarizable. In a number of instances,

[1] Garrison: Jour. Am. Chem. Soc., **45**, 37 (1923).

however, the idea of physical reversibility has taken the place of that of thermodynamic reversibility and polarization has not been properly connected with irreversibility. As in any thermodynamically irreversible process the energy relations of an irreversible electrochemical reaction are indefinite in that the available work term may have any value between its maximum value and zero. The requirements of reversibility in an electrochemical reaction are, first, the potential of each electrode will not vary from its normal equilibrium value by more than an infinitely small amount, and second, diffusion of any substance in the system will take place only between points at an infinitely small difference in pressure. It appears advisable to use these terms only in this strict sense and to introduce other terms which express the physical conditions of reversible equilibria. The term polarization has sometimes been used to describe this physical characteristic but in its more rigorous definition, polarization is always irreversible.

A "primary" reversible electrochemical reaction will be defined as a reaction which may proceed reversibly to an appreciable extent at an electrode at constant electrode potential. A "secondary" reversible electrochemical reaction will be defined as one which may proceed reversibly but only as the electrode potential continually increases or decreases.

This distinction may be made clearer by an example. Pure mercury in contact with an electrolyte containing a mercury salt in solution and also some of the solid salt has frequently been called a "nonpolarizable" electrode, and when the solid salt is absent a "polarizable" electrode. These terms are misleading in that they convey the idea that the passage of current in the first case is reversible and in the second case irreversible because of the physical nature of the electrode. For, quoting a recent and accurate text book of physical chemistry:

"The name 'polarization' [is] used in general to denote the production by the passage of the current of any change in the solution adjoining the electrode or in the surface of the

electrode which makes its potential deviate from its *normal* value." In polarization therefore the concentration of some substance is locally changed in the neighborhood of the electrode and after a time the concentrations become equalized by the irreversible process of diffusion and the electrode potential returns to its normal value. The mercury electrode in either of the above cases may be polarized by high current densities or may behave reversibly at low current densities. The mercury ion equilibrium in the first case is primary, since during reaction the mercury ion concentration is kept constant as long as there is any solid salt left. It is secondary in the second case for as reaction proceeds reversibly the mercury ions throughout the solution change their concentration. This change is not due to polarization since the potential of the electrode does not vary from its normal value at any time. Changes in electrode potential in a secondary reaction are analogous to changes in pressure in the reversible isothermal expansion of a gas.

Assuming that an electrode has reached equilibrium and behaves reversibly some conclusions may now be drawn from the established laws of electrochemistry.

1. The concentrations of the reactants of a primary reaction determine the potential of the electrode by the well known logarithmic relation, and

2. The potential of the electrode as thus determined fixes the concentrations of the reactants of all the secondary equilibria.

A certain change in the solubility of the mercury salt in the above example alters the potential of the electrode accordingly, since by definition the primary reaction may be displaced without appreciable change in concentration thus proceeding until all the secondary reactions have come into equilibrium. On the other hand a change in the concentration of one of the reactants of a secondary equilibrium does not alter the potential of the electrode in the presence of a primary reaction, unless it indirectly shifts the primary equilibrium. If in the above example the solid salt were mercurous chlo-

ride then an increase of hydrogen ions in solution by the addition of sulphuric acid would not alter the electrode potential, the mercury equilibrium would be shifted slightly to bring the hydrogen and oxygen pressures into equilibrium with the electrode potential.

3. When the potential of the electrode is changed from the outside by an infinitely small value ($dv$) the primary equilibrium is displaced quantitatively in accordance with Faraday's laws and

4. The secondary reactions because of their rapid changes in pressure require only a negligible fraction of the current to bring them again into complete equilibrium with the new electrode potential.

5. If no primary reactions are possible then on altering the normal electrode potential from the outside by a small amount ($dv$) the reaction which proceeds with the smallest changes in pressure, that is the reaction which resembles a primary one most closely, is displaced quantitatively in accordance with Faraday's laws with the exception of the small amount of current necessary to keep the other secondary reactions in equilibrium. Unlike the electrode having a primary reaction the potential must be repeatedly changed from the outside in order that the reaction may continue.

To apply this classification to the reactions of the cuprous oxide electrode it is necessary to know at least in a relative way the changes in the concentrations of each substance in equilibrium with the electrode. Let us consider a copper electrode coated with cuprous oxide and placed in a normal aqueous $K_2SO_4$ solution. All the ions in the solution must establish an equilibrium at the surface of the electrode, thus

$$(1)\quad 2H^+ \longleftrightarrow H_2\ (\text{gas}) + 2\ (+)$$
$$(2)\quad 2O^= \longleftrightarrow O_2\ (\text{gas}) + 4\ (-)$$
$$(3)\quad K^+ \longleftrightarrow K\ (\text{metal}) + (+)$$

For the sake of simplicity it is assumed that the sulphate ion is not capable of an equilibrium. Under these conditions (3) as an ideal secondary reaction for the concentration of

potassium metal is infinitely small compared to the massive metal at any electrode potentials we shall consider. The gas equilibria (1) and (2) are also secondary since the electrode is not supposed to be in equilibrium with a gas phase at constant pressure.

Cuprous oxide has a finite solubility and as a result the following equilibria are established,

(4) $Cu_2O(solid) \longleftrightarrow Cu_2O(dissolved) \longleftrightarrow 2Cu^+ + O^=$

(5) $Cu^+ \longleftrightarrow Cu + (+)$

(6) $Cu \longleftrightarrow Cu^{++} + (=)$

It may readily be seen that reaction (5) is a primary reaction as long as solid cuprous oxide and massive copper are present. Reaction (6) although dependent on (5) is a secondary reaction since the cupric ion concentration may vary in the solution. However, as long as massive copper is present it has only one variable reactant and therefore resembles a primary reaction more closely than the gas equilibria.

If the normal electrode potential were displaced from the outside, reactions (5) and (4) would proceed according to Faraday's laws. If this potential were higher than the equilibrium potential (4) and (5) would proceed to the left and $Cu_2O$ would be formed at the expense of copper. This would continue as a primary reaction at the same electrode potential until the copper were exhausted or until it became coated with such dense cuprous oxide that it no longer behaved as massive copper toward the solution.

Some data on the variation of solution pressure with amount of metal have been obtained by Oberbeck[1] and Königsberger and Müller,[2] in which they show that the solution pressure of a metal is independent of the amount of metal present until the amount becomes very small and then its apparent concentration varies rapidly as the amount decreases.

Therefore at the point where copper begins to be exhausted

[1] Wied. Ann., 31, 336 (1887).

[2] Phys. Zeit., 6, 847, 849 (1905).

and the massive metal is cut off from contact with the electrolyte by the cuprous oxide coating, the concentration of the copper becomes variable and reaction (5) is no longer primary. This explains the experimental fact that the equilibrium potential is higher for very dense cuprous oxide coatings than for others. It was also found experimentally that this condition was brought about by passing a current in such a direction that the cuprous oxide coating was formed at the expense of copper.

A simple calculation is all that is necessary to explain the formation of cuprous oxide at the expense of copper when in contact with atmospheric oxygen. At the electrode potential of —0.09 volt with respect to the normal calomel element and in a solution where $OH^-$ ions approximate one mole per liter, the pressure of oxygen gas in equilibrium must be approximately $^1/_{2000}$ of an atmosphere. When brought in contact with oxygen at $^1/_5$ atmosphere this reaction is polarized and as oxygen diffuses through the solution to the electrode and ionizes, the electrode becomes more positive. This is equivalent to a slight current forming cuprous oxide.

It was found experimentally that a pure copper electrode in $K_2SO_4$ solution is not sensitive to visible radiation. This electrode has necessarily set up all the equilibria (1), (2), (3), (5), and (6). The light-sensitive reaction must therefore be introduced by the presence of solid cuprous oxide. From experiments Nos. 4 and 5 we may conclude that reaction (4) is shifted to the right by the radiation. If we start with this assumption all the characteristics of the influence of light which have been found for these cells may be explained by the established laws of electrochemistry.

In the case of an electrode containing massive copper, equilibrium (5) was found to be primary, and reaction (2) secondary. If the reaction (4) were displaced to the right by the radiation the concentrations of both the cuprous ions and the oxygen ions increase simultaneously. The electrode potential will be determined by the cuprous ion concentration since it is primary. This accounts for the positive effect.

If the velocity of formation of ions is proportional to the intensity of the light then the concentration of cuprous ions at equilibrium is proportional to the intensity and the photo-potential should increase with the logarithm of the intensity. This maximum photo-potential would also remain constant with constant illumination provided no current was permitted to flow. Therefore the properties which we must attribute to the photo-chemical reaction are in agreement with the Einstein photo-chemical law in that the number of quanta available for shifting the reaction constant is proportional to the light intensity.

It was proven that reaction (5) is secondary when the cuprous oxide becomes of sufficient density to limit the amount of copper available for reaction. At this point all the reactions of the electrode are secondary. To trace the effect of an increased ionization of cuprous oxide it is necessary to know how the reactions come again into equilibrium and which reaction resembles a primary one most closely. In this case it is possible that the oxygen equilibrium behaves more like a primary one than does the copper equilibrium, making the light effect negative.

There are two ways in which the cupric ions may adjust themselves to the new concentration of cuprous ions, as follows:

(7) $2\,Cu^{+} \longrightarrow 2Cu + 2(+) \longrightarrow Cu + Cu^{++}$

(8) $Cu^{+} \longrightarrow Cu + (+) \longrightarrow Cu^{++} + (-)$

As the cuprous ions increase they deposit on the electrode as copper but this greatly increases the concentration of the copper. This necessitates the solution of cupric ions as in (7) or (8). Suppose that the first small amount of cuprous ions liberated reacts as in (7). Although equivalent quantities of copper and cupric ions are formed, under the conditions specified the copper concentration may increase faster than the cupric ion concentration for an addition of the same amount of material. As a result the products of reaction (7) accelerate reaction (8), which results in a more negative electrode potential.

The increased oxygen ion concentration also tends toward a negative photo-potential the reaction being now relatively less secondary than the reaction $Cu^{+} \longrightarrow Cu + (+)$.

Therefore when the concentration of copper is very small at the start and the light increases the concentrations of the cuprous and oxygen ions simultaneously, the electrode must become negative in order to establish the other secondary equilibria. If the concentration of copper were infinitely small it can easily be seen how the negative photo-potential may become large.

With increasing intensity of the light more cuprous oxide ionizes and enough copper forms through reaction (7) to behave as massive copper. After this point reaction (5) is again primary, the products of reaction (7) no longer accelerate reaction (8) and a further increase in intensity produces the positive recoil. This explains those electrodes which have a temporary negative light effect followed by a permanent positive effect.

By reaction (4) the cuprous ion concentration is dependent on the oxygen ion concentration and by reaction with water the oxygen and hydrogen ions are interdependent. Thus by adding hydrogen ions cuprous ions are liberated which react according to (7) and (8) and by the reverse cuprous ions and copper are removed. This explains the decomposition of cuprous oxide in acid solution and the effects on the positive and negative light effects.

By applying the mass law to reaction (8) it is evident that in the case of large negative light effects cupric ions reduce the maximum negative photo-potential. In other cases the additions of cupric ions may reduce the amount of copper and develop the negative effect by reversing reaction (7).

It appears from experiment 10 above that an increase in the frequency of the light influences either the rate or the amount of oxide ionized. This point requires more experimental data.

In connection with this theory of cuprous oxide cells it is interesting to note that cuprous chloride electrodes as well

as silver halide electrodes behave in some ways like the cuprous oxide electrodes. It has been known for a long time that moist cuprous chloride decomposes in light as follows:

$$2CuCl \longrightarrow Cu + CuCl_2$$

but the mechanism of this reaction in which an equivalent of copper and cupric chloride are formed has not been satisfactorily explained. An explanation is evident, however, by applying this theory and substituting chlorine for oxygen. Dry cuprous chloride and silver halides are stable in light, and according to this theory the "catalytic" action of moisture is the action of a solvent which must moisten the solid to permit electrochemical equilibrium.

From this we may conclude that the influence of the radiation in such cases is primarily a separation of the charged elements as ions followed by the establishment of an electrochemical equilibrium. In some instances the limit of solubility from an electrochemical standpoint is reached and a spontaneous discharge of ions takes place with the liberation of the elements.[1]

**Summary**

The formation of cuprous oxide electrodes and the conditions under which they have both a positive and a negative light effect have been described and the general characteristics of each effect discussed.

The positive photo-potential was found approximately proportional to the log of the light intensity and increased with increasing hydrogen ion concentration.

The maximum negative photo-potential is proportional to the light intensity for low intensities and constant at high intensities, while the positive recoil following the negative maximum, increased with the intensity. The maximum negative photo-potential decreased with increasing hydrogen ion concentration. For large effects the negative photo-

[1] Nernst: Ber. deutsch. chem. Ges., **30**, 1547 (1897); Bodländer: Zeit. phys. Chem., **27**, 55 (1898).

potential decreased and for small effects increased with increasing cupric ion concentration.

The characteristics of the cuprous oxide electrodes which are now known were all explained from the proven laws of electro-chemistry by the assumption that the light shifts the equilibrium constant of the reaction

$$Cu_2O \text{ (solid)} \longleftrightarrow Cu_2O \text{ (dissolved)} \longleftrightarrow 2Cu^+ + O^=$$

causing the cuprous oxide to behave as though its solubility was increased in the light. The results are what would be expected if the Einstein photo-chemical law applied to this reaction in a qualitative manner. The active frequencies are as yet undetermined.

The theory is also applicable to the silver halide electrodes as well as the copper electrodes since they behave in the same way and is opposed to the theory that the primary effect of radiation is either photo-electric in its nature or causes a direct separation of the uncharged elements.

The theory that the effect of the light is a separation of the charged elements as ions or thereby an increase in the solubility of the salt and that the decomposition is made complete only by electrochemical equilibrium is supported by the experimental fact that the perfectly dry salts are stable in light.

The author wishes to thank Prof. H. A. Wilson, F.R.S., for his suggestions and interest in this work.

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# THE REDUCTION OF COPPER OXIDE BY CARBON MONOXIDE AND THE CATALYTIC OXIDATION OF CARBON MONOXIDE IN PRESENCE OF COPPER AND OF COPPER OXIDE

BY HOWARD ALGERNON JONES AND HUGH STOTT TAYLOR

The mechanism of even simple chemical reactions and of simple catalytic actions is by no means so fully investigated as could be desired, nor is it possible to state definitely in many cases how such reactions occur. Reasoning by analogy is apt to lead to quite erroneous conclusions and such conclusions tend to retard chemical progress. The truth of these statements may be very well illustrated by detailed investigations of such apparently simple reactions as the reduction of oxides by various reducing gases and the catalytic oxidation of such gases in presence of metallic oxides or their reduced metals. A simple statement of a reaction by chemical formulae such as:—

$$CuO + H_2 = Cu + H_2O$$

fails to reveal the complexities of the reduction process as the recent study of this reaction by Pease and Taylor[1] has shown. Nor does the corresponding equation

$$2H_2 + O_2 \xrightarrow{Cu} 2H_2O$$

give any real picture of the mechanism of the catalytic change.

The following investigation attempts to extend our knowledge of these simple processes by a thorough study of the reduction of copper oxide by carbon monoxide and of the catalytic combination of carbon monoxide and oxygen in presence of copper oxide and of reduced copper. It will be seen that these reactions show striking similarities in certain aspects to the corresponding reactions with hydrogen. At the same time there are marked and fundamental differences, which, as will be shown, are of great importance in processes,

[1] Pease and Taylor: Jour. Am. Chem. Soc., **43**, 10, 2179 (1921).

such as the preferential combustion of carbon monoxide in hydrogen, having important technical possibilities.

An investigation of the reduction of copper oxide by carbon monoxide has been carried out by Wright, Luff and Rennie.[1] Carbon monoxide generated by treating potassium ferrocyanide with sulphuric acid and purified by caustic soda, silver nitrate and sulphuric acid was passed at a constant rate through a U-tube containing weighed amounts of copper oxide obtained by calcining the nitrate. The temperature of the U-tube was maintained constant at various fixed temperatures by means of vapor baths and the amount of reduction determined by weighing the U-tube after a lapse of time. Experiments were carried out over a range of temperature from 84° to 185°. Measurements were also made of the amount of reduction of copper oxide in sealed tubes, filled with carbon monoxide and maintained at constant temperature for periods up to 6 hours. Using the continuous flow method, an initial period of "incubation" was observed during which no measurable amount of reduction took place, this period varying in duration inversely with the temperature. The reduction appeared to start at some particle of oxide (as evidenced by the appearance of copper nuclei at this point) and was propagated from particle to particle through the mass. The amount of reduction and hence the rate of carbon dioxide formation over any definite time interval increased very rapidly after the start (induction period), passed through a maximum and as the oxide was converted to metal became again immeasurably small.

In an earlier paper by Wright and Luff[2] the following statement is made: "In the course of some other experiments of the same kind, it was noticed that when the carbon oxide was not purified from small quantities of admixed air, the amount of carbon dioxide collected greatly *exceeded* that corresponding to the loss of weight; thus in two experiments the following numbers were obtained:—

[1] Wright, Luff and Rennie: Jour. Chem. Soc., 35, 475 (1879).

[2] Wright and Luff: Jour. Chem. Soc., 33, 1 (1878).

| Time of exposure | Oxygen removed, calculated from carbon dioxide found, that originally present being 100 percent | Oxygen removed, calculated from the loss in weight |
|---|---|---|
| (1) 90 minutes | 155.0 percent | 71.9 percent |
| (2) 220 minutes | 113.0 percent | 72.0 percent |

whence it is evident that, either the partially reduced oxide acted catalytically in causing combination between the free oxygen and the carbon oxide in the gaseous mixture, or the nearly reduced oxide took up the free oxygen and was then again reduced in virtue of the reactions:

$$Cu_xOy + 0 = Cu_xO_{y+1}$$
$$Cu_xO_{y+1} + CO = Cu_xOy + CO_2$$

thus forming more carbon dioxide than that corresponding to the difference between the original oxygen in the cupric oxide employed and that left associated with the copper after the action was completed."

Beyond the observation that a mixture of carbon monoxide and air, when passed over partly reduced copper oxide, gives an abnormally large amount of carbon dioxide when calculation is made on the basis of the oxygen content of the copper oxide, the above authors arrived at no definite conclusions as to the mechanism of such action. A thorough and more detailed study of these points might, it was thought, assist in explaining this mechanism.

In claiming protection for the process of preferential combustion of carbon monoxide in hydrogen, Harger and Terry[1] cite the use of copper and of copper oxide in addition to various other metals and oxides.

E. K. Rideal[2] in a study of the preferential nature of the above process concluded that in presence of copper oxide, a mixture containing 14 percent carbon monoxide, 11.5 percent oxygen and 74.5 percent hydrogen gave a ratio of 0.466 carbon monoxide to 1 hydrogen by volume burned when passed at

[1] Harger and Terry: Brit. Pat., **127**, 609 (1917).
[2] E. K. Rideal: Jour. Chem. Soc., **115**, 993 (1919).

a rate of 33 cc per minute at 280°. At lower temperatures the ratio CO: $H_2$ of the burnt gases shows a continuous increase. Rideal furthermore suggests that the two oxidation processes may be related to one another by the equation

$$\frac{-\frac{d\,C_{co}}{dt}}{-\frac{d\,C_{H_2}}{dt}} = \frac{(CO)}{(H_2)(O_2)^{1/2}}$$

Various assumptions were made as to mechanisms which would result in this ratio and also as to the adsorptions of the several gases concerned. None of the theories as to mechanism received any detailed test nor are the assumptions as to adsorptions in agreement with the recently published data of Taylor and Burns[1] relative to the metal catalysts nor with the data of Dr. A. F. Benton[2] on metallic oxides. In the latter work it has been shown that strong preferential adsorption of carbon monoxide occurs with but small adsorptions of oxygen and hydrogen by active oxide masses. Some evidence as to reaction mechanism will be adduced in this communication.

Due to the increased importance of the problem of the removal of small percentages of carbon monoxide from air, the Chemical Warfare Service of the U. S. Army during the late war made a series of investigations in order to develop suitable catalysts for this work.[3] As a result of this war work, Lamb, Scalione and Edgar[4] have made use of a catalyst consisting of 60 percent manganese dioxide and 40 percent cupric oxide called Hopcalite, to burn carbon monoxide preferentially when present in concentrations up to 1 percent in hydrogen. Their communication appeared subsequent to the completion of this work and they conclude that the results obtained are

[1] Taylor and Burns: Jour. Am. Chem. Soc., **43**, 6, 1273 (1921).

[2] Benton: Ibid., **45**, 887 (1923).

[3] Lamb, Bray and Frazer: Jour. Ind. Eng. Chem., **12**, 213 (1920); Rogers, Piggot, Bahlke and Jennings: Jour. Am. Chem. Soc., **43**, 9, 1973 (1921); Merrill and Scalione: Ibid., **43**, 9, 1982 (1921).

[4] Lamb, Scalione and Edgar: Ibid., **44**, 4, 738 (1922).

not in conflict with the computations put forward by E. K. Rideal, relative to the simultaneous oxidation of carbon monoxide and hydrogen. The mechanism of preferential catalytic oxidation of carbon monoxide in admixture with hydrogen is not discussed by them.

It is suggested[1] that the mechanism of the catalytic oxidation of carbon monoxide in concentrations up to 5 percent in air may possibly be explained by a chemical theory. This theory is based on the alternate reduction and oxidation of any one or possibly all of the various oxides as used in mixtures by the above authors in order to obtain suitable catalysts. They further suggest that the oxide upon which the catalytic activity of the mixture depends is not reoxidized by oxygen fast enough to maintain its catalytic action when present alone and hence the function of the other oxide or oxides is to increase the velocity of the reoxidation of the active constituent of the catalyst mixture.

## Experimental

A sketch of our apparatus is shown in Figure 1. Electrolytic oxygen from tank (A) was passed through heated palladized asbestos in the tube (B) to convert the small percentage of hydrogen in the gas to water, thence through a phosphorus pentoxide drying tube (C). From (C), the pure dry oxygen was passed through a Nichrome tube filled with graphite and resting in a furnace (D) maintained at 1050–1100° C. The carbon monoxide thus formed was led through a heated silica tube (E), containing copper turnings, to convert any traces of oxygen present at this point to carbon dioxide, through the soda-lime towers (F) to remove carbon dioxide, through the flow-meter (H), the phosphorus pentoxide in (K) and finally, into the electrically heated furnace (L) which contained the copper oxide. The furnace consisted of two co-axial glass tubes, the inner one containing the copper

[1] Rogers, Piggott, Bahlke and Jennings: Jour. Am. Chem. Soc., **43**, 9, 1973 (1921).

oxide charge while the outer one was wrapped on the outside with nichrome wire and covered with magnesia pipe covering thus serving as a heating jacket. Temperatures were always read on a mercury-filled thermometer with the bulb directly in contact with the oxide charge. The thermometer passed out through the outer jacket at the top. Near the bottom of the outer jacket was sealed a T-tube (M), through which the gases were admitted, passed up between the outer and inner tube and down through the oxide in the inner tube. An electrolytic generator (N), was used for obtaining the small quantities of oxygen used in the work. This oxygen was passed through heated palladized asbestos in silica tube

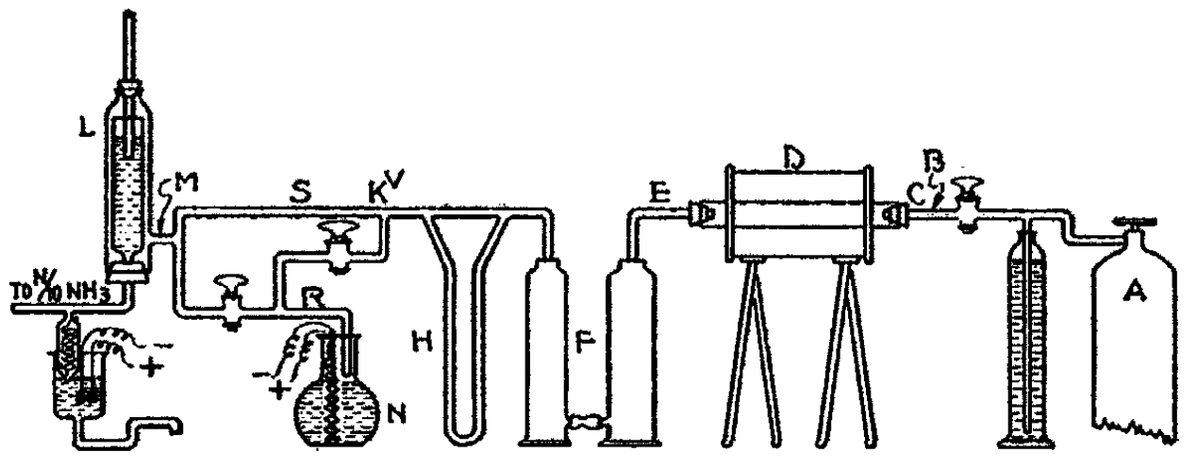



Fig. 1

(P), over phosphorus pentoxide in (R) and admitted to the carbon monoxide stream at the T-tube (M). When carbon dioxide was wanted, the necessary amount of oxygen gas was admitted to the carbon monoxide at point (V) and burned to carbon dioxide over heated copper in silica tube (S).

Rates of reduction were measured by determining the rate of carbon dioxide formation. This was accomplished in a portion of the work by means of an apparatus reported by Rideal and Taylor.[1] They measured the fall in conductivity of one-two hundredth normal lime water caused by absorption of carbon dioxide which precipitates calcium carbonate. Since we were dealing with much higher con-

[1] Rideal and Taylor: The Analyst, **44**, 89 (1919).

centrations of carbon dioxide the heavy precipitate of calcium carbonate might clog the absorption system and collect around the electrodes, thereby creating a disturbing influence on conductivity measurements. For this reason, we took advantage of the fact that one-tenth normal ammonia water has a much lower conductivity than one-tenth normal ammonium carbonate and used one-tenth normal ammonia for the absorbing medium. The effluent gases from the furnace (L) were passed co-currently with a constant flow of

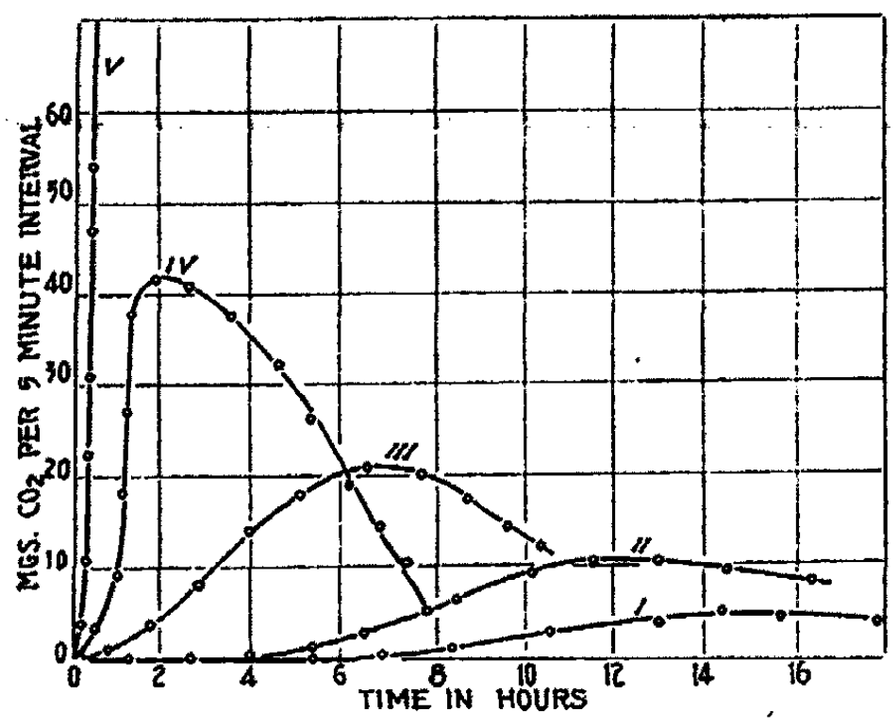



Fig. 2
Curve I, reduction at 80°
Curve II, reduction at 90°
Curve III, reduction at 100°
Curve IV, reduction at 125°
Curve V, reduction at 150°

calibrated ammonia water through a spiral condenser coil and into the conductivity cell maintained at constant temperature. In some of the experiments, the carbon dioxide was absorbed by soda-lime and weighed.

Rates of reduction are expressed throughout in terms of milligrams of carbon dioxide formed in a 5-minute interval. The rate of flow of carbon monoxide was maintained constant at 50 cc per minute. Samples of 5 cc apparent volume of

copper oxide weighing within a few tenths of 10 g were always employed. Since the containing tube was 2.5 sq. cm. in cross section, this gave a layer of oxide about 2 cm deep. An imported copper oxide intended for organic analysis (8–10 mesh) was used.

It has been shown[1] that the initial temperature at which reduction of metallic oxides by carbon monoxide occurred, was consistently inferior in the cases investigated, to the initial temperature at which hydrogen causes reduction. This is verified by comparing our curves for reduction in Figure 2 with those for hydrogen obtained by Pease and Taylor.[2] It will be seen that these possess the characteristics as reported by Wright, Luff and Rennie. There is the incubation period at the lower temperatures shortening with increase in temperature until it is practically non-existent at 125° and higher temperatures. The induction period shows a more pronounced rate of increase of reduction with time the higher the temperature; in fact, reduction increases so rapidly at 150° that we were unable to control the temperature after the last point marked on the curve. At 125°, the duration of the induction period is again rather short when a maximum is reached corresponding to 83 mg of carbon dioxide formed per 5-minute interval and the reduction falls off to a minimum from this point. If all the carbon monoxide passed had been converted to carbon dioxide, the rate would have corresponded to 450 mg in 5 minutes.

The characteristics of the reduction were made clear by examination of numerous samples in the various stages of the same. The reduction appeared to start (as evidenced by the appearance of the red speck of copper) at some particle in the lower half of the charge at the lower temperatures (below 125°). At 125° and 150°, the reduction generally commenced at some point near the middle of the charge, while at still

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[1] Wright and Luff: Jour. Chem. Soc., 33, 1, 504 (1878); Fay, Lane, Seeker and Ferguson: Poly. Eng., 10, 72 (1910).

[2] Pease and Taylor: Jour. Am. Chem. Soc., 43, 10, 2179 (1921).

higher temperatures, the initial action would usually be observed in the first layer of oxide where contact with the carbon monoxide was first made.

### Effect of Copper

It was shown[1] that copper is an auto-catalyst for the reduction of copper oxide by hydrogen by virtue of the increased area of copper-copper oxide interface formed; the reduction occurring most readily and for the most part at this

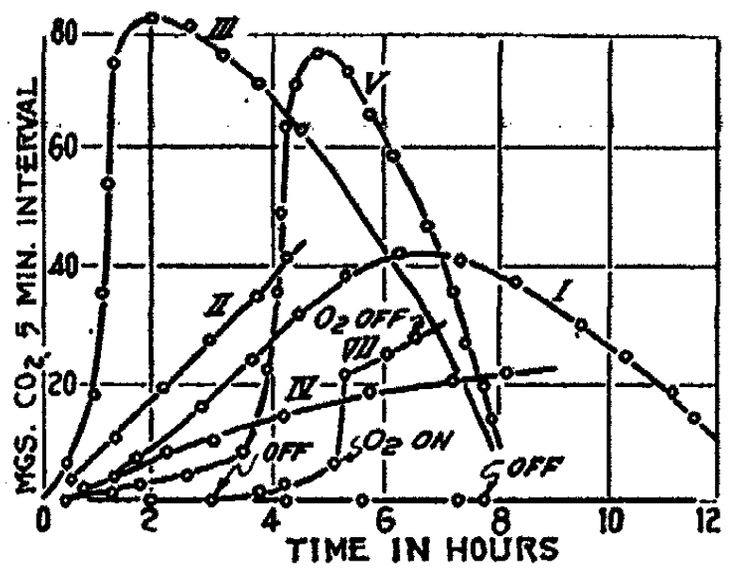



Fig. 3

Curve I, reduction at 100°
Curve II, effect of copper on reduction at 100°
Curve III, reduction at 125°
Curve IV, effect of 20 mg equivalent of oxygen on reeuction at 25°
Curve V, effect of 20 mg carbon dioxide on reduction at 125°
Curve VI, effect of 20 mg equivalent of oxygen on reduction at 100°
Curve VII, effect of 20 mg equivalent of oxygen on reduction at 100°

point. It seemed desirable to try this same effect of copper on the reduction by carbon monoxide. This was done with a layer of freshly reduced granules placed on top of the oxide and reduced at 100°. The result is shown graphically by Curve II, Figure 3. Curve I, Figure 3 represents the reduction by carbon monoxide of pure copper oxide at 100°. A comparison of the curves shows that the incubation period is practically eliminated, it being brief though measurable

[1] Pease and Taylor: Jour. Am. Chem. Soc., **43**, 10, 2179 (1921).

normally. An examination of this sample after reduction had proceeded as far as indicated showed that the initial action had begun at the top of the charge in contact with the copper but reduction had also set in at the bottom of the charge so that the copper-copper oxide interface area was greater than usual, thus explaining the slightly greater rate of reduction in Curve II. It had been noted that ordinarily the top layer of oxide was last reduced at 100° so that this was evidence of the auto-catalytic nature of the reduction.

### Effect of Carbon Dioxide

Twenty mg of carbon dioxide per 5-minute interval were added to the carbon monoxide by means of the arrangement of apparatus previously described. The milliammeter reading of the oxygen generator was 0.292 amp. which generated sufficient oxygen to give the stated amount of carbon dioxide when passed with carbon monoxide over heated copper. In the 250 cc of carbon monoxide which passed in 5 minutes, this is equivalent to 4.5 percent by volume. The reduction at 125° with this quantity of carbon dioxide passed with the carbon monoxide is shown in Curve V, Figure 3. Curve III, Figure 3 represents the normal reduction at 125°. A comparison of these curves shows that whereas normally there is no measurable incubation period at 125°, the presence of this small quantity of carbon dioxide in the carbon monoxide causes an incubation period of about one hour while the time of induction is also lengthened 2 hours. Pease and Taylor have shown that a very small quantity of water vapor inhibits the reduction of copper oxide by hydrogen most probably as a result of an adsorbed, protective layer of water vapor on the surface of the copper oxide which effectively prevents the formation of copper nuclei at this temperature. Dr. A. F. Benton has found in this laboratory that carbon dioxide is adsorbed by copper oxide though in all probability it is not so strongly adsorbed as water vapor. That carbon dioxide has little effect on the reduction at the copper-copper oxide interface is plainly evident since the carbon dioxide was run

during the entire experiment and once the formation of the copper nuclei was well started, the reduction follows the regular curve. The effect, therefore, is probably to form a slight protective film on the copper oxide surface and thus retard the primary reaction, i. e., the formation of copper nuclei.

### Effect of Oxygen

Since carbon monoxide and hydrogen, with more than sufficient oxygen to burn completely all the carbon monoxide present, is passed over copper oxide as a preferential combustion catalyst, we believed that probably some important data could be obtained to assist in explaining the mechanism of this reaction by experiments at various temperatures with a known percentage of oxygen present in the carbon monoxide passed through the copper oxide mass. The effect on the reduction of copper oxide by carbon monoxide containing about 2.6 percent oxygen by volume was therefore tried at 80°, 90°, 100°, 125°, and 150°. The milliammeter setting was again 0.292 amp. This is oxygen equivalent to 20 mg of carbon dioxide per 5-minute interval. The curves for the reduction of copper oxide at 80° and 90° by carbon monoxide containing this amount of oxygen are not included since the effect is exactly similar to that at 100°, the time of passage of the gases being 8 and 9 hours, respectively, for these temperatures.

The effect of oxygen on the reduction at 100° is shown by Curve VI, Figure 3. Curve I, Figure 3 represents the straight reduction at this temperature. The gases were passed for 7.5 hours at 100° and the rate of carbon dioxide formation never exceeded 0.4 mg which is within the experimental error, so that the curve is drawn as a straight line along the X axis, i. e., the reduction is immeasurable over this period. Furthermore, an examination of the sample at the end of the experiment showed no visible copper nuclei present. The effect of oxygen on the reduction at 125° is shown by Curve IV, Figure 3. Curve III, Figure 3 is the normal reduction at this temperature. We find from Curve IV, Figure 3 that the carbon

dioxide formation attains a rate of 7 mg per 5-minute interval after 2 hours has elapsed, whereas normally, the rate passes through a maximum corresponding to 83 mg of carbon dioxide per 5-minute interval in this time. The straight reduction is about 90 percent completed at the end of 8 hours, while with this small amount of oxygen, the curve does not pass through a maximum and only attains a 22 mg rate per 5-minute interval in this time. The sample showed on examination at the end of the run that copper nuclei were present in only very small amount in several particles at the center of the charge. Curve II, Figure 4 shows the effect of oxygen on the initial stages of the reduction at 150° while Curve I, Figure 4, is the straight reduction. The reduction begins normally at 150° as soon as pure carbon monoxide comes in contact with the copper oxide but the effect of oxygen is to cause over a ten minute incubation period which, though short, is nevertheless measurable. Reduction in absence of oxygen attains a rate of 148 mg when 25 minutes have elapsed while with oxygen present, the rate is only 8 mg in the same elapsed time. Again, an examination of samples showed fewer visible copper nuclei

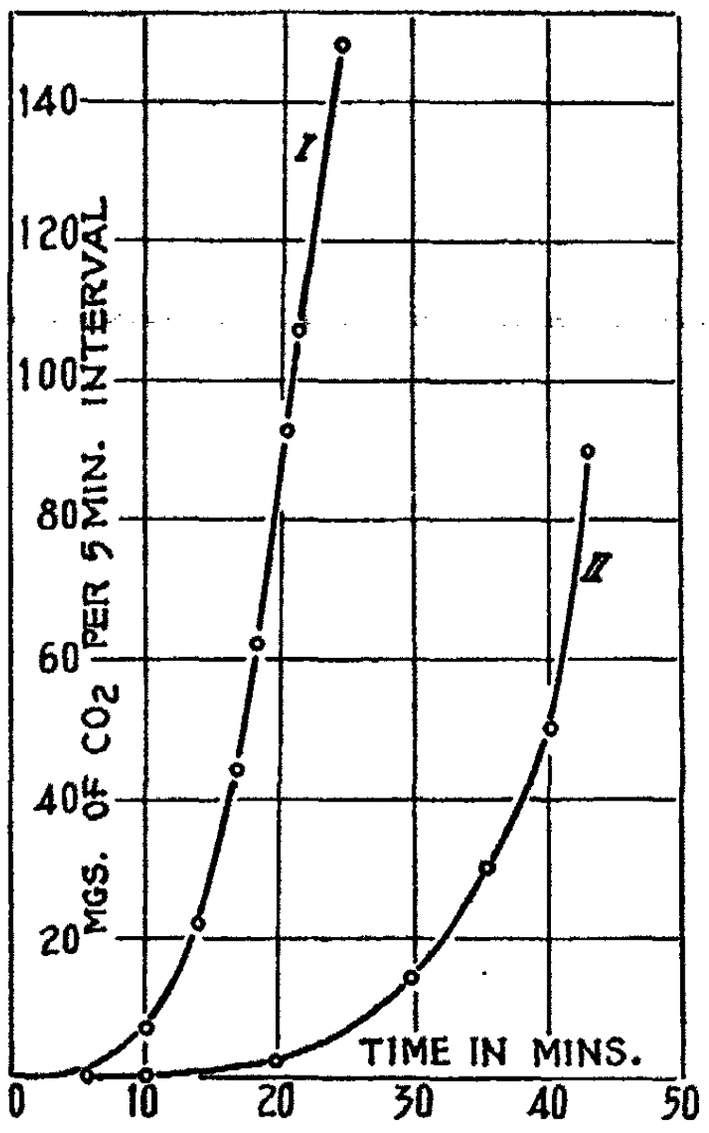



Fig. 4
Curve I, reduction at 150°
Curve II, effect of 20 mg equivalent of oxygen on reduction at 150°

present at the end, when oxygen was passed with the carbon monoxide.

In order to throw more light on the mechanism of the effect of oxygen on the reduction, an experiment was performed in which a 20 mg equivalent of oxygen was passed with the carbon monoxide over a charge of copper oxide for 3 hours at 100°; the oxygen being shut off at the end of this time and the rate of reduction measured to determine the effect on the induction period. When the rate of reduction was found to be increasing in the usual manner, the oxygen was again turned in, the rate of carbon dioxide formation having attained a value of 6 mg in 5 minutes. If the effect of oxygen on the reduction by hydrogen[1] were taken as a criterion, our curve should show a sudden drop to a minimum at this point. However, on taking into consideration the adsorption values of carbon monoxide and hydrogen on copper as determined by Taylor and Burns along with the earlier observations of Wright and Luff as stated previously, we believed that the effect of oxygen with carbon monoxide at this point might possibly give results which are entirely different from those of oxygen with hydrogen. Taylor and Burns showed that, with reduced copper, the adsorption of carbon monoxide is strong, while that of hydrogen is of a much lower order comparable with that of oxygen. Hence, in a carbon monoxide-oxygen mixture, it would be anticipated that the carbon monoxide would be preferentially adsorbed. The results of Pease and Taylor indicate that in a hydrogen-oxygen mixture, the oxygen is adsorbed at the copper-copper oxide interface. The actual result which we obtained is shown in Curve VII, Figure 3. The rate of carbon dioxide formation was found to rise from 6 mg to 21.5 mg immediately the oxygen was admitted and the curve rose gradually from this point. This extremely interesting and fundamentally important result led us to try the same effect of oxygen on the reductions at 90° and 100° with the oxygen turned in at 3 different stages of the same in each

[1] Pease and Taylor: Jour. Am. Chem. Soc., 43, 10, 2179 (1921)

case. These results are shown graphically by Curves I and II, Figure 5. To gather more definite information as to the amount of oxygen in the effluent gases from the furnace chamber in the course of one of these experiments, the gases from the carbon dioxide recording instrument were passed first through soda-lime, over phosphorus pentoxide, and finally over hot copper turnings and the resultant carbon dioxide taken up in a U-tube containing soda-lime with a phosphorus

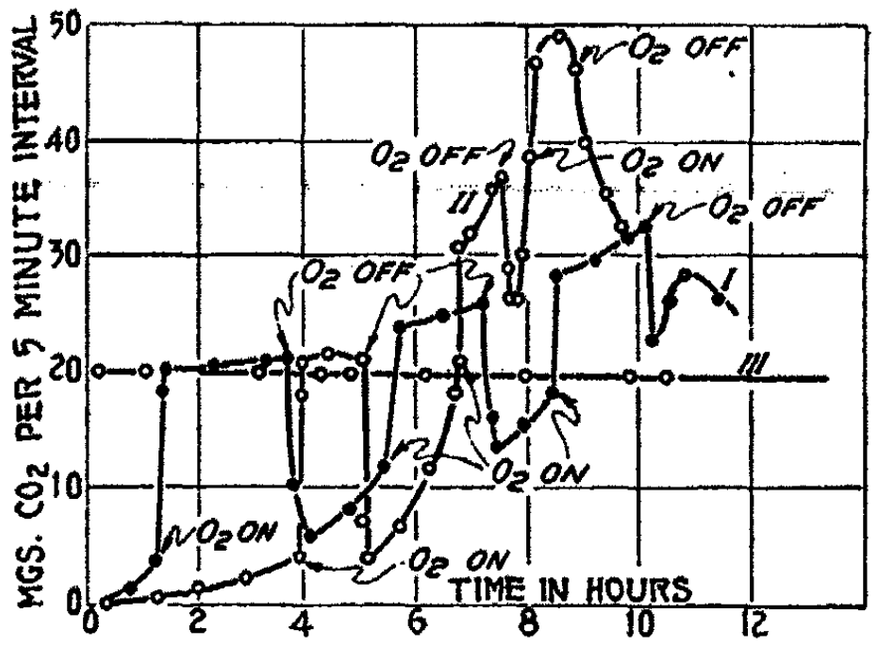



Fig. 5

Curve I, effect of 20 mg equivalent of oxygen added after start of reduction at 90°

Curve II, effect of 20 mg equivalent of oxygen added after start of reduction at 100°

Curve III, effect of 20 mg oxygen passed with carbon monoxide over reduced copper oxide

pentoxide tube following next the soda-lime. These two U-tubes were weighed at frequent intervals during the experiment at 100° while the oxygen was on. Their total gain in weight represents the carbon dioxide equivalent of the oxygen coming through the furnace chamber unchanged. These data are presented in Column IV, Table I.

We may consider Curve II, Figure 5 as a general example of the effect of oxygen on the reduction. When the reduction rate was 4 mg, a 20 mg equivalent of oxygen was turned

in and the rate rose immediately to 21 mg. During this first period, while oxygen was on, there was oxygen equivalent to 1.5 mg carbon dioxide coming through unchanged. The difference, or the equivalent of 18.5 mg carbon dioxide, had reacted. In both the latter periods of "oxygen on" at 100°, the entire amount of oxygen admitted had reacted. It is evident therefore, that even in the presence of the small amount of copper produced by the time the reduction rate corresponds to 4 mg per 5-minute interval, $\frac{18.5}{20.0} \times 100$ or 92 percent of the oxygen was converted to carbon dioxide. At this stage of the reduction of the copper oxide, very few nuclei of copper are discernible. When more nuclei are present, that is, when the reduction rate has reached 20 mg, carbon dioxide per 5-minute interval, the oxygen conversion is quantitative.

Table I is self-explanatory and is derived entirely from the curve and the data in Column IV.

TABLE I

| I | II | III | IV | V | VI |
|---|---|---|---|---|---|
| Period of "oxygen on" | Reduction rate at start of period | Reduction rate at end of period | Amount of un-converted oxygen | Initial reading with "oxygen on" | Last reading with "oxygen on" |
| First | 4.0 mg | 4.3 mg | 1.5 mg | 21.0 mg | 21.3 mg |
| Second | 21.0 mg | 26.5 mg | 0.00 mg | 31.2 mg | 37.3 mg |
| Third | 39.0 mg | 38.0 mg | 0.00 mg | 47.0 mg | 47.0 mg |

NOTE:—The rates are all expressed as mg $CO_2$ per 5-minute interval.

It may be seen from Curve II, Figure 5 that when the oxygen is admitted for the first time, the rate of reduction is 4 mg carbon dioxide per 5-minute interval. Since 18.5 mg equivalent of the oxygen admitted is converted to carbon dioxide, we find that the rate of reduction of the *original* copper oxide falls from 4 mg to a value of 2.5 mg carbon dioxide per 5-minute interval. Similarly, at the end of the oxygen run

the rate of reduction of the original oxide is 2.8 mg carbon dioxide per 5-minute interval, instead of 4.3 mg which is the first reading after turning off the oxygen. In the second period of oxygen admission, the value of 21 mg carbon dioxide per 5-minute interval rises to 31.2 mg immediately the oxygen is admitted. Again, knowing that the 20 mg equivalent of oxygen is quantitatively converted to carbon dioxide, we see that the rate of reduction of the *original* oxide falls from 21 to 11.2 mg carbon dioxide per 5-minute interval. The rate of reduction of the *original* oxide reaches a value of 17.3 mg carbon dioxide per 5-minute interval at the end of this period of oxygen admission, while the reduction occurs at a 26.5 mg. rate immediately the oxygen is turned off. At the start of the third period, the reading is 39 mg carbon dioxide per 5-minute interval. When the oxygen is in and quantitatively converted to carbon dioxide, the reading is 47 mg carbon dioxide per 5-minute interval. This gives a value of 27 mg for the reduction of the *original* oxide or a falling off in this value of 12 mg when the oxygen is admitted. We see further that the rate of reduction attains a maximum while the oxygen is in and falls off rapidly when the oxygen is turned off.

As stated previously, Pease and Taylor found that at temperatures below 200°, the effect of oxygen turned in, while reduction of copper oxide by hydrogen was under way, was to inhibit the reduction process. At the same time, the amount of water vapor formed per 5-minute interval fell off to a very low value, a few mg at most. The conclusion to be drawn from a comparison of our results with carbon monoxide and oxygen over partly reduced copper oxide with those observed by the above authors using hydrogen and oxygen warrants special consideration.

In both cases, it is possible to pass mixtures of hydrogen with a small percentage of oxygen present and of carbon monoxide containing a small percentage of oxygen over the copper oxide mass for an indefinite period without measurable quantity of reaction product, either water vapor or carbon dioxide, being formed. This has been demonstrated with hydrogen-

oxygen mixtures over copper oxide at 150° and with a carbon monoxide-oxygen mixture at 100°. Hence, the explanation for the fundamentally different results obtained must be sought in the action of the reduced copper on the two mixtures.

Therefore, a sample of the copper oxide was completely reduced to metal at 150° and the 20 mg equivalent of oxygen turned in at 200°. The initial reading showed that the entire amount of oxygen was being quantitatively catalysed to carbon dioxide. The temperature was then allowed to drop in steps of 10° each until finally, and much to our surprise, we were effecting complete catalysis of the oxygen in the mixture with no heat on the furnace, the temperature of the copper maintaining itself at 37° C by virtue of the heat of the reaction. In the next experiment, the oxygen was admitted when the copper was at room temperature, 25°. Again, the oxygen was quantitatively converted to carbon dioxide from the start and the temperature rose to 37°, the gases being passed for many hours with the same effect throughout.

Through a study of the mechanism of the catalysis of hydrogen-oxygen mixtures, Pease and Taylor conclude that their results are best explained on the basis of a chemical action or the reaction may be said to proceed through an intermediate compound stage. They present definite evidence of the alternate oxidation and reduction of the copper to give as end products, water vapor and metallic copper, though an oxide of copper is no doubt formed in an intermediate stage of the process.

In a hydrogen-oxygen mixture containing a few percent of oxygen, the oxygen is not quantitatively converted to water vapor when passed over copper until a temperature of 200° is reached. In a similar mixture of carbon monoxide and oxygen, the oxygen passed is quantitatively converted to carbon dioxide at temperatures as low as our arrangement of apparatus permitted, namely 37° C. We subsequently showed that this reaction went extremely rapidly, *even at* 0° C.

We believe that a suitable explanation could be obtained for our totally different result with a carbon monoxide-oxygen

mixture by a consideration of the relative values of carbon monoxide and hydrogen on copper as determined by Taylor and Burns. We thought it best however, to attempt a direct experimental check on the possibilities of alternate oxidation and reduction of the copper which would be direct evidence either for or against an explanation of the mechanism of the catalysis of carbon monoxide-oxygen mixtures over copper on the basis of an intermediate chemical compound stage. This was done in the following manner.

Carbon monoxide was passed over reduced copper at room temperature at the usual 50 cc per minute rate. Twenty mg equivalent of oxygen was then admitted and the quantitative conversion to carbon dioxide allowed to proceed for 5 hours, the temperature maintaining itself at 40°. The carbon monoxide was shut off at the end of this time and pure dry oxygen gas allowed to pass over the copper maintained at 40° for several days. It had been noted previously that active copper, reduced at low temperatures gradually became oxidized on long standing at room temperature in air. After this treatment, the carbon monoxide alone was passed for a period of three hours without the least measurable amount of carbon dioxide being formed at 40°. The same quantity of oxygen as before was admitted at this point and passed for several hours without a trace of carbon dioxide being formed. On shutting off the oxygen, and raising the temperature rapidly to 180°, the surface was again reduced to copper as evidenced by the amount of carbon dioxide formed while the temperature was being raised. The reduction did not attain measurable proportions until the temperature had reached 90°–100°. By the time 180° was reached, the rate of carbon dioxide formation had fallen to practically zero once more, the time necessary to raise the temperature being only twenty minutes. The carbon monoxide was passed for a time at this higher temperature to insure complete reduction, after which the heating current was turned off and the sample allowed to attain 40° once more. The 20 mg equivalent of oxygen was admitted and the initial reading showed quantitative con-

version to carbon dioxide. When this constant result was noted for a period of several hours, the experiment was discontinued.

This experiment is presented in a graphic form in Curve I, Figure 6. It is apparent therefore that this result is very direct evidence against a theory of intermediate compound formation, i. e., alternate oxidation and reduction of the copper to explain the mechanism of the catalytic combination of carbon monoxide and oxygen over copper.

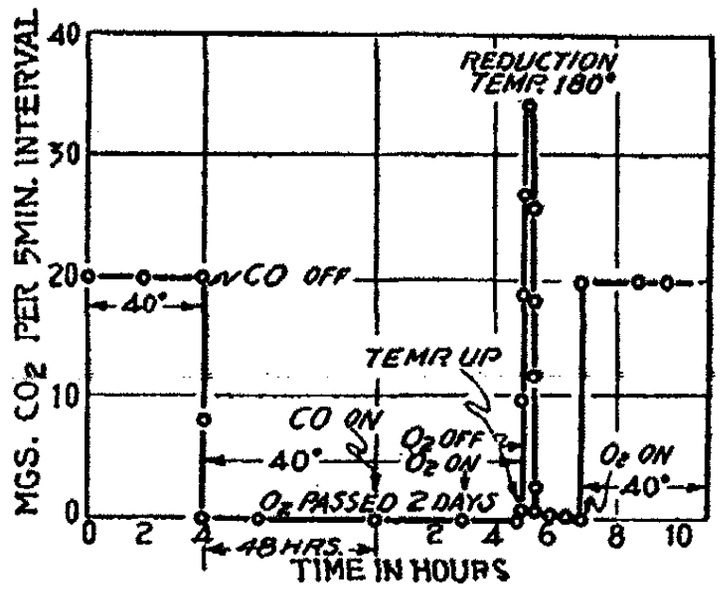



Fig. 6

Hoping to obtain more evidence which would assist in explaining the mechanism of the reaction:

$$2CO + O_2 \xrightarrow{Cu} 2CO_2$$

we next made measurements of this reaction by a static method. A large reaction tube was filled with (8–10) mesh copper oxide, sealed to a capillary T-tube and this in turn connected with a Toepler pump and a measuring burette by means of a three way cock. The free end of the T-tube was sealed to one arm of a mercury manometer. The copper oxide was then reduced in situ with hydrogen at a temperature of 200° and this sample used for reaction velocity measurements. It was found, however, that *the reaction was practically complete in less than 1 minute* after admitting the carbon monoxide-oxygen mixture in a stoichiometric ratio to the catalyst maintained at a temperature of 0° C. Obviously, no data could be obtained from such an active catalyst so, after many trials of various forms of copper oxide using higher temperatures

of reduction, a measurable reaction was obtained as follows. A wire form of copper oxide was reduced with hydrogen at a temp. of 300–350° and subsequently subjected to a long

TABLE II

| Time in minutes | $-dp$ in mm | $\frac{dx}{dt}$ in $\frac{\text{mm}}{\text{min.}}$ | Initial p.p. Carbon Monoxide | Initial p.p. Oxygen |
|---|---|---|---|---|
| *Experiment 1.* | | | | |
| 0 | 0 | | 480 | 235 |
| 0.6 | 59 | 98.3 | | |
| 1.5 | 76 | 19.0 | | |
| 2 | 81 | 10.0 | | |
| 3 | 91 | 10.0 | | |
| 4 | 99 | 8.0 | | |
| 7 | 116 | 5.66 | | |
| 12 | 134 | 3.6 | | |
| 16 | 145 | 2.2 | | |
| 21 | 155 | 2.0 | | |
| 26 | 163 | 1.6 | | |
| 31 | 170 | 1.4 | | |
| 37 | 176.5 | 1.08 | | |
| 41 | 181 | 1.12 | | |
| 46 | 186 | 1.00 | | |
| 57 | 195 | 0.82 | | |
| 66 | 201 | 0.66 | | |
| 76 | 208 | 0.70 | | |
| 86 | 213 | 0.50 | | |
| 96 | 218 | 0.50 | | |
| *Experiment 2.* | | | | |
| 0 | 0 | | 224 | 107 |
| 0.6 | 7 | 11.7 | | |
| 2 | 11 | 3.0 | | |
| 5 | 18 | 2.33 | | |
| 10 | 26 | 1.6 | | |
| 16 | 33 | 1.17 | | |
| 33 | 46 | 0.77 | | |
| 55 | 59 | 0.59 | | |
| 65 | 63 | 0.40 | | |
| 80 | 68 | 0.333 | | |
| 97 | 73 | 0.29 | | |
| 110 | 77.5 | 0.35 | | |
| 125 | 81 | 0.233 | | |

*Experiment 3.*

| | | | | |
|---|---|---|---|---|
| 0 | 0 | | 462 | 225 |
| 1.1 | 5 | 4.54 | | |
| 3 | 10 | 2.63 | | |
| 6 | 14 | 1.33 | | |
| 14 | 23 | 1.12 | | |
| 19 | 27.5 | 0.90 | | |
| 24 | 31.0 | 0.70 | | |

*Experiment 4.*

| | | | | |
|---|---|---|---|---|
| 0 | 0 | | 506 | 245 |
| 0.85 | 80 | 94.1 | | |
| 1.7 | 96 | 18.8 | | |
| 3 | 112 | 12.3 | | |
| 5 | 130 | 9.0 | | |
| 10 | 158 | 5.6 | | |
| 14 | 171 | 3.25 | | |
| 18 | 179 | 2.0 | | |

period of heating at 450–500° C in hydrogen (18 hours). By this treatment, we obtained a copper surface sufficiently low in activity to enable us to obtain measurements of the reaction to be studied at the boiling point of benzene.

The equation for the reaction

$$2CO + O_2 = 2CO_2$$

shows that when the reaction occurs there appear only two molecules of carbon dioxide to replace two molecules of carbon monoxide and one of oxygen so that there is a volume diminution of one-third. The progress of the reaction was then made clear by using a constant volume method in which the fall in pressure was measured on the manometer.

For purposes of calculation, the free space of the system was measured with nitrogen and an adsorption isotherm of carbon monoxide measured on this relatively inactive copper at a temperature of 80° C. Measurements had previously been obtained on the adsorption isotherms of both carbon monoxide and carbon dioxide at several temperatures on a much more active copper.

The preceding data in Table II were obtained in several

typical experiments on the reaction velocity measurements of $2CO + O_2 = 2CO_2$ over copper at 80° C.

Expt. 1 was made using the partial pressures of carbon monoxide and oxygen as recorded in the table. It may be noted that an amount of carbon monoxide somewhat greater than that called for by the stoichiometric equation was used.

Expt. 2 was performed for the purpose of studying the effect of carbon dioxide on the rate of the reaction. This was accomplished by using approximately half the amount of the mixed gases in the second case and comparing the initial rate of reaction observed with that measured in the first experiment when the values for the concentrations of carbon monoxide and oxygen had reached the initial values of these same as used in Expt. 2.

The curves presenting these results in graphic form are shown in Figure 7. Curve I represents Expt. 1; Curve II, Expt. 2, and so on. The values $dp$ are plotted against elapsed time throughout.

From a comparison of Curves I and II, it will be seen that the values for the initial concentrations as used in Expt. 2 were attained after 10 minutes elapsed time in Expt. 1. In the ensuing 86 minutes, the system experienced a fall in pressure of 90 mm in Expt. 1 while in the first 86 minutes Expt. 2 showed only 70 mm decrease in pressure. This may be observed also by a comparison of the $dx/dt$ values in the table for these experiments.

Since it was thought that the velocity of the reaction should be the same or even more rapid in Expt. 2, owing to the initial absence of carbon dioxide and since experiment showed the reverse to be true, we concluded that in all probability the copper was undergoing oxidation without subsequent reduction of the oxide formed even though there was a slight excess of carbon monoxide present.

To confirm this belief, Expt. 3 was performed. Here the ratio of carbon monoxide to oxygen was the same as in

Expts. 1 and 2 while an initial pressure of the mixture comparable to that in Expt. 1 was used.

It was apparent after a short time had elapsed that the velocity of the reaction had again decreased. From the curves, we see that in 24 minutes the system experienced a decrease in pressure of 31 mm in Expt. 3 while in Expt. 1, a decrease of 160 mm was observed in the same elapsed time and Expt. 2 where only half the concentration of gases was used decreased 40 mm in pressure over the same time interval.

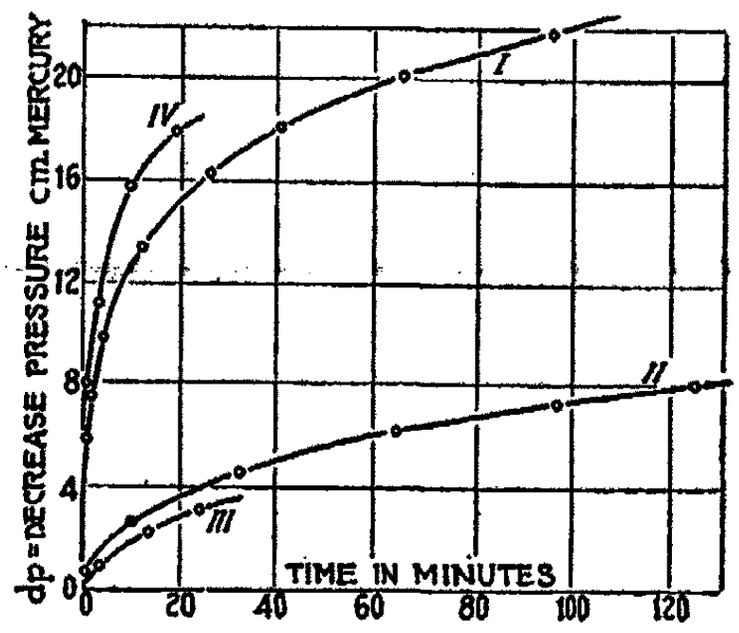



Fig. 7

Reaction Velocity Measurements

Curve I, a stoichiometric mixture of carbon monoxide oxygen over copper at 80° using one atmosphere

Curve II, a half atmosphere of a stoichiometric mixture at 80°

Curve III, stoichiometric mixture using one atmosphere at 80°

Curve IV, effect of treating copper surface with hydrogen at 200° after experiments represented in Curves I–III. One atmosphere of a stoichiometric mixture used in this curve

This was then additional evidence of the decrease in the velocity of the reaction in successive experiments. In order that we could state positively whether the copper was undergoing oxidation without subsequent reduction of the oxide, the copper was subjected to treatment with hydrogen at 200° when it was noted that marked amounts of water collected in the capillary tubes. After thoroughly pumping out, a stoichiometric ratio of $2CO : O_2$ was used to obtain the data as tabulated under Expt. 4, Table II and plotted on Curve IV, Figure 7.

It is evident from a comparison of Curve IV with Curves I, II and III in Figure 7, that the surface of the copper has be-

come activated by this treatment with hydrogen. A decrease in pressure of 179 mm. in 18 minutes is observed in Expt. 4 as against a decrease of 149 mm in the same elapsed time in Expt. 1 while in Expt. 3, which was also performed before the treatment with hydrogen at 200°, the same time interval indicated a decrease in pressure of only 26 mm.

A comparison of Curve IV with Curve I in Figure 7 further shows the fact that the copper is more active in Expt. 4 than in Expt. 1 due in all probability to the low temperature oxidation and subsequent reduction with hydrogen at 200°, which treatment was found previously to give a very active catalyst. It follows that there is but one conclusion to be drawn on the basis of these results. Copper oxide reduced at 200°–300° gives a very active catalyst for the carbon monoxide-oxygen combination; the reaction being practically instantaneous at 0° C. On decreasing the activity of this surface by heating for long periods at high temperatures in order to obtain measurable reaction velocity data, it is found that the copper oxidizes to an appreciable extent at 80° C in presence of excess of carbon monoxide. In successive experiments without subsequent reduction of the oxide formed, the activity of the catalyst, and hence the rate of the reaction is found to decrease rapidly. When this surface layer of oxide, which may be observed by the darkened color of the catalyst, is reduced at 200° with hydrogen, the copper becomes more active with each successive treatment so that finally one arrives at the starting point with a very active copper catalyst, i. e., the carbon monoxide-oxygen combination reaches equilibrium in less than 1 minute at 0° C.

## Conclusions

The importance of the interface between the two phases copper-copper oxide in the reduction of copper oxide by carbon monoxide has been demonstrated in the present work. It has been shown that low temperature reduction of copper oxide by carbon monoxide is negligible until copper nuclei are established in the copper oxide mass. Subsequent re-

action then occurs at the boundary copper-copper oxide as may be observed by the ever increasing area of the red copper extending outwards from the original nuclei. The amount of carbon dioxide produced per unit of time as a result of such reduction at the interface, increases steadily with increasing extent of interface, attains a maximum and then steadily diminishes as the reduction of the oxide is completed. This phenomenon of the activity existing at the copper-copper oxide interface had previously been demonstrated in the study made by Pease and Taylor on the reduction of copper oxide by hydrogen. It is another case of a variety of such phenomena recently indicated by Langmuir[1] in the cases of dissociation involving calcium carbonate and salt hydrates. Langmuir's conclusion that this interface phenomenon is general for reactions involving two solid phases is strengthened by our observations on copper-copper oxide and by further examples found in the literature and summarized in a recent article by Taylor.[2]

Carbon dioxide when present in small concentrations in carbon monoxide has been shown to exert a retarding effect on the primary reaction of the reduction of copper oxide, i. e., the formation of copper nuclei. As previously stated, carbon dioxide is markedly adsorbed by copper oxide. There is the possibility therefore, that the carbon dioxide is adsorbed to form a slight protective film on the copper oxide surface which would satisfactorily account for the retardation effect observed. The lengthening of the time of induction observed probably finds explanation in the fact that carbon dioxide is measurably adsorbed by copper at the copper-copper oxide interface at which point the reduction process has been shown to occur.

Oxygen present in small concentration has been shown to produce a pronounced retardation of the reduction process.

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[1] Langmuir: Trans. Faraday Soc., Sept. (1921); Jour. Am. Chem. Soc., 38, 2263 (1916).

[2] H. S. Taylor: Jour. Franklin Inst., 194, 1 (1922).

The effect of oxygen on the reduction at low temperatures is probably to oxidize the copper atoms to copper oxide as quickly as they are formed, thus suppressing the spread of the copper-copper oxide interfaces so that, under the conditions chosen, the reduction does not assume measurable proportions. As the temperature is raised, however, the rate of formation of copper nuclei exceeds the rate of re-oxidation of the copper atoms by the small amount of oxygen present so that reduction increases gradually with time. The evidence obtained, along with many visual observations, lends support to the view that the mechanism in this case is one of alternate reduction of the copper oxide, forming carbon dioxide and copper, and regeneration of the copper oxide by oxidation of the copper.

The experiments with oxygen admitted after the copper nuclei formation was well under way pointed to a possible fundamental difference between the mechanism of carbon monoxide-oxygen combination over copper and that obtaining over copper oxide. A consideration of these experiments along with those subsequently performed with completely reduced copper definitely established this fundamental difference. The combination of carbon monoxide and oxygen over copper oxide is found to be a relatively slow process, the mechanism being one of alternate reduction and oxidation at an interface. In contrast to this relatively slow process for the combination of carbon monoxide with oxygen, is that taking place practically instantaneously over a reduced active copper. In this case, it has been established very definitely that the mechanism is certainly not one of intermediate compound formation, i. e., alternate oxidation and reduction, but rather the oxidation of an adsorbed layer of carbon monoxide on the copper surface. This conclusion aids in explaining the observation that a small amount of oxygen, initially present in the carbon monoxide, may completely suppress the spread of the copper-copper oxide interface at certain temperatures while oxygen, admitted after copper nuclei have been formed in sufficient amount, combines directly with the carbon monoxide, adsorbed on the copper, to give the

greatly increased quantities of carbon dioxide observed under these conditions.

It has been shown by Taylor and Burns that hydrogen is very markedly adsorbed by nickel. As stated previously, they have also noted marked adsorption of carbon monoxide on copper while the adsorption of oxygen is negligible on the same metal. From a consideration of some unpublished data obtained in this laboratory, Pease and Taylor conclude that the mechanism for the combination of hydrogen and oxygen over reduced nickel is best explained on the basis of the adsorption theory of contact catalysis. This reaction also occurs at room temperature under conditions from which they conclude that here again the oxygen combines directly with the adsorbed oxidizable gas, i. e., hydrogen. As noted previously, Pease and Taylor from a study of the catalytic combination of hydrogen and oxygen over copper, conclude that an explanation for the mechanism of this reaction is based on intermediate compound formation, i. e., alternate oxidation and reduction. Taylor and Burns have also shown that the adsorptions of both hydrogen and oxygen on copper are small.

This striking parallelism to be observed in the mechanism obtaining in the cases of carbon monoxide-oxygen combination over copper and hydrogen-oxygen combination over nickel when considered along with the totally different mechanism observed in the combination of hydrogen-oxygen mixtures over copper, lend especial weight to the conclusions drawn by Taylor and Burns from a study of the adsorption of gases by various metal catalysts.

As a result of the static measurements carried out in this work, the conclusion is drawn that oxygen is a "poison" in the combination of carbon monoxide and oxygen over copper. Poisons are now classified in heterogeneous catalytic work as either permanent or transitory. So called "permanent poisons" usually are found to react chemically with a catalyst reducing its activity continuously and progressively with extended use in presence of the poison.

Transitory poisons in gas reaction are most generally

to be explained on the basis of preferential adsorption of the poison from the gas mixture, even though this poison is present in only minute quantities. The adsorption is, however, reversible and the poisoning effect disappears either wholly or in part on removal of the transitory poison from the gas mixture.

On the basis of this classification and the data obtained by us, oxygen may be said to be a "permanent poison" for the carbon monoxide-oxygen combination over copper. In this case, copper oxide is formed, the activity of the catalyst decreases rapidly and regeneration of the copper, by reduction of the oxide, is necessary to restore the activity. This is entirely analogous to the permanent poisoning of an iron catalyst in ammonia synthesis by formation of iron sulphide when sulphur compounds are present in the gases used. In this case, it is necessary to oxidize the sulphide and then regenerate the metal by reduction of the oxide.

As a result of some static experiments on the velocity of carbon monoxide-oxygen combination over copper oxide at 184–218°, we conclude that concordant results are unattainable in successive experiments. The mechanism for this reaction has been shown to be one of alternate reduction and oxidation. The velocity of the reaction shows a steady increase in successive experiments due, in all probability, to the reduction proceeding more rapidly in each successive case at a constant temperature.

## Summary

1. The reduction of copper oxide by carbon monoxide has been shown to be an auto-catalytic process, copper being the auto-catalyst; the reduction occurring at a copper-copper oxide interface.

2. The retarding effects of carbon dioxide and oxygen on the primary reaction of the reduction process, i. e., the formation of copper nuclei, have been pointed out.

3. The mechanism for the combination of carbon mon-

oxide-oxygen mixtures over copper oxide has been shown to be alternate reduction and oxidation of the copper oxide.

4. The mechanism for the combination of carbon monoxide-oxygen mixtures over copper has been shown to be the oxidation of an adsorbed layer of carbon monoxide.

5. It has been established that oxygen is a "permanent poison" in the combination of carbon monoxide with oxygen over copper.

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# ELECTROLYTIC PREPARATION OF PARA-AMIDOPHENOL

BY J. C. WARNER[1] AND O. W. BROWN

In previous papers,[2] the results of a study of the various factors influencing the electrolytic preparation of ortho-amidophenol and its recovery from solution have been given. The purpose of the present investigation was to make a similar study of the factors influencing the electrolytic preparation of para-amidophenol.

In the past, para-amidophenol has been prepared by a great variety of methods. Paul[3] prepared it by reducing para-nitrophenol with tin and hydrochloric acid. Grandmougin,[4] in a similar manner accomplished the reduction by the use of iron and acetic acid. He also reduced para-nitrophenol to para-amidophenol in an alkaline solution by means of sodium hyposulphite. Para-nitrosophenol, reduced by means of sodium sulphide, likewise yields para-amidophenol.

Grandmougin[5] has prepared para-amidophenol in the following manner:—Aniline is diazotized and coupled to phenol forming para-hydroxyazobenzene. This compound is then reduced forming para-amidophenol and aniline. The aniline is distilled from the mixture and the para-amidophenol is crystallized from the mother liquor. This process has been used by manufacturers in this country.

Nitrobenzene is directly reduced to para-amidophenol by means of zinc dust[6] and sulphuric acid at 50° to 80° C

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[1] This paper is constructed from a dissertation presented by J. C. Warner to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Trans. Am. Electrochem. Soc., **41**, 143 (1922).

[3] Zeit. angew. Chem., **9**, 594 (1896).

[4] Jour. prakt. Chem., **76**, 135 (1907).

[5] Ibid., **76**, 126 (1907).

[6] German Pat., 96,853 (1898).

Noyes and Clement,[1] Gattermann,[2] Stroji,[3] and Darmstäder[4] have accomplished this direct reduction by the electrolysis of a solution of nitrobenzene in strong (80–90 percent) sulphuric acid. In recent years, McDaniel, Schneider, and Ballard of the Eastman Kodak Company[5] attempted to develop this method into a commercial process for the preparation of para-amidophenol. It has, however, proven too costly for successful operation.

Mignonac,[6] Brochet,[7] and Brown and Carrick[8] have prepared para-amidophenol by the catalytic reduction of para-nitrophenol. The vapor pressure of para-nitrophenol, however, is so low at the temperature at which the reaction is best carried out, that the process must of necessity be very slow.

Elbs,[9] in an article entitled, "Quantitative Research on Processes of Reduction," gives the results of some experimental work upon the electrolytic reduction of para-nitrophenol to para-amidophenol. In this work, he based his calculation of yields upon the quantity of hydrogen evolved at the cathode, assuming that all of the hydrogen not evolved was used in reducing para-nitrophenol to the corresponding amine. Later, in his book entitled, "Electrolytic Preparations" (page 88), Elbs has given directions by which he states that para-nitrophenol may be reduced to para-amidophenol with a material yield of 80 percent. A systematic study of the various factors influencing this reduction, however, has not been recorded.

In our investigation, the influence of various factors upon

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[1] Ber. deutsch. chem. Ges., **26**, 990 (1893).
[2] Ibid., **26**, 1846 (1893).
[3] Jour. Soc. Chem. Ind., **37**, 459A (1918).
[4] German Patents, 150,800 (1904); 154,086 (1904).
[5] Trans. Am. Electrochem. Soc., **39**, 319 (1921).
[6] Bull. Soc. chim. France, **7**, 270 (1910).
[7] Eng. Pat., 16936 (1913); French Pat., 458,033, 1912; U. S. Pat., 1,247,629.
[8] Jour. Am. Chem. Soc., **41**, 436 (1919).
[9] Jour. prakt. Chem., **43**, 39 (1891).

the reduction of para-nitrophenol to para-amidophenol at copper and lead cathodes has been studied and a satisfactory method for the recovery of para-amidophenol from solutions has been developed.

## Experimental

The apparatus used was similiar to that described in our previous papers. In all experiments, the cathode liquor consisted of 400 cc of caustic soda or sodium carbonate solution in which was dissolved various quantities of para-nitrophenol. The container for the cathode solution was an 800 cc pyrex beaker. The anode solution, consisting of about 100 cc of 15 percent caustic soda was placed in a porous cup 10 cms high and 5 cms in diameter. The porous cup was suspended in the cathode liquor. The anode, in all experiments, was an iron wire gauze having a surface of 1.2 square decimeters (counting both sides). The temperature of the cathode liquor was regulated by means of an electric hot plate beneath the beaker and glass cooling coils in the cathode compartment through which water could be circulated. A glass stirrer, driven at about 800 r.p.m. by means of a small electric motor, was placed in the cathode compartment between the cathode and the porous cup.

At the end of each experiment, the cathode, stirrer, porous cup, and cooling coils were washed off into the cathode liquor and the latter transferred to a 1000 cc graduated flask and diluted to the mark. The quantity of para-amidophenol produced was determined by titration with standard sodium nitrite solutions as described in a previous article.

Commercial para-nitrophenol, without purification, was used throughout this investigation. When reductions were carried out using para-nitrophenol which had been purified by recrystallization from water, the same yields were obtained as when the commercial product was reduced under like conditions. These experiments led us to the conclusion that the commercial para-nitrophenol was quite pure.

### Reduction at a Copper Cathode

In this part of the investigation, the cathode was an 18 mesh copper wire gauze. The diameter of the wires in the gauze was 0.041 cm. The area of the gauze was one square decimeter (counting both sides).

### Sodium Hydroxide Electrolyte

The influence of current density at the cathode upon the efficiency of the reduction process is shown by the results of experiments given in Table I. In all of these experiments the theoretical number of ampere hours was used. Hence, material yield and current efficiency in percent of theory have the same numerical values.

TABLE I

Influence of Current Density

Cathode solution; 400 cc 5 percent NaOH 5 grams para-nitrophenol
Temperature; 62° ± 2° C
Ampere hours used; 5.78 (theory).

| Cathodic C. D.-Amps. per sq. dcm. | Voltagedropthrough cell 5 min. after start | Material yield and current efficiency. Percent | Av. material yield and current efficiency. Percent |
|---|---|---|---|
| 1 | 2.0 | 92.7 | |
| 1 | 2.1 | 91.2 | 91.9 |
| 2 | 3.5 | 92.0 | |
| 2 | 2.7 | 91.1 | 91.7 |
| 2 | 3.0 | 92.0 | |
| 4 | 3.8 | 90.6 | |
| 4 | 4.3 | 89.4 | 90.0 |
| 6 | 6.2 | 88.8 | |
| 6 | 5.3 | 87.1 | 87.9 |
| 10 | 7.1 | 82.8 | |
| 10 | 7.3 | 82.2 | 82.8 |
| 10 | 6.4 | 83.0 | |
| 10 | 7.1 | 83.5 | |

The data given in Table I are shown graphically in Figure 1. From the figure, it is evident that there is a gradual decrease in current efficiency and material yield as the current density is increased.

The influence of concentration of caustic soda in the cathode liquor was next studied. The results of these experiments are recorded in Table II.

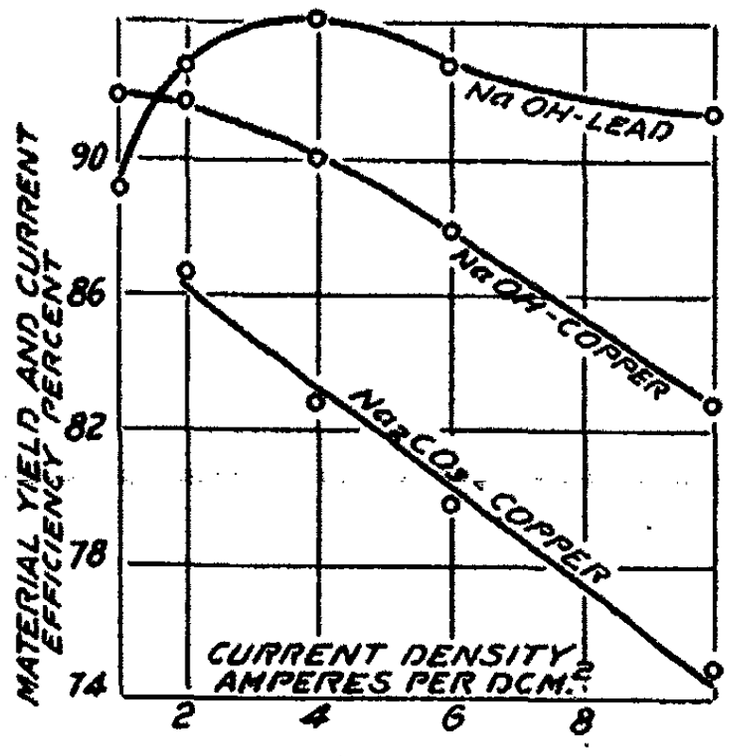



Fig. 1

TABLE II

Influence of Concentration of Caustic Soda

Cathode solution; 400 cc NaOH solution. 5 grams para-nitrophenol.
Cathodic current density; 4.0 amps. per sq. dcm.
Temperature; 62° ± 2° C.
Ampere hours used; 5.78 (theory).

| Conc. NaOH in cathode liquor. Percent by weight | Voltage drop through cell, 5 min. after start | Current efficiency and material yield. Percent | Av. current efficiency and material yield. Percent |
|---|---|---|---|
| 3 | 4.4 | 88.4 | 88.6 |
| 3 | 4.1 | 88.8 | |
| 5 | 3.8 | 90.6 | |
| 5 | 4.3 | 89.4 | 90.0 |
| 8 | 3.6 | 92.1 | |
| 8 | 3.4 | 91.8 | 91.9 |
| 10 | 3.4 | 90.9 | |
| 10 | 4.8 | 91.2 | 91.1 |
| 10 | 4.7 | 91.2 | |
| 15 | 4.6 | 88.3 | 88.1 |
| 15 | 3.8 | 87.9 | |

The results shown in Table II are shown graphically in Figure 2. Current efficiency and material yield increase with increased concentrations of caustic soda until a concentration of eight percent is reached. Thereafter, there is a regular decline as the concentration increases. The increase in yields at first is probably due to the fact that the solution becomes more conducting as the concentration of caustic increases. The decrease in current efficiency and material yield when more concentrated solutions of caustic soda are used

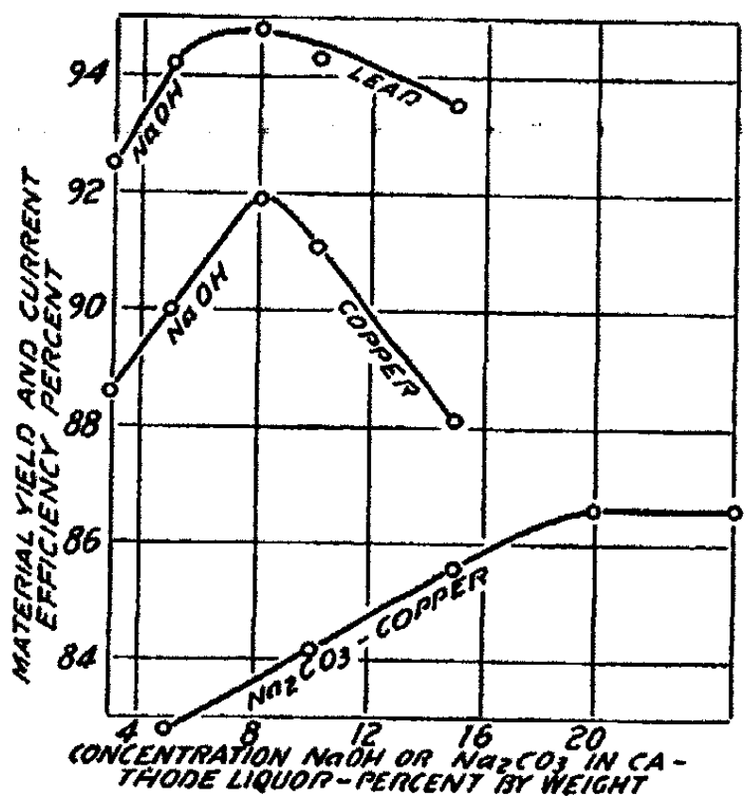



Fig. 2

may be due to the decreased solubility of the sodium salt of para-nitrophenol in the stronger caustic or possibly because the para-amidophenol is less stable in the more concentrated alkali.

The relation between concentration of para-nitrophenol in the cathode solution and current efficiency is shown by the experiments recorded in Table III.

The results given in Table III are shown graphically in Figure 3. Current efficiency and material yield increase as the quantity of para-nitrophenol in the cathode liquor

is increased until a concentration of ten grams in 400 cc is reached. Further increases in concentration of para-nitro-

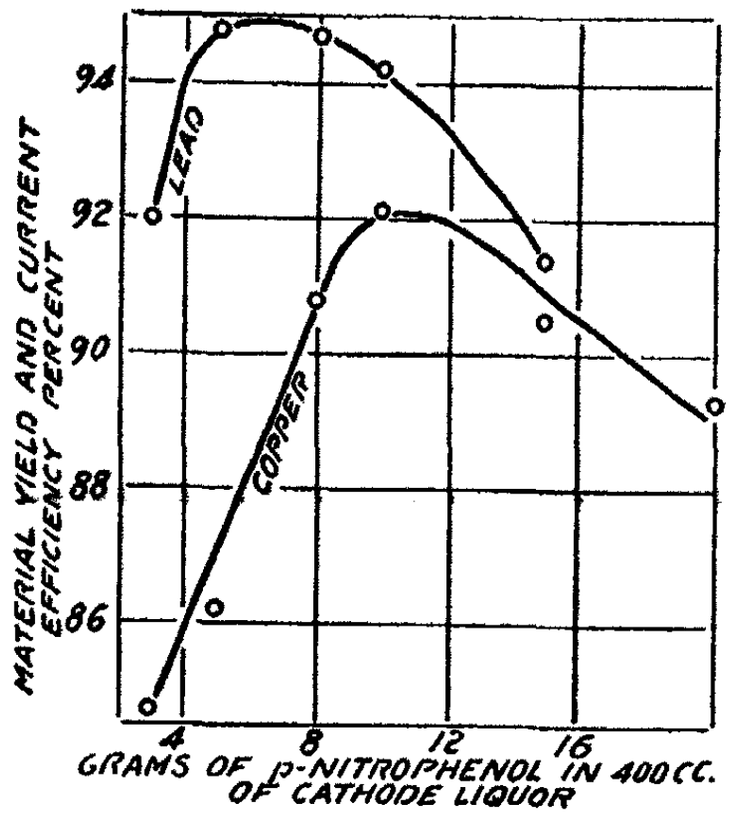



Fig. 3

TABLE III

Influence of Concentration of Para-nitrophenol

Cathode solution; 400 cc 5 percent NaOH
para-nitrophenol
Cathodic current density; 4.0 amps. per sq. dcm.
Temperature; 62° ± 2° C

| Gms p-nitro phenol in 400 cc cathode solution | Voltage drop through cell, 5 min. after start | Ampere hours used | Current efficiency and material yield. Percent | Av. current efficiency and material yield. Percent |
|---|---|---|---|---|
| 3 | 6.2 | 3.47 | 85.4 | 84.7 |
| 3 | 5.4 | 3.47 | 84.0 | |
| 5 | 4.9 | 5.78 | 86.2 | 86.2 |
| 5 | 5.3 | 5.78 | 86.2 | |
| 8 | 5.1 | 9.25 | 90.4 | 90.8 |
| 8 | 5.3 | 9.25 | 91.2 | |
| 10 | 6.5 | 11.56 | 92.3 | 92.1 |
| 10 | 6.3 | 11.56 | 91.9 | |
| 15 | 6.2 | 17.30 | 90.4 | 90.5 |
| 15 | 5.4 | 17.30 | 90.7 | |
| 20 | 5.2 | 23.12 | 89.4 | 89.3 |
| 20 | 5.3 | 23.12 | 89.2 | |

phenol cause a decrease in current efficiency. Since the quantity of para-nitrophenol remaining in solution when hydrogen begins to be evolved at the cathode is constant, one would expect current efficiency to increase as the concentration of para-nitrophenol was increased because the unchanged nitrophenol would be a smaller percentage of the total quantity to be reduced. The decline of the later portion of the curve is undoubtedly due to the fact that the beneficial influence of

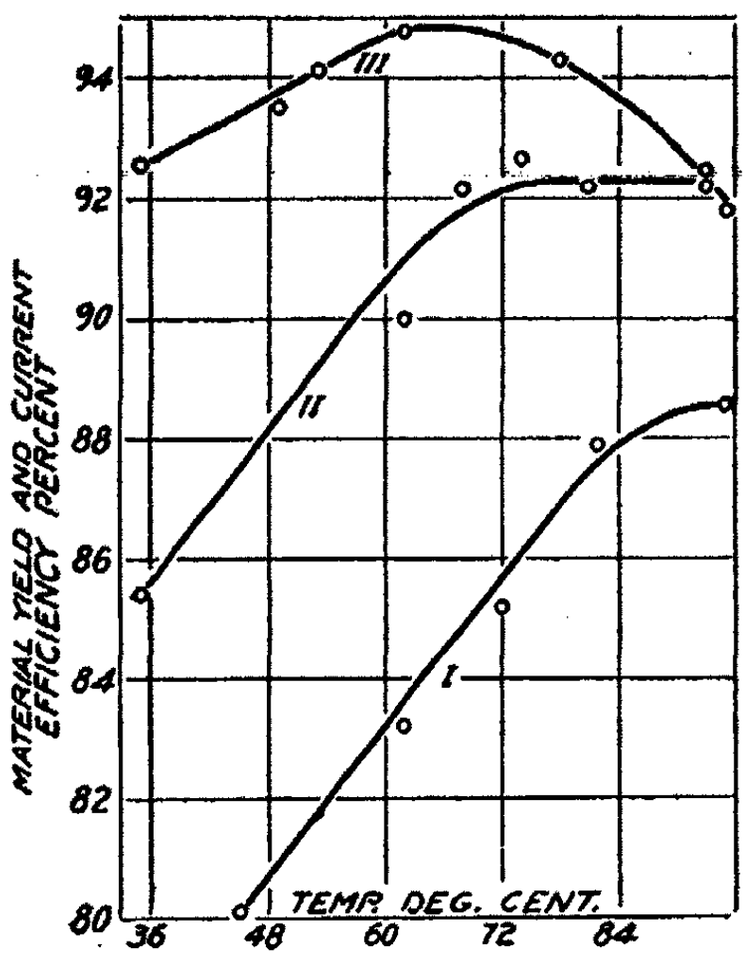



Fig. 4

increased concentrations of para-nitrophenol is more than counterbalanced by losses. These losses are probably due to increased decomposition of the para-amidophenol when longer periods are required for the reduction and to increased loss by diffusion into the porous cup. The diffusion of para-amidophenol into the cup would be dependent upon the difference in concentrations of the amine outside and inside the cup and upon the time for diffusion.

The results of experiments which show the influence of temperature are recorded in Tables IV and V.

TABLE IV

Influence of Temperature at 10.0 Amperes per Square Decimeter

Cathode solution; 400 cc 5 percent NaOH
5 grams para-nitrophenol
Ampere hours used; 5.78 (theory)

| Temperature Degrees Centigrade | Voltage drop through cell 5 min. after start | Current efficiency and material yield. Percent |
|---|---|---|
| 45 | 8.7 | 80.1 |
| 45 | 9.3 | 80.1 |
| 62 | 6.4 | 83.0 |
| 62 | 7.1 | 83.5 |
| 72 | 7.0 | 85.2 |
| 82 | 7.2 | 87.9 |
| 95 | 7.1 | 88.6 |

TABLE V

Influence of Temperature at 4.0 Amperes per Square Decimeter

Cathode solution; 400 cc 5 percent NaOH
5 grams para-nitrophenol
Ampere hours used; 5.78 (theory)

| Temperature Degrees Centigrade | Voltage drop through cell 5 min. after start | Current efficiency and material yield. Percent |
|---|---|---|
| 35 | 5.4 | 85.8 |
| 35 | 5.1 | 85.1 |
| 62 | 3.8 | 90.6 |
| 62 | 4.3 | 89.4 |
| 68 | 4.7 | 92.2 |
| 74 | 4.0 | 92.7 |
| 81 | 4.1 | 92.2 |
| 93 | 3.7 | 92.2 |

The results given in Tables IV and V are shown graphically in Figure 4. With a current density of 10.0 amperes per sq. dcm., the current efficiency and material yield increase as the temperature is increased (Curve I) until a temperature

of about 80° C is reached. Thereafter, the beneficial influence of higher temperatures is partly counterbalanced by losses and the increase in efficiency is no longer as great. This decrease in the beneficial influence of temperature might possibly be due to a lowering of the cathodic overvoltage. This, however, is hardly a likely cause, since in a similar study of

TABLE VI

Current Efficiency and Material Yield with Current less than and in Excess of Theory

Cathode solution; 400 cc 8 percent NaOH
10 grams para-nitrophenol
Cathodic current density; 2.0 amps. per sq. dcm.
Temperature; 72°—74 C

| Ampere hrs. Percent of theory | Voltage drop through cell 5 min. after start | Current efficiency. Percent of theory | Av. current efficiency. Percent | Material yield. Percent | Av. material yield. Percent |
|---|---|---|---|---|---|
| 25 | 3.1 | 99.8 | 100.3 | 25.0 | 25.0 |
| 25 | 3.6 | 100.8 | | 25.0 | |
| 51 | 3.2 | 100.4 | 99.8 | 51.0 | 51.0 |
| 51 | 3.4 | 99.2 | | 51.0 | |
| 75 | 3.2 | 98.5 | 98.75 | 73.9 | 74.1 |
| 75 | 3.4 | 99.0 | | 74.2 | |
| 90 | 3.3 | 97.4 | 97.4 | 87.7 | 87.7 |
| 90 | 3.4 | 97.4 | | 87.7 | |
| 100 | 3.3 | 93.1 | 92.7 | 92.2 | 92.7 |
| 100 | 3.9 | 92.2 | | 93.1 | |
| 110 | 3.2 | 85.5 | 85.4 | 94.1 | 94.0 |
| 110 | 3.6 | 85.3 | | 93.9 | |
| 120 | 3.0 | 78.0 | 78.1 | 93.6 | 93.9 |
| 120 | 3.4 | 78.2 | | 94.2 | |

the effect of temperature upon the preparation of ortho-amidophenol, material yield and current efficiency were found to increase directly with the temperature. It seems reasonable to suppose that the explanation of the difference in these two cases is to be found in the difference in the stability of the ortho and para-amidophenols.

At a current density of 4.0 amperes per sq. dcm. (Curve II), material yield and current efficiency increase with an

increase in temperature up to about 70° C. Thereafter, an increase in temperature causes no further increase in yield.

Since, in all the preceding experiments, the theoretical number of ampere hours was used, some experiments were carried out in which the relationship between current efficiency and material yield was studied when various numbers of ampere hours, greater and less than theory, were used. The results of these experiments are given in Table VI.

The results shown in Table VI are plotted in Figure 5. The current efficiency curve remains practically horizontal until about 65 percent of the theoretical number of ampere

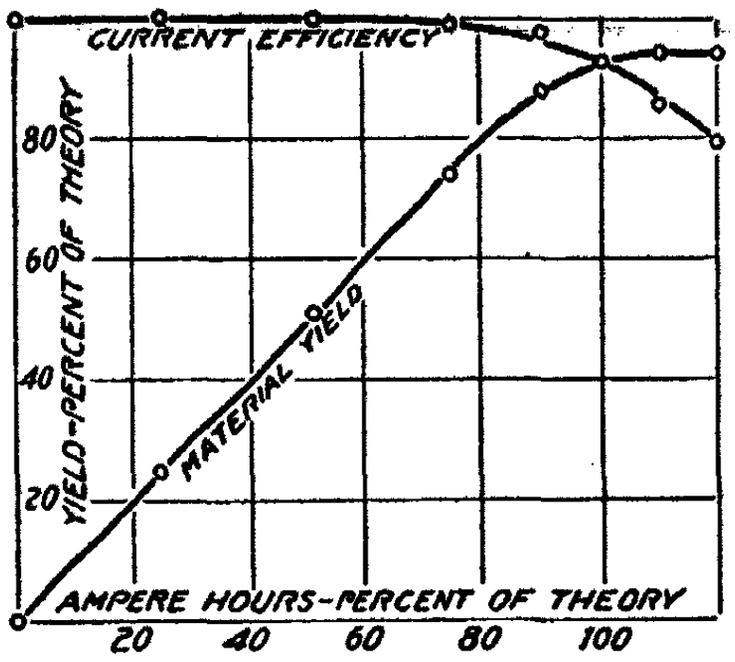



Fig. 5

hours have been passed. Thereafter, there is a downward trend of the efficiency curve. From these data, it is evident that under the conditions of these experiments, theoretical current efficiency is obtained as long as the concentration of para-nitrophenol does not drop below about 0.9 gram in 100 cc of cathode solution. Material yield increases with the number of ampere hours until current in an amount equal to 110 percent of theory has been passed, but under these conditions the use of current in excess of this amount does not cause an increase in material yield.

### Sodium Carbonate Electrolyte

The following experiments were carried out in order to compare the reduction of para-nitrophenol to para-amido-phenol in a sodium carbonate electrolyte to the reduction in solutions of caustic soda. In these experiments, the same apparatus was used, and the same conditions were maintained as in similiar experiments with NaOH.

The results of experiments showing the influence of current density upon current efficiency and material yield are given in Table VII.

TABLE VII

Influence of Current Density

Anode liquor; 15 percent NaOH
Cathode liquor; 400 cc 5 percent $Na_2CO_3.10H_2O$
5 grams para-nitrophenol
Temperature; 62° ± 2° C
Ampere hours used; 5.78 (theory).

| Cathodic C. D. amps. per sq. dcm. | Voltage drop through cell 5 min. after start | Current efficiency and material yield. Percent | Av. current efficiency and material yield. Percent |
|---|---|---|---|
| 2 | ... | 86.3 | 86.6 |
| 2 | ... | 86.9 | |
| 4 | 5.8 | 82.8 | 82.8 |
| 4 | 6.5 | 82.8 | |
| 6 | 5.2 | 79.8 | 79.8 |
| 10 | 8.0 | 75.0 | 75.0 |
| 10 | 9.0 | 75.0 | |

The data given in Table VII are shown graphically in Figure 1. From the curve, it can be seen that material yield and current efficiency decrease as the current density is increased. The yields at all current densities are lower than the yields obtained at corresponding current densities when NaOH is used as solvent for the para-nitrophenol. The voltage drop through the cell in all of these experiments was greater than in corresponding experiments with NaOH.

The influence of the concentration of sodium carbonate in the cathode liquor upon current efficiency and material

yield is given by the results of experiments recorded in Table VIII.

TABLE VIII

Influence of Concentration of Sodium Carbonate

Anode liquor; 15 percent NaOH
Cathode liquor; 400 cc sodium carbonate solution
5 grams para-nitrophenol
Cathodic current density; 4.0 amps. per sq. dcm.
Temperature; 62° ± 2° C
Ampere hours used: 5.78 (theory)

| Conc. $Na_2CO_3.10H_2O$ in cathode liq. Percent by wgt. | Voltage drop through cell 5 min. after start | Current efficiency and material yield. Percent | Av. current efficiency and material yield. Percent |
|---|---|---|---|
| 5 | 5.8 | 82.8 | 82.8 |
| 5 | 6.5 | 82.8 | |
| 10 | 5.0 | 84.2 | 84.2 |
| 15 | 3.8 | 85.6 | 85.6 |
| 15 | 4.6 | 85.6 | |
| 20 | 4.1 | 86.3 | 86.6 |
| 20 | 4.1 | 86.9 | |
| 25 | 4.0 | 86.3 | 86.6 |
| 25 | 4.6 | 86.9 | |

The results recorded in Table VIII are plotted in Figure 2. Current efficiency and material yield increase with increased concentration of sodium carbonate in the cathode liquor until a concentration of 20 percent $Na_2CO_3.10H_2O$ is reached. Thereafter, increase in the concentration causes no further increase in yield. The limit of solubility of sodium carbonate in water prevented the use of stronger solutions of the carbonate.

Para-nitrophenol is more readily soluble in sodium carbonate solutions than in solutions of sodium hydroxide. Solution in the former is always accompanied by the evolution of carbon dioxide.

Although the course of the reduction in sodium carbonate solutions has not been as thoroughly investigated as the reduction in solutions of caustic soda, it seems that sufficient data have been obtained to prove that sodium carbonate is

inferior to sodium hydroxide for use in the electrolytic reduction of para-nitrophenol to the corresponding amine.

### Sodium Bicarbonate and Sulphuric Acid Electrolytes

Although the reduction in these electrolytes has not been thoroughly investigated, experiments conducted in this laboratory by Mr. Levi H. Wellman, show that sodium bicarbonate and sulphuric acid are both inferior to sodium hydroxide and sodium carbonate solutions as electrolytes in carrying out this reduction.

### Reduction at a Lead Cathode

The reduction at a lead cathode was studied only in a sodium hydroxide electrolyte. From experience with the electrolytic preparation of ortho-amidophenol, one would expect lead to be a very good electrode material to use in the reduction of para-nitrophenol to the corresponding amine. The results of the following experiments show that this expectation is fulfilled.

The apparatus used and the conditions maintained in these experiments were the same as in the previous experiments except that the copper cathode was replaced by a cathode covered with spongy lead. The sponge lead cathode was prepared by plating lead on an 18 mesh copper wire gauze, having a surface of one sq. dcm. (counting both sides), from a bath of 15 percent NaOH solution in which litharge had been dissolved. Sheet lead anodes were used and a current of 10.0 amperes was passed for a period of ten minutes. The cathodes prepared in this manner were kept under water until used.

The results of experiments showing the influence of cathodic current density upon current efficiency and material yield are recorded in Table IX.

The results given in Table IX are plotted in Figure 1. As the current density is increased, the current efficiency increases at first until a current density of 4.0 amperes per sq. dcm. is reached. Thereafter, there is a gradual decrease

TABLE IX

Influence of Current Density

Cathode solution; 400 cc 5 percent NaOH
5 grams para-nitrophenol
Temperature; 62° ± 2° C
Ampere hours used; 5.78 (theory)

| Cathodic C. D. amps. per sq. dcm. | Voltage drop through cell 5 min. after start | Current efficiency and material yield. Percent | Av. current efficiency and material yield. Percent |
|---|---|---|---|
| 1 | 1.7 | 88.7 | |
| 1 | 1.8 | 89.4 | 89.1 |
| 2 | 2.0 | 92.8 | |
| 2 | 2.8 | 92.8 | 92.8 |
| 4 | 2.5 | 94.5 | |
| 4 | 3.5 | 93.8 | 94.2 |
| 6 | — | 92.8 | |
| 6 | — | 92.8 | 92.8 |
| 10 | 3.9 | 91.4 | |
| 10 | 4.8 | 91.4 | 91.4 |

TABLE X

Influence of Concentration of NaOH

Cathode solution; 400 cc NaOH solution
5 grams para-nitrophenol
Cathodic current density; 4.0 amperes per sq. dcm.
Temperature; 62° ± 2° C
Ampere hours used; 5.78 (theory)

| Conc. NaOH in cathode liquor. Percent by weight | Voltage drop through cell 5 min. after start | Current efficiency and material yield. Percent | Av. current efficiency and material yield. Percent |
|---|---|---|---|
| 3 | 2.1 | 92.6 | 92.5 |
| 3 | 3.1 | 92.4 | |
| 5 | 2.5 | 94.5 | 94.2 |
| 5 | 3.5 | 93.8 | |
| 8 | 2.5 | 94.8 | 94.8 |
| 8 | 3.3 | 94.8 | |
| 10 | 2.7 | 94.5 | 94.3 |
| 10 | 3.4 | 94.2 | |
| 15 | 3.2 | 93.5 | 93.5 |
| 15 | 4.0 | 93.5 | |

in yield as the current density is increased. The shape of the current density curve with a lead cathode is similiar to the corresponding curve obtained in the study of the reduction of ortho-nitrophenol at a lead cathode

The influence of the concentration of caustic soda in the cathode liquor is shown by the data recorded in Table X.

The results from Table X are shown graphically in Figure 2. As the concentration of caustic soda in the cathode liquor is increased, there is a rather rapid increase in the current efficiency until a concentration of eight percent is reached. A further increase in the concentration of caustic soda causes a gradual decrease in current efficiency.

The data given in Table XI show the relation between the temperature of the cathode liquor and the current efficiency and material yield.

TABLE XI

Influence of Temperature

Cathode solution; 400 cc 8 percent NaOH
5 grams para-nitrophenol
Cathodic current density; 4.0 amperes per sq. dcm.
Ampere hours used: 5.78 (theory)

| Temperature degrees Centigrade | Voltage drop through cell 5 min. after start | Current efficiency and material yield. Percent |
|---|---|---|
| 33 | 3.5 | 92.7 |
| 33 | 4.5 | 92.5 |
| 49 | 2.8 | 93.5 |
| 53 | 3.0 | 94.1 |
| 62 | 2.5 | 94.8 |
| 62 | 3.3 | 94.8 |
| 73 | 2.5 | 94.1 |
| 78 | 2.7 | 94.5 |
| 93 | 2.5 | 92.5 |
| 95 | 3.0 | 91.8 |

The data given in Table XI are graphically represented in Figure 4 (Curve III). There is a gradual increase in yield as the temperature is increased until a temperature of 65° to 70° C is reached. As the temperature is increased above

this point there is a decrease in yield. The counteracting influences which cause yields to decrease as the temperature is raised above 70° C may be an increase in the rate of decomposition of the para-amidophenol, a lowering of the cathodic overvoltage of lead, or the influence of temperature upon the nature of the lead which is redeposited upon the cathode. At high temperatures (90–95° C), the redeposited lead seems to be much more crystalline and hence would afford a much smaller active cathode surface.

The influence of the concentration of para-nitrophenol in the cathode liquor upon current efficiency is shown by the results of experiments recorded in Table XII.

TABLE XII

Influence of Concentration of Paranitrophenol

Cathode solution; 400 cc 8 percent NaOH
Para-nitrophenol
Cathodic current density; 4.00 amperes per sq. dcm.
Temperature; 62° ± 2° C

| Gms. p-nitrophenol in 400 cc of cathode solution | Voltage drop through cell 5 min. after start | Ampere hours used | Current efficiency and material yield. Percent | Av. current efficiency and material yield. Percent |
|---|---|---|---|---|
| 3 | 3.5 | 3.47 | 91.9 | 92.0 |
| 3 | 5.0 | 3.47 | 92.2 | |
| 5 | 2.5 | 5.78 | 94.8 | 94.8 |
| 5 | 3.3 | 5.78 | 94.8 | |
| 8 | 3.5 | 9.25 | 94.7 | 94.7 |
| 8 | 3.5 | 9.25 | 94.7 | |
| 10 | 3.5 | 11.56 | 94.5 | 94.2 |
| 10 | 3.5 | 11.56 | 93.8 | |
| 15 | 3.5 | 17.30 | 91.6 | 91.4 |
| 15 | 3.3 | 17.30 | 91.2 | |

The results given in Table XII are plotted in Figure 3. It is evident from the curve that current efficiency increases with an increase in the concentration of para-nitrophenol in the cathode liquor until a concentration of about 6 to 7 grams of para-nitrophenol in 400 cc of cathode solution is

reached. A further increase in concentration causes a decrease in yield. The changes in the direction of the curve may be explained in the same way as the changes of the similar curve obtained from a study of the reduction at a copper cathode. The difference in the maximum points on the two curves may be due to the different concentrations of NaOH used as electrolyte.

### Recovery of Para-Amidophenol from Solution

As has been mentioned in a previous paper,[1] ortho-amidophenol can very conveniently be liberated from its alkaline solutions by saturating a solution of the amine with carbon dioxide, whereupon the free base separates out as small plate-like crystals. By filtering, washing, and drying, ortho-amidophenol may be obtained which ranges in purity from 97–99 percent. When an attempt was made to recover para-amidophenol from its alkaline solutions by the same method, very unsatisfactory yields of only fairly pure material were obtained. The best sample obtained by this procedure was only 90 percent pure and possessed a dark brown color.

By use of a different method, however, it has been possible to recover para-amidophenol of high purity from alkaline solutions of the amine with very good yields. The method which has been used successfully involves the liberation of the amine from alkaline solutions (to which a small amount of sodium bisulphite has been added) by means of the addition of (1:1) sulphuric acid.

A number of experiments were carried out to study to some extent the effect of the quantity of sodium bisulphite added. The alkaline solutions of para-amidophenol were in all cases obtained by electrolytically reducing para-nitrophenol in alkaline solutions at a lead cathode under like conditions. Each solution contained 10.9 grams of para-amidophenol and was allowed to stand at room temperature for 16 hours, was then placed in a bath of running water while the para-amidophenol was liberated by the dropwise addition

of (1:1) sulphuric acid until a phenolphthalein end-point was reached. The liquor was then filtered by means of suction and the para-amidophenol washed twice with cold distilled water, sucked as dry as possible on the Beuchner filter, and then dried over night in a vacuum desiccator. The dry para-amidophenol was weighed and the purity determined. The results of these experiments are given in Table XIII.

TABLE XIII

Influence of $NaHSO_3$ upon the Recovery of Para-amidophenol

| Gms $NaHSO_3$ added to 500 cc of solution | Gms para-amidophenol recovered | Percent purity | Gms pure p-amidophenol | Percent recovery |
|---|---|---|---|---|
| 0.0 | 9.2 | 96.4 | 8.87 | 81.3 |
| 5.0 | 9.3 | 98.7 | 9.18 | 84.2 |
| 10.0 | 9.5 | 98.1 | 9.32 | 85.5 |

From this data, it seems evident that there is no advantage in the use of more than small amounts of sodium bisulphite in the recovery. If the para-amidophenol is liberated immediately after being prepared, good yields of very pure material can be obtained without the addition of the bisulphite. When para-amidophenol was liberated immediately after the reduction from a solution containing 10.9 grams of the amine, 9.0 grams of para-amidophenol, 98.4 percent pure, were obtained. The mother liquor, after filtering off the precipitated para-amidophenol, still contained 2.06 grams of the amine.

The para-amidophenol remaining in the mother liquor may be almost completely recovered by making slightly acid, evaporating to dryness on the steam bath, powdering the residue, extracting it with small quantities of boiling alcohol, and evaporating the alcohol under vacuum. When this procedure was followed in the recovery of para-amidophenol from 400 cc of an alkaline solution containing 10.9 grams of the amine and 5 grams of sodium bisulphite, the following results were obtained.

| | | |
|---|---|---|
| Weight ppt. p-amidophenol—gms | 9.4 | |
| Purity—percent | 99.2 | |
| Weight pure p-amidophenol—gms | | 9.32 |
| Weight p-amidophenol from residue—gms | 1.6 | |
| Purity—percent | 87.7 | |
| Weight pure p-amidophenol—gms | | 1.40 |
| Total pure p-amidophenol-gms | | 10.72 |
| Loss—gms | | 0.18 |
| Loss—percent | | 1.65 |

The para-amidophenol obtained by extracting the residue from the evaporation of the mother liquor might be further purified by recrystallization from a suitable solvent. The ash content of the samples of the amine from residues was about 4.0 percent. The ash content of the samples of precipitated para-amidophenol was in all cases less than one percent.

This procedure has also proven itself superior to the carbon dioxide method for the liberation of ortho-amidophenol from its alkaline solutions. By this method, ortho-amidophenol ranging in purity from 99.5 to 99.7 percent may be obtained.

As the best procedure for the laboratory preparation of para-amidophenol, the following is recommended. Prepare a lead cathode by plating sponge lead on a copper gauze from a solution of litharge in 15 percent caustic soda at a current density of 10.0 amperes per sq. dcm.

Start the reduction with a cathode solution of 8 percent NaOH containing about 3 to 4 grams of para-nitrophenol per 100 cc. Use as anode an iron wire gauze and as anode liquor a 15 percent solution of NaOH. Maintain the cathode liquor at a temperature of 65–75° C. Start the reduction with a current density of 10.0 amperes per sq. dcm. When one half the nitrophenol has been reduced, add one half the original amount of the nitrophenol. Continue the reduction at a current density of 10.0 amperes per sq. dcm. until 95 percent of the theoretical number of ampere hours has been

passed. Finish the reduction with a current density of 4.0 amperes per sq. dcm., passing a ten percent excess of current.

At the end of the reduction, wash off the porous cup, cathode, and stirrer into the cathode liquor with as small a quantity of water as possible. Add about 1 gram of sodium bisulphite for each 100 cc of cathode liquor and cool to room temperature. Liberate the amine by the dropwise addition of (1 : 1) sulphuric acid to a phenolphthalein end-point. Filter on a Beuchner funnel with suction, wash the residue twice with cold distilled water, suck as dry as possible on the filter bed, and dry in a vacuum dessicator. Make the mother liquor slightly acid with sulphuric acid and evaporate to dryness on a steam bath, powder the dry residue, and extract several times with small quantities of boiling absolute alcohol. Evaporate the alcohol from the amidophenol in a vacuum desiccator.

A 90 to 95 percent yield should be obtained in the reduction and practically all of this can be recovered. About nine tenths of the amine should be obtained from the precipitation as a product ranging in purity from 98.5 to 99.5 percent. One-tenth can be obtained by extraction of the residue from the mother liquor as a product ranging in purity from 85 to 90 percent.

## Summary and Conclusions

1. Lead is superior to copper for use as a cathode in the reduction of para-nitrophenol to para-amidophenol. Lead cathodes also permit the use of higher current densities during the reduction.

2. An electrolyte containing NaOH gives higher current efficiencies and material yields of para-amidophenol than electrolytes containing sodium carbonate, sodium bicarbonate or sulphuric acid.

3. With a copper or lead cathode, the highest current efficiencies and material yields are obtained with an electrolyte containing about eight percent NaOH.

4. At a copper cathode, the highest current efficiencies

and material yields are obtained when a current density of 1 to 2 amperes per sq. dcm. is used.

5. The most favorable concentration of para-nitrophenol in the cathode liquor is 2.0 to 3.0 grams of the nitrophenol in 100 cc.

6. With a current density of 4.0 amperes per sq. dcm., the most favorable temperature is 65° to 75° C. With a current density of 10.0 amperes per sq. dcm., the reduction is best carried out near the boiling point.

7. When solutions of 10 grams of para-nitrophenol in 400 cc of 8 percent caustic soda were reduced at a copper cathode with a current density of 2.0 amperes per sq. dcm., and at a temperature of 72°–74° C, the following results were obtained.

*a.* Theoretical current efficiency was obtained as long as the concentration of para-nitrophenol did not drop below about 1.0 gram in 100 cc.

*b.* Material yields increased as the number of ampere hours was increased until ten percent in excess of the theoretical amount of current was used. The use of a larger excess of current causes no further increase in material yield.

8. Para-amidophenol of high purity (99.0–99.5 percent) can be obtained from alkaline solutions of the amine by neutralization with sulphuric acid in the presence of sodium bisulphite, filtering, washing with water, and drying under vacuum.

9. The para-amidophenol remaining in the mother liquor after precipitation with sulphuric acid can almost all be recovered by making the mother liquor slightly acid, evaporating to dryness on a steam bath, and extracting the dry residue with small portions of boiling absolute alcohol. The alcohol should then be evaporated from the para-amidophenol under vacuum.

10. On standing, alkaline para-amidophenol solutions decompose quite rapidly. If small quantities of sodium bisulphite are added, this decomposition is prevented.

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# THE PHYSICO-CHEMICAL PROPERTIES OF STRONG AND WEAK FLOURS, V. THE IDENTITY OF THE GLUTEN PROTEIN RESPONSIBLE FOR THE CHANGES IN HYDRATION CAPACITY PRODUCED BY ACIDS*

BY PAUL FRANCIS SHARP AND ROSS AIKEN GORTNER**

In the preceding paper of this series[1] a method was described for the reduction of the concentration of the soluble electrolytes present in the original flour down to a point where they exerted little effect on increased imbibition produced by various acids. Later it was found that the centrifuging of the flour-in-water suspension advocated in the method, could be replaced by simple decantation, the two methods giving identical results and the decantation method being much easier. In the decantation method the weighed amount of flour was made up to 1 liter with distilled water and shaken at intervals over a period of 45 minutes, the material was then allowed to settle for 10 to 15 minutes, the supernatant liquid decanted, the residue shaken with an additional 500 cc of distilled water, the material allowed to settle, the supernatant liquid decanted and the residue made up to a total volume of 100 cc. This 100 cc was then taken for the viscosity determination according to the method previously described.[2]

We had suspected for some time that the glutenin was

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[1] R. A. Gortner and P. F. Sharp: "The Physico-Chemical Properties of Strong and Weak Flours, IV." Jour. Phys. Chem., 27, 567 (1923).

[2] R. A. Gortner and P. F. Sharp: "The Physico-Chemical Properties of Strong and Weak Flours, III." Ibid., 27, 481 (1923).

the protein mainly responsible for the changes in imbibition of the flour or of the gluten under the influence of acids and alkalies. The determinations reported in this paper were carried out in order to test this supposition and to ascertain which protein and what quantity of protein was removed along with the electrolytes in the extraction method described above.

Duplicate 9 gram and 18 gram portions of flour 1009 (a strong patent flour, milled from hard red spring wheat grown in the Red River Valley) were extracted for the removal of the electrolytes by the centrifuge method and the amount of protein (N × 5.7) removed by this treatment was determined. The flour residue was then extracted for two hours in a mechanical shaker with alcohol, 100 cc of 95 percent alcohol being added to the residue which contained enough water to dilute the alcohol to about 70 percent. The alcohol was removed by centrifuging and the flour residue was treated with two successive portions of 100 cc each of 70 percent alcohol. The three alcoholic extracts were combined and the protein thus removed was determined. The flour residue was again treated with 50 cc of 70 percent alcohol and agitated in a mechanical shaker for 30 minutes, the mixture centrifuged, and the protein in the alcohol again determined. The residue was extracted a third time in a similar manner and the protein in the extract again determined. The residue was then extracted with 50 cc of 95 percent alcohol followed by 50 cc of ether and the protein in these extracts determined. The residue was then air dried and finally suspended in 100 cc of distilled water and the imbibition capacity of the remaining protein was measured with a MacMichael viscosimeter. The highest viscosity produced with lactic acid acting on this flour residue, and the protein (N × 5.7) removed in the various extracts are given in Table I.

It is seen from Table I that the treatment with water removes a considerable proportion of the protein, and the results obtained by subsequent extraction with alcohol show that the protein removed is the alcohol soluble protein, gliadin,

for although the individual values in the two columns vary considerably, nevertheless the sums of the two show good

TABLE I

Protein extracted from flour 1009 by (1) two successive extractions of 1 liter and 500 cubic centimeters of water, (2) residue extracted three successive times with 100 cc portions of 70 percent alcohol, (3) is the sum of (1) + (2), (4) residue extracted with 50 cubic centimeters of 70 percent alcohol, (5) residue extracted again with 50 cubic centimeters of 70 percent alcohol, (6) residue from (5) extracted twice with 50 cubic centimeters of 95 percent alcohol followed by 50 cubic centimeters of ether, (7) sum of protein extracted, (8) dry residue was made up to 100 cubic centimeters with water and the highest viscosity obtained with lactic acid determined. The torsion wire read 29.2° with 60% sucrose solution (viscosity 43.86 centipoise).

| Weight of flour taken | Protein in | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| | Water extract | First alcohol extract | (1) + (2) | Second alcohol extract |
| Grams | Percent | Percent | Percent | Percent |
| 18 | 3.93 | 5.16 | 9.09 | 0.19 |
| 18 | 4.66 | 4.33 | 8.99 | 0.18 |
| 9 | 5.88 | 3.22 | 9.10 | 0.17 |
| 9 | 6.04 | 2.83 | 8.87 | 0.17 |
| | | Average = | 9.01 | |

Alcohol soluble protein A.O.A.C. method = 9.04

TABLE I (Cont.)

| Weight of flour taken | Protein in | | | 8 |
|---|---|---|---|---|
| | 5 | 6 | 7 | |
| | Third alcohol extract | 95% alcohol ether extract | Total protein extracted | Viscosity reading |
| Grams | Percent | Percent | Percent | M° |
| 18 | 0.13 | 0.02 | 9.43 | 191 |
| 18 | 0.14 | 0.02 | 9.33 | 195 |
| 9 | 0.13 | 0.02 | 9.42 | . . . |
| 9 | 0.11 | 0.01 | 9.16 | . . . |
| | | Average = | 9.33 | |

Alcohol soluble protein A.O.A.C. method = 9.04

agreement and the average agrees very well with the alcohol soluble protein determined directly according to the A.O.A.C method.[1] The viscosity value is not as high as was found in previous determinations, i. e., 258° M for the 18 grams, where treatment with alcohol was omitted, yet the imbibition here produced is of a high order of magnitude.

The results of this experiment indicated that most of the gliadin could be removed from the flour by simple extraction with distilled water. In order to ascertain how far this was true, 18 gram portions of the flour were shaken with 500 cc of distilled water, the flour particles allowed to settle, and the supernatant liquid decanted into a 2 liter volumetric flask. The extraction was repeated three times more and the protein removed by the two liters of water was determined in an aliquot of the extract. Three samples of flour were thus extracted, the first 8 times, the second 12 times, and the third 16 times, with 500 cc portions of distilled water and the protein removed by the water determined. The remaining residues were each treated with 100 cc of 95 percent alcohol which with the water present in the residue made a final concentration of 70 percent alcohol and the material shaken in a mechanical shaker for 2 hours. The extract was removed by centrifuging and the residue was twice more extracted with 100 cc of 70 percent alcohol. The protein removed in these alcoholic extracts was then determined. The residues were air dried and made up to a total volume of 100 cc with distilled water and the maximum viscosity produced in the presence of lactic acid was determined. The results are given in Table II.

The viscosity values obtained are not as high as those in Table I yet about 1 percent more protein was removed in Table II which would roughly account for the difference. The results indicate that most of the alcohol soluble prote n can be removed by treatment with water, but even after extraction with 16 successive portions of 500 cc each of distilled

[1] "Methods of Analysis." Association of Official Agricultural Chemists, Washington, (1920), p. 167–168.

water approximately 1 percent of alcohol soluble protein remains. Some of the glutenin was undoubtedly removed with the water extract, either in solution or in the form of a suspension which had not settled out.

TABLE II

18 gram portions of flour 1009 were repeatedly extracted with 500 cubic centimeter portions of water and the protein (N × 5.70) in the combined extract determined. The number of extractions is indicated in the table. The remaining residue was finally extracted three times with 100 cc portions of 70 percent alcohol. The protein content of these extracts was determined. The residue was made up to 100 cubic centimeters with water and the maximum viscosity in the presence of lactic acid was determined. The torsion wire used read 29.2° M with a 60 percent sucrose solution whose viscosity is 43.86 centipoise.

| | Percentage protein in | | | |
|---|---|---|---|---|
| | First 4 water extracts | Second 4 water extracts | Third 4 water extracts | Fourth 4 water extracts |
| I | 6.67 | 1.61 | .... | .... |
| II | 6.77 | 1.56 | 0.75 | .... |
| III | 6.77 | 1.43 | 0.63 | 0.52 |

TABLE II (Cont.)

| | Percentage protein in | | |
|---|---|---|---|
| | Alcohol extracts after water extraction | Total protein extracted | Viscosity M° |
| I | 1.85 | 10.13 | ....* |
| II | 1.25 | 10.33 | 157 |
| III | 1.12 | 10.33 | 149 |

* Residue lost by accident.

On the theory that glutenin is solely responsible for the viscosity changes, the lower viscosity readings obtained in Tables I and II could not be accounted for entirely on the basis of the removal of some of the glutenin due to a slight solubility or mechanical dispersion in the water. It is well known that naturally occurring proteins are very sensitive to changes in their environment and it was suspected that

this lower viscosity might be due to either to a denaturizing effect of the 70 percent alcohol or to the subsequent drying of the residue. Sharp and Gortner[1] have shown that gluten cannot be dried in a vacuum oven at a temperature of 50° C without altering its colloidal properties. The above experiment was therefore repeated, except that, instead of drying after the alcoholic extraction, the alcohol was removed by 4 subsequent extractions with 500 cc of distilled water. The maximum viscosity values obtained were, for the 8 extractions 202° M, for the 12 extractions 160° M, and for the 16 extractions 105° M. These experiments indicated that it is the denaturization of the glutenin by the 70 percent alcohol which causes the lowered viscosity readings. The colloidal properties of the glutenin are thus markedly altered by treatment with 70 percent alcohol. Additional proof that this is the case is found in the next experiment.

Three samples of flour of 18 grams each were extracted, the first 8 times with 500 cc of water, the second 12 times and the third 16 times, and the increase in viscosity as produced by various additions of lactic acid then determined on the residue. It will be noted that this is a repetition of the preceding experiments with the exception that the treatments with alcohol are omitted. The results obtained are expressed graphically in Figure 1.

*The maximum viscosity reading, 456° M, is much higher than any of the previous values, yet practically all of the alcohol soluble protein has been removed.* The effect of even 0.10 cc of normal lactic acid is very pronounced, causing an increase in viscosity of over 90 times the value obtained with distilled water (4° M to 365° M). This viscosity is reached *almost instantaneously* on the addition of the lactic acid.

Loeb[2] suggests that the physical behavior of proteins, such as swelling, viscosity changes, etc., which have been

[1] P. F. Sharp and R. A. Gortner: "Physico-chemical Studies of Strong and Weak Flours, II." Jour. Phys. Chem., 26, 101–136 (1922).

[2] J. Loeb: "Proteins and the Theory of Colloidal Behavior," p. 119 (1922).

ascribed by earlier workers to the colloidal state of the proteins, is in reality due to the formation of definite chemical compounds with the acids, alkalies and salts; and that the hydration and viscosity phenomena are due to the osmotic behavior of the protein ions in accordance with the Donnan[1] equilibrium and the colloidal condition, *per se*, does not enter into the swell-

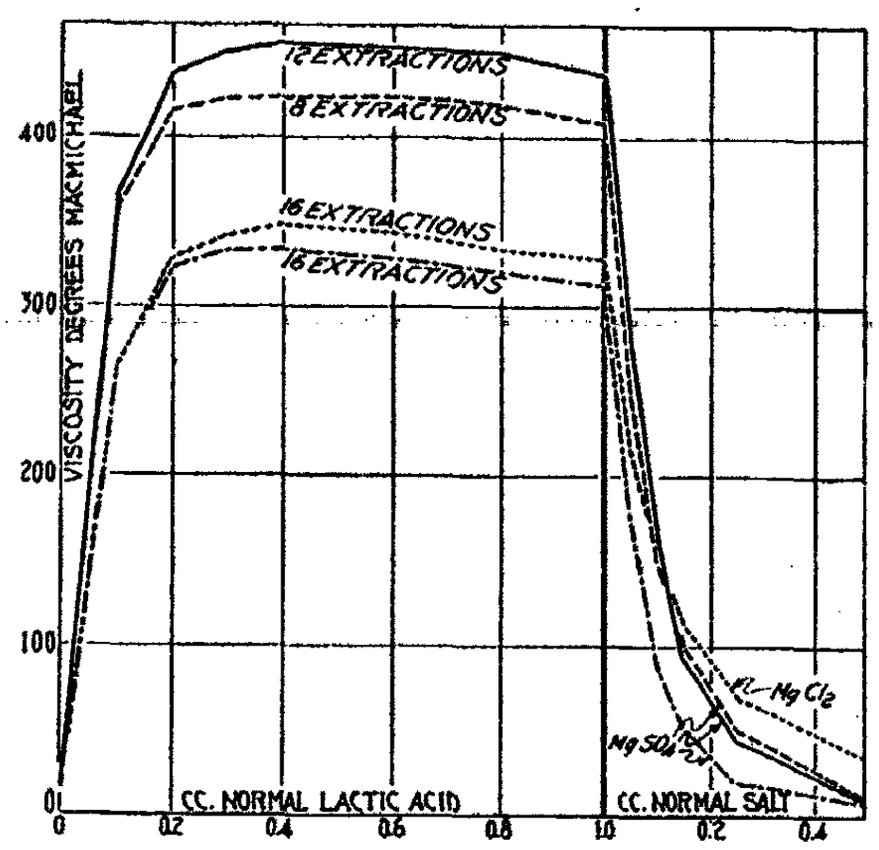



Fig. 1

The effect of repeated extraction of the flour with water on the viscosity as influenced by lactic acid and the effect of adding salts to the system

ing or viscosity changes. Loeb has presented a mass of data in support of his view. It is not our intention to seriously discuss this question in the present paper. We wish merely to point out one or two pertinent facts which may have a bearing upon the question.

In the first place the argument that proteins, such as egg albumen, are known to occur in monomolecular solution (cf. the studies of Sörensen et al.)[2] does not in our opinion

[1] F. G. Donnan: Zeit. Elektrochem., 17, 572–581 (1911).

[2] S. P. L. Sörensen, et al.: "Studies on Proteins," Comptes rendus. Lab. Carlsberg, 12, 1–372 (1915–1917).

preclude the possibility that such solutions may possess purely colloidal reactions. The colloidal state has been defined as depending upon the *size* of the particle, those particles between the diameter of 0.1$\mu$ and 1$\mu\mu$ being within the colloidal realm. Apparently many workers have read into this definition the supposition that such particles must be composed of aggregates of molecules. Such a supposition is apparently not true. Robertson[1] has calculated the diameter of the casein molecules on the assumption that the molecular volume is an additive function of the volume of the constituent atoms. He concludes that the diameter of the casein molecule must be about 2.4$\mu\mu$ providing that the formula is $C_{777}H_{1241}N_{197}O_{250}S_4P_4$ with a molecular weight of approximately 17,000. *Even in monomolecular solution, a particle of such size should show surface phenomena characteristic of the colloidal state. The casein molecule, however, is undoubtedly hydrated in solution so that the actual diameter of the particle in solution must considerably exceed the minimum diameter of 2.1$\mu\mu$.* Ultrafiltration data also indicate that the casein particle as it exists in solution has a relatively large diameter considerably exceeding 2.4$\mu\mu$. Whether or not casein exists in solution in monomolecular aggregates is still unknown. Sörensen,[2] however, has shown that egg albumen solutions are definitely monomolecular solutions which rigidly obey the equilibria demanded by the phase rule. He concludes from direct osmotic pressure measurements that the molecular weight of egg albumen is of the order of 34,000. Ultrafiltration experiments again indicate that these molecules are highly hydrated *and are of colloidal dimensions.* Such solutions undoubtedly show chemical reactions, but *we believe that they must also show surface reactions characteristic of similarly sized particles in the colloidal state.*

Turning again to Figure 1, we note that 0.1 cc of normal lactic acid increased the viscosity of the flour suspension from

[1] T. B. Robertson: "The Physical Chemistry of the Proteins," pp. 343–4 (1918).

[2] S. P. L. Sörensen: loc. cit.

4° MacMichael to 365° M. This increase in viscosity was *practically instantaneous* (within 2 or 3 seconds!) and on the addition of 0.5 cc of normal $MgSO_4$ solution the viscosity fell *practically instantaneously* from 439° M to 11° M. The rate of viscosity change and the extreme lability of the systems suggest very strongly that we are dealing with *surface reactions* characteristic of the colloidal realm, rather than chemical combinations and the subsequent osmosis of the Donnan equilibrium. The real test of Loeb's view that all osmotic and viscosity changes are due to the Donnan equilibrium will come when some one applies it to carbohydrate solutions. With pentosan solutions we have as great viscosity values as are found in protein solutions, nevertheless no one has shown that such gums and mucilages combine with acids and basis in stoichiometrical relationships.

The depressing effect of salts on the viscosity of a flour suspension hydrated by lactic acid is very pronounced as can be seen from Figure 1. The depressing effect of magnesium sulfate is greater than that of magnesium chloride. This is in agreement with the effect of these two salts on the flours which have not been extracted with water.[1]

These experiments indicate that the glutenin is the protein mainly responsible for the increase in imbibition produced by acids acting on flour-in-water suspensions. This conclusion that glutenin is the protein responsible for the imbibition changes between strong and weak flours was reached late in the fall of 1921 and all of the experimental work was completed prior to May 1922. Woodman[2] in a recent paper, and using entirely different methods, reaches a similar conclusion that the difference between a strong and weak flour is due to a difference in the glutenin fraction. Woodman bases his evidence on the optical behavior of the pure flour proteins when racemized at 37° by dilute alkali. He finds the gliadin from both types of flour to be identical, but the natural glutenins

[1] R. A. Gortner and P. F. Sharp: "The Physico-Chemical Properties of Strong and Weak Flours, IV." Jour. Phys. Chem., 27, 567 (1923).

[2] H. E. Woodman: Jour. Agr. Sci., 12, 231–243 (1922).

possess different specific optical rotations and, when treated with alkali, show different racemization curves. Woodman states "The factor which determines the shape of the loaf and which appears to be directly related to the physical properties of the gluten of the flours, is possibly dependent on the particular glutenine mechanism possessed by the wheat. The results of this investigation suggest that the strong wheat synthesizes one type of glutenine and the weak wheat a different type."

Such a conclusion we regard as strongly confirming our experiments as recorded in the present series of papers. Woodman suggests that if the physical properties of strong and weak flours are determined by the glutenin fraction it ought, theoretically, to be possible to prepare a "strong" gluten by mixing the gliadin from a weak flour with the glutenin from a strong flour. He was, however, unsuccessful in such an experiment and believes that his failure was due to two factors (1) "It is not possible by grinding the proteins together to effect the same intimacy of mixture as occurs naturally in the flour" and (2) "The physical properties of the proteins themselves have probably been considerably modified during the process of their isolation as a result of prolonged contact with different reagents (alcohol, ether, alkali etc.)." Here again his second conclusion admirably sustains our findings that treatment of the glutenin with alcohol markedly changes its physical properties. This conclusion we expect to enlarge upon in the seventh paper of this series.

## Summary

1. Glutenin is the protein mainly responsible for the increase in imbibition when flour-in-water suspensions are acted on by acids.

2. A large proportion of the gliadin can be removed from flour by extraction with distilled water while very little of the glutenin is removed by such treatment.

3. The colloidal properties of the glutenin as measured

by changes in rate of imbibition and maximum imbibition capacity are markedly altered by treatment with alcohol of a relatively high concentration.

4. A "strong" flour is apparently characterized by the presence of a glutenin possessing marked colloidal properties whereas the corresponding colloidal properties of the glutenin in a weak flour are much less pronounced.

# CUPRIC OXIDE JELLIES

BY HARRY B. WEISER

Foerster[1] prepared a cupric oxide jelly by the hydrolysis of a solution of cupric ammonium acetate of the formula $Cu(C_2H_3O_2)_2.2NH_3$. The latter was prepared in a very pure crystalline state by addition of excess alcoholic ammonia to an alcoholic solution of cupric acetate and distilling off the excess alcohol. A solution of this highly soluble salt was prepared either by the addition of a very small amount of water or by allowing the salt to deliquesce. On diluting this concentrated solution a jelly was formed which changed in time to a fine powder.

Finch[2] working in Bancroft's laboratory has repeated and extended the investigations of Foerster. He found that a jelly could be obtained simply by adding an excess of water directly to the crystals of cupric ammonium acetate and shaking to ensure rapid solution. Like Foerster, Finch observed that the jelly was not permanent and that quite as good a suspension was obtained which approached a jelly in properties simply by adding ammonia in suitable amount to saturated $Cu(C_2H_3O_2)_2$; but this method was unsatisfactory as a gelatinous precipitate formed in a short time. It was found that a good jelly could be obtained by the addition of 0.5 gm. of $MnSO_4.7H_2O$ to 50 cc. of saturated $Cu(C_2H_3O_2)_2$ and precipitating with 3 cc of diluted ammonia (1 : 1). Since no jelly was obtained by the addition of $NH_4OH$ to a solution of $CuSO_4$ it was thought that the manganese radical was the effective one. This proved incorrect since no jellies could be obtained in the presence of manganese salts other than the sulphate. To reconcile the good effect of a small amount of manganous sulphate with the fact that $CuSO_4$ gave no jelly it was concluded that a small amount of sulphate was the

[1] Ber. deutsch. chem. Ges., **25**, 3416 (1892).

[2] Jour. Phys Chem.., **18**, 26 (1914).

important thing. This was proven to be true. A good jelly resulted by using 50 cc saturated $Cu(C_2H_3O_2)_2$, 4 drops of concentrated $H_2SO_4$ and 3–4 cc diluted ammonia (1:1). $K_2SO_4$ in small amount could be substituted for $H_2SO_4$ but a permanent jelly was not obtained using a small amount of $CuSO_4$. Finch's experiments led to the conclusion that permanent cupric oxide jellies can be formed only by the addition of a suitable amount of ammonia to cupric acetate solution in the presence of a small amount of sulphate ion. No explanation is suggested to account for the facts: first, that a limiting concentration of ammonia is necessary; second, that copper acetate is effective but not copper sulphate, chloride, or nitrate; and third, that the presence of a small amount of sulphate ion in conjunction with copper acetate is necessary for the formation of a permanent jelly.

I have pointed out that in general a jelly will be formed if a suitable amount of a hydrous substance is gotten into colloidal solution and allowed to precipitate at a suitable rate.[1] The presence of salts influence the formation of jellies in so far as the precipitating and stabilizing action of the ions affect the rate of precipitation. Since cupric oxide adsorbs water strongly it possesses the necessary property for forming a jelly providing it is allowed to precipitate at a suitable rate. It seemed probable therefore that the specific conditions for the formation of a cupric oxide jelly as found by Finch, could be explained in the light of the general theory. Some experiments were undertaken with this end in view.

## Experimental

*The precipitation of cupric acetate with ammonia.* A saturated solution of cupric acetate was prepared and found by analysis to be 0.77 N. 25 cc portions were precipitated with 3, 4, 5 and 6 cc respectively of 3 N ammonia. The precipitate which was obtained in each case apparently enclosed all the water and from this point of view might be considered a jelly. The fact that it settled quickly giving a slight super-

[1] Jour. Phys. Chem., **26**, 429, 681 (1922).

natant liquid proved that it was merely a bulky gelatinous precipitate and not a jelly. A similar precipitate was obtained with the sulphate, chloride and nitrate of copper.

The results were what might be expected. Von Weimarn[1] has shown that jelly-like masses of insoluble salts are formed by mixing concentrated solutions of soluble salts containing the desired ions. With the hydrous oxides the concentration of the solutions mixed need not be so great as for a salt that normally precipitates in a very slightly hydrous, crystalline form like $BaSO_4$. Still the general conditions are the same and it has been our experience that the bulky gelatinous precipitates obtained by rapid precipitation cannot be classed true jellies as they are quite different in appearance and in character from the firm uniform jellies obtained by slow precipitation from colloidal solutions. The failure to obtain jellies by direct precipitation led to a quantitative study of Finch's method.

*Experiments with cupric acetate and ammonium hydroxide in the presence of potassium sulphate.* A mixing apparatus was prepared consisting of a glass tube 20 cm long and 4 cm in diameter supplied with rubber stoppers. Through a hole in the center of one stopper was placed a glass rod on the end of which was sealed a 10 cc glass cup. 25 cc portions of cupric acetate were first placed in the tube together with 1, 2, 3 or 4 cc portions of potassium sulphate. In the cup were placed varying amounts of 3 N ammonium hydroxide. The tube was stoppered and inverted with a quick jerk; this ensures rapid uniform mixing. The contents of the mixer was then poured into a large test tube and allowed to stand. Observations were made each hour until a gelatinous precipitate formed, for the first 6 hours and daily thereafter for two weeks. A part of these observations are recorded in Table XIV. Where the term "precipitate" is used, is meant a gelatinous precipitate with considerable supernatant liquid, as distinct from a jelly. It will be noted that in most cases the jellies are not permanent but break down after a few hours.

[1] Grundzüge der Dispersoidchemie, 67 (1914).

The results recorded in Table I show the best conditions for obtaining a firm jelly while closer observations of these experiments indicate the explanation of the results. It was noted at the outset that the addition of less than the equivalent amount of $NH_4OH$ did not produce a precipitate but a perfectly clear solution which starts to precipitate spontaneously after intervals that vary from a few seconds to several minutes depending on the amounts of $K_2SO_4$ and $NH_4OH$

TABLE I

| Solutions added to 25 cc 0.75 N $Cu(C_2H_3O_2)_2$ | | Observations after | | | |
|---|---|---|---|---|---|
| N $K_2SO_4$ cc | 3N $NH_4OH$ cc | 4 hours | 1 day | 7 days | 14 days |
| 1 | 3 | Precipitate | ——— | ——— | ——— |
| 2 | 3 | Soft jelly | Precipitate | ——— | ——— |
| 3 | 3 | Precipitate | ——— | ——— | ——— |
| 4 | 3 | Precipitate | ——— | ——— | ——— |
| 1 | 4 | Good jelly | Soft jelly | Precipitate | ——— |
| 2 | 4 | Good jelly | Good jelly | Precipitate | ——— |
| 3 | 4 | Good jelly | Fair jelly | Precipitate | ——— |
| 4 | 4 | Good jelly | Precipitate | ——— | ——— |
| 1 | 5 | Good jelly | Good jelly | Fair jelly | Precipitate |
| 2 | 5 | Good jelly | Good jelly | Good jelly | Good jelly |
| 3 | 5 | Good jelly | Good jelly | Fair jelly | Precipitate |
| 4 | 5 | Precipitate | ——— | ——— | ——— |
| 1 | 6 | Fair jelly | Precipitate | ——— | ——— |
| 2 | 6 | Fair jelly | Precipitate | ——— | ——— |
| 3 | 6 | Fair jelly | Precipitate | ——— | ——— |
| 4 | 6 | Precipitate | ——— | ——— | ——— |

added. We have seen that a comparatively slow precipitation from colloidal solution favors the formation of a firm jelly so that the problem resolved itself into finding the most favorable conditions of precipitation. A firm jelly that remained unbroken for more than 3 months was obtained by adding 5 cc of 3 N $NH_4OH$ to 25 cc of 0.75 N $Cu(C_2H_3O_2)_2$ containing 2 cc of $K_2SO_4$. With too little $K_2SO_4$ a gelatinous precipitate formed at once on adding the equivalent amount

of $NH_4OH$; the same is true with an excess of $K_2SO_4$. With a suitable amount of sulphate and too little $NH_4OH$ not enough precipitation takes place to form a firm jelly. This was observed with 3 cc, which is one-half the equivalent of the copper present. With too much $NH_4OH$ not only does precipitation take place too rapidly but a portion of the copper goes to the deep blue copper ammonium complex. This was observed with 6 cc of $NH_4OH$, an amount equivalent to the copper. The conditions that we have found most favorable are similar to those of Finch[1] who obtained the best results by adding

TABLE II

| Solutions added to 25 cc 0.77 N $Cu(C_2H_3O_2)_2$ | | Observations after | | | |
|---|---|---|---|---|---|
| N $CuSO_4$ cc | 3N $NH_4OH$ cc | 4 hours | 24 hours | 7 days | 14 days |
| 1 | 5 | Good jelly | Good jelly | Fair jelly | Precipitate |
| 2 | 5 | Good jelly | Good jelly | Good jelly | Fair jelly |
| 3 | 5 | Good jelly | Fair jelly | Precipitate | ——— |
| $(NH_4)_2SO_4$ | | | | | |
| 1 | 5 | Soft jelly | Fair jelly | Precipitate | ——— |
| 2 | 5 | Good jelly | Good jelly | Good jelly | Good jelly |
| 3 | 5 | Good jelly | Good jelly | Good jelly | Precipitate |

3–4 cc of $NH_4OH$ (1:1) to 50 cc of saturated $Cu(C_2H_3O_2)_2$ containing 0.5 g $MnSO_4.4H_2O$. This sulphate is equivalent to 2.24 cc of N salt in 25 cc as compared with 2 cc which we have found most satisfactory.

Since $K_2SO_4$ and $MnSO_4$ seem equally satisfactory there seemed no reason why other sulphates including $CuSO_4$ might not be used. The results with $CuSO_4$ and $(NH_4)_2SO_4$ recorded in Table II confirm this view.

A close observation of the formation of the jellies showed that in every case the presence of sulphate prevented immediate precipitation; but with too little sulphate the precipitation

[1] Loc. cit.

was too slow and with too much sulphate, the precipitation was too rapid to form a firm permanent jelly. This action of sulphate was investigated further as described in the next paragraph.

*Action of $NH_4OH$ on copper acetate solution in the presence of ammonium sulphate.* The amount of ammonia necessary to cause a slight permanent precipitate at once when added to copper acetate in the presence and absence of sulphate was determined as follows: 25 cc of 0.75 N copper acetate with or without $(NH_4)_2SO_4$ was placed in the mixing apparatus and a known amount of 3 N $NH_4OH$ in the cup. The mixer was shaken and the solution observed promptly to determine whether or not a precipitate formed at once. By repeated trials the conditions for the formation of a slight permanent precipitate were found with considerable accuracy. The results are given in Table III.

TABLE III

| Solutions mixed | | | Observations |
|---|---|---|---|
| $Cu(C_2H_3O_2)_2$ 0.75 N | $(NH_4)_2SO_4$ N | $NH_4OH$ 3 N | |
| 25 | 0.0 | 1.75 | No precipitate |
| 25 | 0.0 | 2.00 | Very slight precipitate |
| 25 | 0.2 | 2.75 | No precipitate |
| 25 | 0.2 | 3.00 | Slight precipitate |
| 25 | 0.2 | 3.25 | Large precipitate |
| 25 | 0.4 | 3.25 | No precipitate |
| 25 | 0.4 | 3.50 | Slight precipitate |
| 25 | 0.8 | 4-8 | No precipitate. Goes over directly to the blue copper ammonium complex |

It will be noted that 2 cc of 3 N $NH_4OH$ must be added rapidly to 25 cc of 0.75 N $Cu(C_2H_3O_2)_2$ in order to get a slight permanent precipitate at once. A similar precipitate was obtained on adding but 0.10 cc of 3 N $NH_4OH$ to 25 cc of 0.75 N solutions of $CuSO_4$, $Cu(NO_3)_2$ and $CuCl_2$. Thus the acetate is the only one of the four salts which gives colloidal

hydrous cupric oxide of appreciable concentration on adding $NH_4OH$ to the 0.75 N solution. A much higher concentration of the colloid may be obtained by adding to the acetate solution a very small amount of sulphate ion. It is altogether likely that small amounts of multivalent ions other than $SO_4''$ would be equally effective but none of the common ions can be employed on account of the insolubility of their copper salts. The colloids obtained in this way of whatever concentration are so instable that spontaneous precipitation takes place on standing. It is this combination of circumstances that enables one to prepare a stable cupric oxide jelly by regulating the conditions so that a suitable concentration of colloid precipitates at a suitable rate.

## Summary

The results of this investigation may be summarized as follows:

1. Hydrous cupric oxide jellies are formed when a suitable concentration of colloidal oxide is precipitated at a suitable rate. The desired conditions may be realized by adding ammonia to cupric acetate in the presence of a small amount of sulphate and allowing the colloidal solution to precipitate spontaneously.

2. Jellies are not formed by adding ammonia to sulphate, chloride or nitrate since no colloid forms but immediate precipitation results with the formation of a gelatinous precipitate. Jellies are not formed by adding ammonia to cupric acetate alone since a colloid of suitable concentration cannot be prepared in this way.

3. The results of the experiments on the formation of cupric oxide jellies are in accord with the author's general theory.

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# NEW BOOKS

**Physikalische Chemie der Zelle und der Gewebe.** *By Rudolf Höber. Part I. Fifth edition. 25 × 17 cm; pp. xv + 544. Leipzig: Wilhelm Engelmann, 1922. Price: 5751 marks.*—In the fifth edition the essentially physical chemical material is in the first part, while the second part is to deal primarily with physiological phenomena. The chapters in the first part are entitled: theory of solutions and the osmotic pressure of body liquids; electrolytic dissociation; quantitative determination of hydrogen ion concentration and its physiological significance; surface phenomena; colloids; reaction velocity and the effect of enzymes on it. One chapter from the second part is included: the osmotic properties and permeability of cells and tissue.

The book is full of interesting facts, of which only a few can be mentioned. The freezing points of the body fluids of sea-animals varies from —2.3° which is practically the freezing point of sea water to —0.7° for whales, which is about normal for land animals, p. 34. The two extremes are simple enough; but why should we have intermediate cases at —1.04° and apparently nothing below that until one gets to —2.3°?

Sodium urate has a relatively low solubility when added direct to water, but a relatively high apparent solubility when uric acid is added to a solution of a sodium salt of a weak organic acid, p. 84. Höber concludes, apparently correctly, that in the second case we have sodium urate in colloidal suspension; but one would have liked to have seen this confirmed by adding the organic acid to a hot concentrated solution of sodium urate. It seems probable that the organic acid acts as a peptizing agent; but this has not been proved.

Quantitative data are given on p. 116 for the magnitude of the salt error in titration, and the account of buffer action on p. 120 is good. The reviewer would have liked to see some proof, p. 126, that the inflection in the titration curve necessarily corresponds to stoichiometric relations. The limitations should be stated. We are often told that the third hydrogen in phosphoric acid can be titrated with Poirrier Blue and yet we are told elsewhere that trisodium phosphate is completely hydrolyzed to caustic soda and disodium phosphate. The reviewer doubts the possibility of titrating a non-existent acid.

The author is quite definite that albumin forms colloidal solutions, p. 100, and he does not agree with Loeb that the Hofmeister series, p. 267, is a vain thing. For a long time the reviewer did not understand why Loeb considered the liquefaction of gelatine by potassium iodide solution as having nothing to do with swelling. The reason apparently is that Loeb considers swelling as due to hydration whereas liquefaction is melting. As the railway guard once remarked: "cats is dogs and rabbits is dogs but turtles is insects."

The author cites Burton's experiments on the reversal of the electrical charge on colloidal silver by adding aluminum salts, p. 189; but, like the rest of us for so many years, he does not draw the conclusion that, in so far as an aluminum salt is adsorbed by a silver electrode, it must change the so-called solution pressure of the silver. This is interesting because he practically had the thing worked out if one takes this observation in conjunction with the action of alcohol

and other non-electrolytes on colloidal solutions, pp. 243, 244, 291. Another interesting point which calls for study is that alcohol has more effect on gelatine in presence of a mixture of sodium and calcium chlorides, p. 281, than in presence of either salt alone.

On p. 194 the author cites the adsorption of the color bases, chrysoidin and malachite green, by alumina, which is a mordant for acid dyes, as a case of selective adsorption. This may be the case; but it is more likely that the alumina had not been washed entirely free from the precipitating base.

The chapter on colloids, pp. 208–292, is pretty nearly a treatise on colloid chemistry, and is supplemented by adsorption potentials, p. 199, negative osmosis, p. 201, immuno-chemistry, p. 285, etc., occurring elsewhere. The experiments on the osmotic pressure of Congo red, p. 217, rather suggest the occurrence of a colloidal ion such as McBain found in the soaps. The author accepts the conclusions of Hatschek that in a 9.4% solution of casein, the free water occupies only twelve percent of the total volume, p. 247. This seems to be in line with the statement, p. 404, that roughly one-fourth of the water in the blood corpuscles is not present as free water.

On p. 274 is the interesting statement that the trivalent cation of hexamminocobalti chloride, $[Co(NH_3)_6]Cl_3$, has only a very slight precipitating action on albumin. We know that enzymes are extremely specific in their action which means selective adsorption of some kind. Höber points out, p. 334, that even in true solution inorganic catalysts are sometimes quite specific. "Potassium bichromate accelerates only the oxidation of hydriodic acid by hydrobromic acid and has very little effect on the oxidation by iodic acid or potassium persulphate. Iron and copper salts accelerate the oxidation of potassium iodide by potassium persulphate but not the oxidation of sulphur dioxide."

Höber does not accept at all the view of Arrhenius, p. 285, that the reaction between tetanolysin and antitetanolysin is an ordinary reversible reaction in a homogeneous system. The apparent equilibrium varies with the rate at which the antitoxin is added and the reaction is reversible only at first. Höber considers that the phenomenon is essentially the adsorption of one colloid by another.

Everybody is familiar with the fact that sodium chloride increases the catalytic action of hydrochloric acid on sugar. It is one of our outstanding problems. Few of us keep in mind, however, that it is apparently an anion effect, being greater with bromides than with chlorides, p. 277. The saponification of esters is affected by anions in the order: tartrate, oxalate, $SO_4 > S_2O_3 > CH_3CO_4 > Cl > Br > NO_3 > I$. The effect of cations on the catalysis of esters is: $Li > Na > K > Rb > Cs$, while the reverse order holds for the saponification: $Cs > Rb > K > Li$.

Höber points out that some colloids will diffuse through some colloidal membranes, p. 289. Egg albumin and haemoglobin pass through films of glue; pepsin diffuses into cubes of coagulated albumin; while diastase, invertase, rhamnase, and oxidase penetrate a gelatine jelly.

Many plant cells are less readily affected by solutions of salts of the alkaloids than by the free bases, p. 418. The assumption made is that the cell wal. is practically impermeable to the alkaloid cation. Consequently the toxicity of the salts increases with increasing weakness of the acid because this means more hydrolysis. The facts could also be accounted for if one assumed that the alka-

loid cation could penetrate the cell wall but had a low toxicity. The way to differentiate between these two hypotheses would be to inject the alkaloid salt of a strong acid into the cell.

There are a number of interesting things about blood corpuscles, pp. 442, 448, 453. While the blood corpuscles of most animals are impermeable to grape sugar, there is a good deal of evidence that this is not true for the blood of men and apes. While the blood corpuscles are practically impermeable to salts, this is because the cations cannot pass through, the walls being readily permeable to bromide, chloride, nitrate, and sulphate ions. Without going into the question as to how the salts get there, it is interesting to note that there are no sodium salts in the blood corpuscles of the horse, the pig, and the rabbit, while the potassium content is high. With the dog and the cat there is at least ten times as much sodium as potassium. On the other hand the composition of the serum is practically the same for the five animals.

The haemoglobin problem is only just touched on in this section, p. 460, a fuller discussion being reserved by the author for a later chapter. A few words on it will not be out of place. Haemoglobin and oxygen give a dissociation curve corresponding to a binary compound. Since haemoglobin is not in true solution, the significance of the data has been called in question. The difficulty can be avoided by postulating that the dispersed phase, if sufficiently finely divided, does not behave like a phase of constant composition. We know this to be true in certain cases. Tannin and substantive dyes are adsorbed just as though they were in true solution. On the other hand salts have a very special effect on the adsorption of substantive dyes because they change the stability relations. We get something similar with haemoglobin.

"The relation between the percentage saturation of haemoglobin and the oxygen pressure can be represented by an equilateral hyperbola in the case of a pure haemoglobin solution. If salts are added the form of the curve changes, varying with the nature and the concentration of the salt. How that is to be explained will be told later. Barcroft and Camis have shown that if one adds to a pure haemoglobin solution the mixture of salts which chemical analysis has shown to be present in the blood of any particular kind of animal, the saturation curve will be identical with that for the blood of that species. A solution of haemoglobin will give the curve for dog's blood if the salts in dog's blood are added, and will give the curve for man's blood if the salts in man's blood are added. The difference in the saturation curves for different kinds of animals is therefore due to differences in the salt present and not to differences in the haemoglobins."

Höber gives an excellent discussion of the general question of semipermeability, p. 476–544; but he is rather stumped by the fact that it is apparently necessary to postulate that a given cell wall is both permeable and impermeable for the same substance. A lipoid film will account for a great many of the phenomena; but it would not let water through, so we have to add lecithin, p. 502. A great many of the acid dyes are insoluble in lipoids but penetrate certain cells readily, p. 519. Worse than that, one finds that among the substances for which the cells are normally impermeable are grape sugar, fruit sugar, cane sugar and other carbohydrates, the amino-acids and the acid amides, and many other substances which are foodstuffs for the cells, which are brought to the cells from the

outside and which are found inside the cells, p. 503. "What the cell can use, it shuts out, and what it cannot use, it lets in."

This difficulty may disappear if we do not insist on continuous impermeability. Osterhout has shown that the electrical conductance varies with the ratio of calcium to sodium salts. Höber quotes the work of Loeb and of Osterhout on the antagonistic action of calcium and sodium salts; but he does not refer to Clowes who explained this phenomenon. It may easily be that slight, temporary changes in the composition of the fluid around the cells may alter the permeability very much. This is the more probable because we know that with death the cell wall becomes permeable and because Czapek has shown that the surface tension has a marked effect on permeability. Our laboratory conclusions as to permeability are based to a large extent on experiments with sodium salts, which would naturally give the maximum impermeability. It is worth noting that haemoglobin comes out of the blood corpuscles of different animals at varying salt concentrations, p. 398, although the blood from different animals is practically isotomic. Haemoglobin comes out of man's blood at 0.45% NaCl whereas the blood is isotonic with 0.9–1.0% NaCl. *Wilder D. Bancroft*

**The Book of the Sky.** *By M. Luckiesh. 21 × 14 cm; pp. xi + 236. New York: E. P. Dutton and Co., 1922. Price: $3.50.*—In the foreword the author says: "Since the advent of flying with its modern safety, convenience, and extensive possibilities, the aerial world becomes more important and interesting to mankind. It is believed that this little volume, which touches upon so many aspects of the sky and upon what may be seen and felt in cloudland, will interest the general reader whether he is one who flies in reality or would fly on the wings of his imagination or would be content merely to admire the sky and to learn its meanings."

The chapters are entitled: man unshackled; the countenance of nature; the formation of clouds; the thunderstorm; cloud-forms; beyond an overcast sky; cloud levels; mingled moods; sunset colors; afterglow, a polar climb; cloud capers; a night flight; annihilating distance; a philosophy for flying; aerial antics; the supremacy of air-travel; meteorology; winds; weather and the sky; the convoy.

"It should not dull the beauty of sunsets to know that the colors are born in the smudge of the earth-haze. In fact, this should exalt the atmospheric haze, for without it the sky would vary little in color from that at noonday. In fact, even the delicate pastel shades of the clouds low down in the sky at noon would disappear and the clouds would appear as boldly against the deep blue as those in the zenith," p. 90.

"When the sun is setting blood-red at the earth's surface the aerial observer at an altitude of two or three miles sees the color scheme spread out before him. The lowest clouds are tinged with red, the next higher are of an orange tint; those at his level are a brilliant yellow; and the fibrous cirri two or three miles above him are still bathed in the yellowish white sunlight. Before the direct sunlight reaches the clouds at low altitudes it must pass through great depths of the densest haze. In reaching the higher clouds, the depth of the path of the sun's rays through the haze is considerably less than in the preceding case, fur-

thermore, the density of the haze diminishes somewhat with altitude. From his position three miles above the earth the observer sees the sun practically free from haze and if he were among the cirrus clouds, scarcely any dust haze would be between him and the sun."

"Considering the latitudes of the United States at other times than an equinox, an aircraft would not need to climb as fast as one thousand feet per minute for the first five minutes to see two very distinct sunsets with a sunrise between them on the same evening." p. 99.

At one time in eastern Iowa there were extremely brilliant glows about an hour after sunset, which were seamed with straight radial shadows pointing toward the sun. "There is a possibility that on these occasions of extraordinary afterglow, there were witnessed the shadows cast by the Rocky Mountains eight hundred miles to the west," p. 101.

"The terms 'canopy' and 'dome' as applied to the sky do not arise from pure fancy. As one observes the heavens he becomes conscious of an illusion of the sky which makes it appear like a dome. Whether this illusion is due to a suggestion of a dome shape by the sky itself or arises from our own inner reasoning, the author is unable to determine; however, it is a recognized illusion. In fact, experiments have been made to determine the apparent shape of the sky dome as it appears to groups of observers. The results indicate that most persons would consider it a flattened dome, that is, not a true hemisphere," p. 128.

The author believes that "one may find it possible to convince himself that living is a product of time multiplied by intensity; in other words, that living is not measured in terms of duration. One person may live a whole lifetime with unobservant eyes and unresponsive sensibility and still not accumulate as much living as another who drinks of the joys of life as he passes along a brief interval. From this viewpoint it is essential to compare the beauties, thrills, wonders, inspirations, and emotions in the aerial world with those of the more prosaic worlds with which mankind is familiar. There can be no ennui for mankind in cloudland for a long time to come," p. 159.

"The utmost freedom of an airplane strongly impresses one when in the air. Furthermore, on looking down into the depths of air somewhat visible owing to the luminous haze, and viewing airplanes far below and on all sides, one is likely to be further impressed with the fact that, after all, the air is fluid. By some such process of analysis and through certain obvious associations, it becomes easy to liken the airplane to a fish free to swim in any direction in its element. To the author the bird analogy is inadequate and the fish analogy has been drawn upon to supplement the deficiencies of the former. This may appear to be a minor point but it is important in awakening the imagination to the possibilities of flying and in aiding in visualizing the details of some of the most startling aerial antics," p. 164.

"Doubtless, most of the weather-lore was fairly dependable in the localities in which it originated and, notwithstanding the fact that it usually expresses weather-signs indirectly, it may often be traced to a logical source. It appears that most of it evolved from the accumulated experiences of years of everyday observation of the sky and the weather. However, the weather-signs differ somewhat in various parts of the world; hence, those sayings which have

been transplanted into regions remote from their sources are liable to appear to be merely 'rhyme' without the 'reason.' Nevertheless, it is interesting and worth while to analyze the weather-lore which has been handed down through many generations and to attempt to ascertain its foundations. In other words, it is hardly safe to laugh at the picturesque sayings of the weather-wise layman regardless of their apparent lack of connection with the sky or with other direct weather-signs," p. 213.

"Local weather conditions are quite varied owing to local influences but sky-signs are usually plentiful and reliable. However, the details of such weather may be best studied by observation fortified by a knowledge of the details of general storms. This phase of weather becomes exceedingly obvious to the aerial traveler. For example, during a dry spell when there is not enough moisture in the air from which cumulus clouds may form over wide areas, it is not unusual to look down upon clouds floating over woods, river valleys, and swampy regions with no clouds appearing elsewhere. The local variations of weather conditions and of the appearance of clouds very soon impress the observant cross-country traveler in cloudland. The details of local conditions cannot be adequately discussed within the boundaries of a single chapter, therefore, they will be left to each interested reader so observe and to analyze in his own locality. It should be noted that local variations are usually merely a matter of intensity and that principles remain fairly definite and universal over the entire globe. Superposed on the general and local storms or weather, there are always the diurnal weather conditions. Today one of these may dominate, tomorrow, another, but local or diurnal conditions can hardly convert the foul-weather cirrus into the fair-weather cumulus clouds," p. 221.

The cloud pictures deserve a word of mention; they are extraordinarily good. *Wilder D. Bancroft*

**Synthetic Colouring Matters. Dyestuffs derived from Pyridine, Quinoline, Acridine, and Xanthene.** *By J. T. Hewitt.* 23 × 15 *cm; pp. xi* + 405. *New York and London: Longmans, Green and Co., 1922. Price: $4.75.*—The chapters are entitled: pyridine and its homologues; quinoline, its homologues and derivatives; quinophthalone and flavaniline; the cyanine group; synthesis of acridine and its derivatives; general account of the acridine dyestuffs; amino derivatives of acridine; amino derivatives of 5-phenylacridine; phenonaphthacridines; the pyrone ring; fluorone and fluorim compounds; pyronines and rosamines; the constitution of fluorescein and its analogous compounds; fluorescein and related dyestuffs; hydroxyl derivatives of fluoran other than fluorescein; constitution of the rhodamines; manufactures of rhodamines; rhodols and unsymmetrical rhodamines; anisolines.

The book is essentially a reference book. It is a collection of facts with no general statements to speak of. Even in the chapter entitled "General Account of the Acridine Dyestuffs," we find only the methods of making chrysaniline, benzoflavine, flaveosin, acridine orange, naphthacridine, tolunaphthacridine, trypaflavin, and the anthraquinone acridines.

On p. 3, under pyridine and its homologues, the author says that "it is generally only such compounds as may be represented by tautomeric formulas,

i. e., can possess a quinonoid configuration, which form real dye stuffs." In a foot-note is the statement that "the author is not making a confession of quinonoid faith, but is simply pointing out a new fact. Thus in the azo-series, the dyestuffs are possibly (probably) not quinonoid, nevertheless they may be written with a tautomeric quinonoid structure."

When discussing Skraup's synthesis of quinoline, p. 38, the author says that "the nitro-groups simply furnish a convenient source of oxygen to get rid of excess of hydrogen which would convert quinoline into reduction products and so diminish the yield." If this is so, it ought to be possible to get the same results with air or with any suitable oxidizing agent.

Under chrysophenol, p. 169, is the statement that "the crystalline material in the tube, obtained in accordance with the equation,

$$C_{19}H_{18}N_3 + H_2O + 2HCl = NH_4Cl + C_{19}H_{11}ON_3.HCl$$

was regarded as a mixture of ammonium chloride and chrysophenol hydrochloride by Claus and Fischer and Körner. On account of the apparent homogeneity of the product, Dunstan and Hewitt consider that it may be a double salt." It would have been so simple a matter to decide this question definitely that it seems a pity it should have been left open.

The commercial development of eosine is rather interesting, p. 290. "In the autumn of 1871, Baeyer handed a specimen of fluorescein to Caro of the Badische Anilin and Soda Fabrik and received news from him a few days afterwards that he had discovered a beautiful dyestuff by brominating the compound. Baeyer suggested to Emil Fischer the desirability of examining fluorescein more fully and as a result the diacetyl and dibenzoyl derivatives, the chloride and sulphate were prepared and described. Meanwhile Caro undertook the task of preparing the necessary intermediates on a technical scale and discovered the method of purifying tetrafluorescein by means of its potassium salt, so that by the summer of 1874 the Badische Company were in the position to place the salt on the market under the name of Eosine. At that date the German Patent Law afforded very little protection and the decision was made to keep the process a secret. By December 1874, Gnehm suspected that eosine was allied to Baeyer's phthalein dyestuffs, and shortly afterwards Hofmann revealed the secret which had been kept for almost a year."

While reference is made on p. 77 to work on isocyanines done in the United States, it is probable that the Kodak Laboratory is not enthusiastic over the chapter on the cyanine group.

The reviewer was specially interested in the first sentence in the book. "The three bases, pyridine, quinoline, and acridine, although colourless, exhibit selective absorption in the ultraviolet, and furnish compounds by substitution which are often coloured and sometimes behave as dyestuffs." One wonders whether it would be possible to make suitable ultraviolet filters out of the three compounds and suitable derivatives. *Wilder D. Bancroft*

**The Theory of Development.** *By A. H. Nietz.* 22 × 15 *cm; pp.* 190. *New York: D. Van Nostrand Company, 1922. Price: $2.50.*—This is the second of the monographs on the theory of photography from the Research Laboratory

of the Eastman Kodak Company, and, as such, is very welcome. "The present monograph presents the results of investigations undertaken to determine the reduction potentials of certain organic developers, and to establish the connection between these potentials and the developing characteristics of the various compounds. It was originally intended to use both electrometric and photographic methods, but since the results obtained by the latter method are complete, it has been decided to publish these at the present time.

"In the course of the work a large amount of sensitometric data has been accumulated, as well as much information relative to various other aspects of the process of development. The inclusion of what may seem an unwarrantedly large amount of these data seems justified by the desire to render the information obtained as useful as possible for future work as well as to support the various conclusions reached."

On p. 13 the author says: "Chemically, photographic development is now understood to be a reduction process. Many of the features of its mechanism, however, are relatively unknown, as, for example, the differentiation by certain reducing agents between the silver halide which has been affected by light and that which has not. To clear up these matters and to determine the nature of the latent image will require extensive experimental work on details which at first seem to have little bearing on the subject. Although it is impossible at present to rate the various phases of possible investigation according to their importance, it is evident that all effects of development must be eliminated one by one. The study of development characteristics and of the reduction potentials of developers is thus of greatest importance."

The volume contains a mass of data on reduction potentials and on rate of development. It represents an enormous amount of work. Whether this work has been done wisely is an open question which time alone can answer definitely. The Kodak Laboratory undoubtedly thought that this was the way the theory of development should be studied. The reviewer does not think so. It seems to him that it would have been wiser to determine qualitatively the factors on which development depends instead of plunging quantitatively on what is undoubtedly a minor factor in development, the reduction potential. We know this to be a minor factor because all of the developers in use will develop unexposed silver bromide in the absence of gelatine.

The author practically ignores the function of the gelatine and is not at all interested in the question whether a solvent or peptizing action of the developer is or is not an important factor, perhaps the most important factor. The Research Laboratory at Kodak Park has such wonderful facilities that one wishes they would study their problems a bit instead of making measurements first and thinking afterwards. *Wilder D. Bancroft*

**Données Numériques sur les Colloïdes.** *By G. Rebière. 28 × 23 cm; pp. vii + 11. Paris: Gauthier-Villars et Cie, 1922. Price: 6 francs, paper; 12 francs, bound.*—This is a reprint from the fourth volume of the *Tables annuelles de Constantes et Données numériques*, covering the years 1913–1916. In an introduction written by Duclaux, he claims that Sörensen has proved that albumin has a definite solubility and a definite osmotic pressure. "Albumin is therefore

the first case of the conversion of colloid chemistry to ordinary chemistry. This will not remain an isolated case. Many natural colloids, haemoglobin for instance, will doubtless give the same results when studied by the same methods and with the same care. In spite of the great difficulties inherent in these methods it is to be hoped that such studies of colloids will be undertaken in as many cases as possible.

"The number of investigators who take the chemical view of colloids is actually increasing though they are still in a minority. This point of view meets strong opposition in several countries, and those not the smallest ones. The so-called physical theories are still more in favor. One cannot oppose a chemical to a physical view absolutely and say that one is false and the other true. The question is which is the more serviceable. The nomenclature adopted by the chief protagonists of the physical ideas show that they are not really interested in colloids, but in dispersoids, which means matter more or less disintegrated. The true colloids, on the other hand, those which occur in nature, consist of agglomerated matter and are condensoids. The dispersoids belong under physics and the condensoids under chemistry. The whole quarrel is over the question whether it is more useful to know the properties of proteins or of cellulose than to know those of an emulsion of mercury or oil. A comparison of the two aims shows which one ought to work for first."

The data in the tables are grouped under two heads: properties of colloidal solids, including adsorption of liquids by solids and of adsorption from solutions; and properties and reactions of colloidal solutions, with viscosity, conductance, coagulation, and miscellaneous as the sub-heads. *Wilder D. Bancroft*

**Experimental Physical Chemistry.** *By Benjamin S. Neuhausen. 21 × 14 cm; pp. 53. Philadelphia: H. N. Rudley, 1923. Price: $1.00.*—In the preface the author points out that "in acquainting the medical student with physico-chemical methods it has been usually the custom to prescribe for him a course in the physical chemistry department of his university. As a result he determined the surface tension of carbon tetrachloride or benzene—substances which are of no immediate interest to him—or he studied by the electrometric method the equilibrium of ferric and ferrous ions, while such topics as the influence of the carbon dioxide pressure on blood or serum, which are of great import to such a student, were wholly neglected."

The author therefore gives twelve experiments under four heads. These include, among others: the determination of the freezing point depression of serum; the determination of sodium and chlorine ions in serum; the determination of the albumin-globulin ratio in serum; the use of tributyrin to show lipase in serum; the rate of inversion of cane sugar by the ferment invertase. These may be and doubtless are admirable experiments to supplement a laboratory course in physical chemistry; but it seems like folly to substitute these experiments for the regular ones, which is apparently what the author wishes to do.

*Wilder D. Bancroft*

# A STUDY OF THE FLUIDITY RELATIONSHIPS IN THE SYSTEM, NITRIC ACID, SULFURIC ACID, AND WATER[1]

BY EUGENE C. BINGHAM AND S. BRADFORD STONE

## Introduction

The fluidity relationships existing in ternary mixtures have been the subject of few studies, although previous work of Bingham, White, Thomas, and Cadwell[2] indicates that such studies may give important evidence in regard to the formation of solvates. Ternary mixtures of nitric acid, sulfuric acid, and water are of particular interest because of their wide use in nitration, in connection with which there are important physico-chemical problems.

## HISTORICAL INTRODUCTION

### Nitric Acid

The physical properties of nitric acid have led many observers to the conclusion that it is hydrated in aqueous solution, and the existence of at least fifteen such hydrates has been reported in the literature. Of these only the mono- and tri-hydrates,[3] both of which correspond to maximum points on the freezing point curve, have been isolated.

Hartley[4] concluded that nitric acid of the specific gravity 1.490 was associated because of the pronounced difference in the absorption spectra of the same amounts of concentration and dilute acid. The work of Ramsay and Aston[5] gave an association factor of 1.68 and 1.86 as measured from the

[1] Contributed from the Gayley Chemical and Metallurgical Laboratory of Lafayette College.

[2] Bingham, White, Thomas, and Cadwell: Zeit. phys. Chem., **83**, 641 (1913).

[3] Pickering: Jour. Chem. Soc., **63**, 436 (1893).

[4] Hartley: Ibid., **133**, 663 (1903).

[5] Ramsay and Aston: Ibid., **65**, 167 (1894).

variation of surface energy for 99.8% acid at temperatures of 11.6°, 46.2°, and 78.2°.

Acid of ninety-five percent or over has irregular physical properties.[1] The contractions, conductivities, and to a slighter degree the refractive indices all show pronounced discontinuities at this concentration. This anomalous behavior, according to Veley and Manley,[1] indicates a decomposition into nitrogen pentoxide and water, rather than association. In this connection Küster and Munch[2] state that absolute, colorless nitric acid shows signs of decomposition when heated above its melting point.

The transpiration times of aqueous solutions of nitric acid have been investigated by Graham[3] who found that the mixture showing maximum transpiration time contained 70% $HNO_3$. He used a capillary opening into a bath, and worked with a constant pressure of one atmosphere. Neither the method of preparation of his nitric acid nor the method of determining its purity was described. No precautions were taken against the absorption of water by the very hygroscopic absolute acid. His original values, which were given in sufficient detail to permit their recalculation into terms of absolute fluidity, together with the method of recalculation are given in Table IV.

Bousfield[4] and Poiseuille[5] found that at low temperatures and in dilute solutions nitric acid decreased the viscosity of water, producing the so-called "negative viscosity." This negative curvature disappeared on raising the temperature to 25°.

Chèneveau[6] found that nitric acid-water mixtures of the composition $HNO_3.2H_2O$ displayed a maximum of relative viscosity.

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[1] Veley and Manley: Proc. Roy. Soc., 69, 86 (1901).
[2] Zeit. anorg. Chem., 43, 350 (1907).
[3] Graham: Phil. Trans., 151, 376 (1861).
[4] Bousfield: Jour. Chem. Soc., 107, 1787 (1915).
[5] Poiseuille: Ann. Chim. Phys., 21, 76 (1847).
[6] Chèneveau: Comptes rendus, 155, 154 (1912).

Reyher[1] working at 25° found no indications of negative curvature. This result agrees with that of Bousfield who found that the negative curvature had disappeared at 25°.

### Sulfuric Acid

While the existence of a large number of hydrates of sulfuric acid has been surmised from the properties of its aqueous solution, only the mono-hydrate[2] and the tetra-hydrate[3] have been definitely isolated.

The absolute acid fumes at temperatures above 30° due to a partial dissociation into sulfur trioxide and water.

The viscosities of aqueous solutions of sulfuric acid at 25° have been studied by Dunstan and Wilson.[4] The corrected values[5] are given in Table VIII. They found a maximum viscosity at $H_2SO_4.H_2O$ and a minimum at $H_2SO_4.3H_2O$.

Chèneveau found that a mixture of the composition $H_2SO_4.H_2O$ had a maximum relative viscosity.

Graham measured the transpiration times of mixtures of sulfuric acid and water. Unfortunately he saw no necessity at the time of giving the same amount of detail as in the case of nitric acid, so his results cannot be recalculated in terms of absolute values. The mixture displaying maximum transpiration time contained 17.5% $H_2O$, closely corresponding to the compound $H_2SO_4.H_2O$ (18.36% $H_2O$).

### Mixtures of Nitric and Sulfuric Acids

Saposchnikow[6] found that for mixtures of ninety-nine percent nitric acid with absolute sulfuric acid the vapor pressure followed the law of Henry, being proportional to the

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[1] Reyher: Zeit. phys. Chem., **2**, 744 (1888).

[2] Roscoe and Schorlemmer: "Treatise on Chemistry," 5th Ed., Vol. I, p. 441.

[3] Pickering: Jour. Chem. Soc., **57**, 339 (1890).

[4] Dunstan and Wilson: Ibid., **91**, 85 (1907).

[5] Dunstan: Proc. Chem. Soc., **30**, 104 (1914).

[6] Saposchnikow: Zeit. phys. Chem., **49**, 697 (1904).

amount of nitric acid present over a wide range of concentration. This seemed to him to indicate the absence of solvation. When over seventy percent nitric acid was present in the mixtures, the vapor pressure fell below that calculated from Henry's law. This was ascribed to a decomposition of the nitric acid into nitrogen pentoxide and water. Further evidence of such dehydration of the nitric acid was obtained from the density curves which showed a maximum at about ninety percent sulfuric. The same conclusion was also supported by a study of the nitrogen content of the vapor phase, which in mixtures containing a large excess of sulfuric acid rose above 22.2 percent (the nitrogen content of nitric acid). The conductivity curve of the same mixtures showed that the effect of adding a small amount of the ninety-nine percent nitric to sulfuric acid was to raise the specific conductivity very rapidly and in a manner similar to that of a small addition of water.

### Ternary Mixtures of Nitric Acid, Sulfuric Acid, and Water

Saposchnikow showed that the effect of adding sulfuric acid to nitric acids of the specific gravities 1.48[1] and 1.40[2] was to raise the vapor pressure until, with increasing concentration of sulfuric acid, a maximum of vapor pressure was reached. This he interpreted as due to the sulfuric acid attracting the water combined with the nitric acid and thereby increasing the concentration of free nitric acid molecules. The density curves of mixtures of the above acids with sulfuric acid displayed a maximum density around ninety percent sulfuric, ascribed, as before, to a partial dehydration of the nitric acid. When the sulfuric acid was present in large excess, the vapor phase for the mixture contained a larger amount of nitrogen than corresponded to absolute nitric acid.

Saposchnikow's conclusion, that sulfuric acid when added to a solution of nitric acid is hydrated and produces an increased concentration of free nitric acid molecules, was sup-

[1] Saposchnikow: Zeit. phys. Chem., **51**, 609 (1905).
[2] Saposchnikow: Ibid., **53**, 225 (1905).

ported by the work of Pascal and Garnier[1] on the distillation of such mixtures. On the other hand, Berl and Samtleben[2] in a similar study obtained fundamentally different boiling point and vapor composition curves and concluded that for ternary mixtures with over 32% water, there was no evidence of any water binding action of the sulfuric acid at the boiling point.

## Experimental Details

Two viscometers of the variable pressure type described by Bingham[3] were used, the one (No. 6) for all mixtures having a viscosity in excess of four centipoises, the other (No. 5) for those of lower viscosity. Two bottles containing phosphorus pentoxide were placed in the pressure lines so that only dry air could come in contact with the acid mixtures in the viscometer.

The specific gravities of the more fluid mixtures were measured in a pycnometer of the type described by Bingham, Van Klooster, and Kleinspehn.[4] For the more viscous mixtures which could not be introduced into this instrument, a pycnometer of the Ostwald-Sprengel type was used.

The viscosities were calculated by use of the formula $\eta = CPt - C'\rho/t$, where $C$ and $C'$ are constants of the instrument, $P$ is the corrected pressure, $\rho$ the density of the liquid, and $t$ the time.

The constant for viscometer No. 5 was determined as $1.473 \times 10^{-7}$ by calibration with water distilled first over acid permanganate, and then over alkaline permanganate. The constant for viscometer No. 6 had been determined by Mr. Hyden, as $0.7954 \times 10^{-5}$, by measuring the time of flow of linseed oil in a viscometer previously calibrated with water,

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[1] P. Pascal and Garnier: Ann. Chim., **15**, 253 (1921). See Chem. and Met., **27**, 1025 (1922) for an English translation by Dr. F. C. Zeisberg.

[2] E. Berl and Samtleben: Zeit. angew. Chem., **35**, 206 (1922). See Chem. and Met., **25**, 1103, 1145 (1921) for English translation by Dr. F. C. Zeisberg.

[3] Bulletin **298**, Bureau of Standards.

[4] Bingham, Van Klooster, and Kleinspehn: Jour. Phys. Chem., **24**, 1 (1920).

and then using this linseed oil as a calibrating fluid. His values were checked by calibration with aniline freshly distilled from metallic sodium.

## PREPARATION OF MATERIALS

### Nitric Acid

Nitric acid of less than seventy percent $HNO_3$ was prepared by distillation of Baker and Adamson purest nitric acid under diminished pressure, the receiver being cooled by ice. The distilling apparatus was constructed entirely of glass, and was made by sealing off the neck of one Pyrex distilling flask, and then connecting the side arm *A* (Figure 1) of this flask to the constricted neck of a similar Pyrex flask.

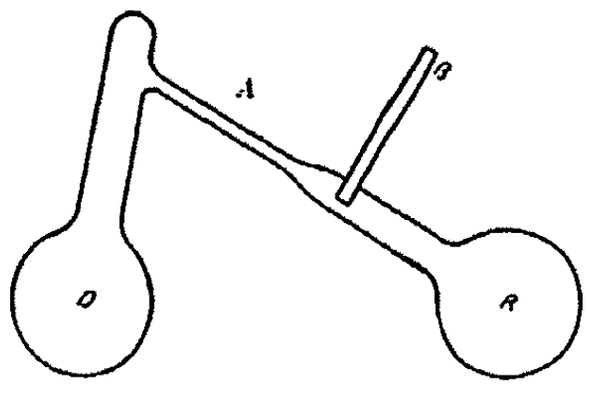



Fig. 1

Liquids were introduced at the side arm *B* and by tilting the apparatus were placed in the distilling end *D* without coming in contact with the receiving end *R*. Rejecting the first and second twenty-five cubic centimeters of distillate, served to wash out any few drops of the original liquid present in *R*. By elevating *R* the distillate was readily removed without contamination from any of the liquid in *D*. After introduction of the liquid into *D*, suction was applied at *B* by means of a water pump, the distilling end *D* placed in a water bath and *R* cooled by ice.

One distillation after rejecting the first and last fractions gave an acid of about 70% $HNO_3$ which contained from nil to 0.00002% nitrogen dioxide from nil to 0.000004% sulfuric acid, and from nil to 0.000003% hydrochloric acid.

For the concentrated nitric acid, Baker and Adamson's purest nitric acid was mixed with an equal weight of sulfuric acid and distilled in the above-described apparatus. The product obtained was mixed with an equal weight of sulfuric acid and then redistilled. The distillate after standing over

barium nitrate and silver nitrate was again distilled. The final product had a slight yellow tinge and became distinctly yellow on dilution with concentrated sulfuric acid. It analyzed 99.2% $HNO_3$, 0.07% $NO_2$ with no traces of sulfuric or hydrochloric acid.

### Sulfuric Acid

Sulfuric acid was prepared by distillation of Baker and Adamson's C. P. sulfuric acid. One distillation gave an acid

TABLE I

Fluidities of Mixtures of Nitric Acid and Water at 10°

| % $HNO_3$ from | | Mean | Vol. % $HNO_3$ | Po gr/cm² | P gr/cm² | Time sec. | $\rho^{10}/_4$ | $\eta$ centi-poises | $\varphi$ abso-lute |
|---|---|---|---|---|---|---|---|---|---|
| Anal-ysis | Density | | | | | | | | |
| 99.24 | 100.00* | 99.19 | 98.77 | 126.85 | 126.39 | 574.6 | 1.5306 | 1.0697 | 93.48 |
| 99.13 | —— | —— | —— | 127.25 | 126.79 | 573.4 | —— | 1.0709 | 93.38 |
| 88.32 | 88.68* | 88.34 | 83.20 | 187.26 | 186.68 | 650.9 | 1.4958 | 1.7898 | 55.87 |
| 88.36 | —— | —— | —— | 187.30 | 186.72 | 651.5 | —— | 1.7918 | 55.81 |
| —— | —— | —— | —— | 187.68 | 187.10 | 649.4 | —— | 1.7897 | 55.88 |
| 77.25 | 77.96* | 77.24 | 68.92 | 198.04 | 197.71 | 854.0 | 1.4612 | 2.4870 | 40.21 |
| 77.23 | —— | —— | —— | 198.47 | 198.14 | 853.0 | —— | 2.4895 | 40.17 |
| 69.84 | 70.03 | 69.86 | 60.23 | 216.82 | 216.45 | 818.3 | 1.4275 | 2.609 | 38.33 |
| 69.89 | 69.60 | —— | —— | 217.22 | 216.89 | 817.3 | —— | 2.611 | 38.30 |
| 62.61 | —— | 62.66 | 52.30 | 216.70 | 216.36 | 830.6 | —— | 2.647 | 37.78 |
| 62.60 | —— | —— | —— | 217.08 | 216.76 | 828.1 | —— | 2.644 | 37.82 |
| 52.10 | 52.19 | 52.13 | 41.57 | 216.96 | 216.57 | 749.2 | 1.3339 | 2.390 | 41.84 |
| 52.19 | —— | —— | —— | 217.30 | 216.86 | 748.2 | —— | 2.390 | 41.84 |
| 38.07 | 38.00 | 38.05 | 28.64 | 216.87 | 216.32 | 578.1 | 1.2427 | 1.842 | 54.29 |
| 38.01 | —— | —— | —— | 217.19 | 216.47 | 578.0 | —— | 1.843 | 54.23 |
| 25.28 | 25.31 | 25.28 | 18.10 | 216.85 | 216.03 | 471.4 | 1.1555 | 1.500 | 66.67 |
| 25.29 | —— | —— | —— | 217.15 | 216.29 | 470.2 | —— | 1.498 | 66.76 |
| 12.66 | 12.65 | 12.65 | 8.65 | 216.66 | 215.64 | 418.4 | 1.0739 | 1.329 | 75.24 |
| 12.63 | —— | —— | —— | 216.94 | 215.90 | 417.9 | —— | 1.329 | 75.24 |

The mean values in Column three are the mean of the analytical values, and of all the values obtained from the density determinations.

The values marked with an asterisk were not used in calculating the mean composition, because the densities observed were known to be too high due to the absorption of water by the acid in the pycnometer.

The volume percentages were calculated from the mean weight percent.

which contained about 98% sulfuric acid, 0.0001% iron, no trace of hydrochloric acid and 0.00011% lead sulfate.

The anhydrous sulfuric acid was made by dissolving sulfur trioxide fumes (obtained by heating oleum) in the pure sulfuric acid previously prepared. The excess of sulfuric acid anhydride was removed by dilution with sulfuric acid.

## Analytical Methods

The compositions of the nitric acid-water mixtures were determined by titration with barium hydroxide solution, and then compared with the values obtained by interpolation from the density tables of Veley and Manley, and Lunge and Rey.[1] The mixtures of sulfuric acid and water were titrated with sodium hydroxide solution, and the values obtained compared with those interpolated from the density table of Domke.[1]

TABLE II

Fluidities of Mixtures of Nitric Acid and Water at 20°

| % $HNO_3$ from | | Mean | Vol. per-cent | Po gr/cm² | P | Time sec. | $\rho^{20}/_4$ | $\eta$ centi-poises | $\varphi$ abso-lute |
|---|---|---|---|---|---|---|---|---|---|
| Anal-ysis | Density | | | | | | | | |
| 99.24 | 100.00* | 99.19 | 98.78 | 126.88 | 125.85 | 492.7 | 1.5108 | 0.9133 | 109.5 |
| 99.13 | —— | —— | —— | 127.29 | 126.26 | 491.1 | —— | 0.9133 | 109.5 |
| 88.32 | 88.79* | 88.34 | 83.36 | 187.31 | 186.44 | 528.7 | 1.4793 | 1.4519 | 68.88 |
| 88.36 | —— | —— | —— | 187.69 | 186.82 | 527.3 | —— | 1.4510 | 68.92 |
| 77.25 | 77.93* | 77.24 | 69.16 | 198.07 | 197.56 | 671.0 | 1.4451 | 1.9524 | 51.22 |
| 77.23 | —— | —— | —— | 198.45 | 197.91 | 669.8 | —— | 1.9626 | 51.21 |
| 69.84 | 69.94 | 69.86 | 60.51 | 216.84 | 216.23 | 640.2 | 1.4131 | 2.039 | 49.04 |
| 69.89 | 69.92 | —— | —— | 217.21 | 216.68 | 640.1 | —— | 2.043 | 48.95 |
| 52.10 | 52.03 | 52.13 | 41.86 | 216.90 | 216.31 | 591.0 | 1.3222 | 1.883 | 53.11 |
| 52.19 | ——* | —— | —— | 217.24 | 216.56 | 590.0 | —— | 1.882 | 53.13 |
| 38.07 | 38.14 | 38.05 | 28.88 | 217.17 | 216.31 | 473.6 | 1.2337 | 1.509 | 66.27 |
| 38.01 | —— | —— | —— | 216.85 | 215.90 | 474.5 | —— | 1.509 | 66.27 |
| 25.28 | 25.26 | 25.28 | 18.28 | 216.85 | 215.27 | 381.6 | 1.1492 | 1.210 | 82.64 |
| 25.29 | —— | —— | —— | 217.15 | 215.61 | 381.0 | —— | 1.210 | 82.64 |
| 12.66 | —— | 12.65 | 8.74 | 216.64 | 215.11 | 333.6 | 1.0698 | 1.057 | 94.61 |
| 12.63 | —— | —— | —— | 216.92 | 215.31 | 333.6 | —— | 1.058 | 94.52 |
| —— | —— | —— | —— | 216.64 | 215.05 | 334.0 | —— | 1.058 | 94.52 |

[1] Landolt and Börnstein's Tabellen, 3d edition.

The average of the values obtained by analysis, and from the density determinations, was taken as the composition of the mixture.

For the ternary mixtures, about one gram of the acid mixture was weighed in a sixty $cm^3$ glass-stoppered flask, and titrated with sodium hydroxide using phenolphthalein as indicator. The sulfuric was estimated by precipitation with barium chloride on the same sample. The average of two determinations was taken as the composition.

### Mixtures of Nitric Acid and Water

Tables I, II, and III give the experimental data for mixtures of nitric acid with water, the results being shown graphically in Figure 2. The mean values in Column three are

TABLE III

Fluidities of Mixtures of Nitric Acid and Water at 40°

| Mean % $HNO_3$ | Vol. % $HNO_3$ | Po gr/$cm^2$ | P gr/$cm^2$ | Time sec. | $\rho^{40}/_4$ | $\eta$ centipoises | $\varphi$ absolute |
|---|---|---|---|---|---|---|---|
| 99.19 | 98.80 | 126.93 | 125.22 | 378.6 | —— | 0.6983 | 143.2 |
| —— | —— | 127.31 | 125.59 | 377.7 | —— | 0.6987 | 143.1 |
| 88.34 | 83.56 | 187.31 | 185.62 | 375.0 | 1.4468 | 1.0253 | 97.53 |
| —— | —— | 187.69 | 185.98 | 374.2 | —— | 1.0251 | 97.55 |
| —— | —— | 187.31 | 185.62 | 374.6 | —— | 1.0242 | 97.64 |
| 77.24 | 69.48 | 198.21 | 197.06 | 452.0 | —— | 1.3120 | 76.22 |
| —— | —— | 197.57 | 197.42 | 451.0 | —— | 1.3115 | 76.25 |
| 69.86 | 60.86 | 216.80 | 215.59 | 427.0 | 1.3835 | 1.356 | 73.75 |
| —— | —— | 217.16 | 215.91 | 427.0 | —— | 1.358 | 73.64 |
| 62.66 | 52.96 | 216.91 | 215.69 | 430.9 | 1.3480 | 1.369 | 73.05 |
| —— | —— | 217.27 | 216.01 | 430.9 | —— | 1.371 | 72.94 |
| 52.13 | 42.22 | 216.87 | 215.57 | 405.0 | 1.2982 | 1.286 | 77.76 |
| —— | —— | 216.87 | 215.57 | 405.0 | —— | 1.286 | 77.76 |
| 38.05 | 29.18 | 216.81 | 214.86 | 326.4 | —— | 1.033 | 96.81 |
| —— | —— | 216.81 | 214.86 | 326.4 | —— | 1.033 | 96.81 |
| 25.28 | 18.50 | 216.85 | 214.25 | 268.8 | 1.1355 | 0.8483 | 117.9 |
| —— | —— | 217.15 | 214.62 | 268.5 | —— | 0.8488 | 117.8 |
| 12.65 | 8.86 | 216.65 | 213.36 | 230.4 | 1.0603 | 0.7241 | 138.1 |
| —— | | 216.93 | 213.63 | 229.8 | —— | 0.7231 | 138.3 |

No values for the composition of the mixtures as calculated from the densities are given, due to lack of any tables for nitric acid-water mixtures at 40°.

the mean of the analytical results and of the composition as determined from the density at 10° and 20° C. For solutions above seventy percent nitric acid, only the analytical values were used to calculate the mean, as it was found that the densities measured in an Ostwald-Sprengler pycnometer were in error through the absorption of water by the acid in the pycnometer. This source of error was afterwards removed by suitable precautions.

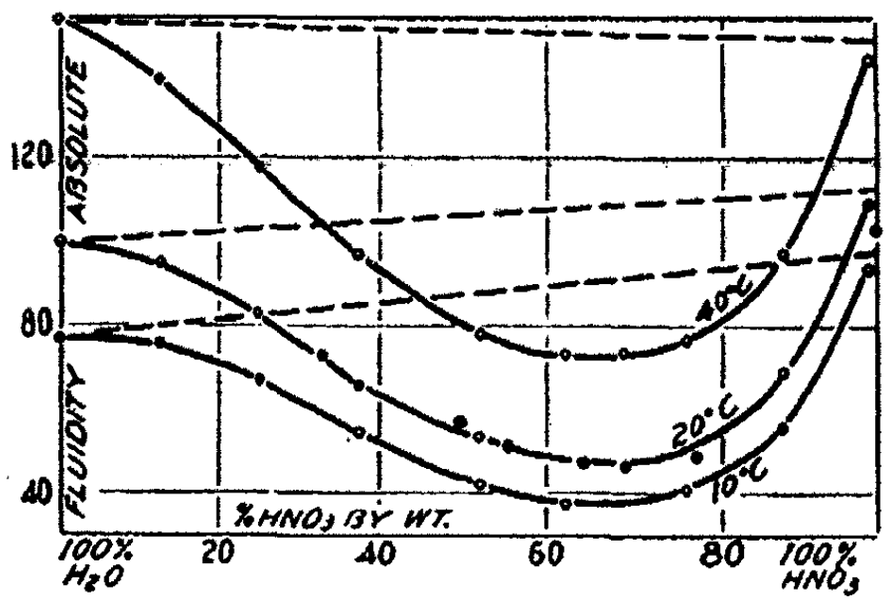



Fig. 2

Fluidity-Weight Concentration Curves for Aqueous Solutions of Nitric Acid

Po is the observed pressure after making certain corrections,[1] P in Column six is the pressure used solely in overcoming viscous resistance,[2] $\rho$ in column eight is the density, $\eta$ is the viscosity in centipoises, and $\varphi$ is the fluidity in absolute units.

The first addition of nitric acid to water depresses the fluidity only very slightly, a so-called "negative viscosity" effect, ascribed to a decomposition of the associated water molecules by the nitric acid.[3] The effect of temperature which gradually eliminates the negative curvature is clearly

[1] Bulletin 278, Bureau of Standards.
[2] "Fluidity and Plasticity," p. 313.
[3] Ibid., p. 184.

seen on comparing the curves for 10°, 20°, and 40° in Figure 2. The disappearance of the negative curvature with increase of temperature is probably due to the smaller association of water at high temperatures. The negative curvature is, as would be expected, more pronounced in very dilute solution, and both Poiseuille[1] and Bousfield[2] found that in dilute solutions of

TABLE IV

Graham's Data[3] for Mixtures of Nitric Acid and Water at 20°

Volume of liquid transpired, V = 8.075 cc
Length of capillary, L = 2.8 cm
Radius of capillary = 0.00471 cm
Time of flow for water under one atmosphere pressure = 348.0 seconds.

By substituting the above values in the equations $C' = \frac{mV}{8l\pi}$ and $C = \frac{\pi g r^4}{8Vl}$ the value of the constants can be obtained, as C′ = 0.1285 and C = 0.00002994/Po
The viscosity of a liquid = CPoT − C′ρ/T, or substituting the values obtained above = 0.00002994T − 0.1285ρ/T

| % $HNO_3$ | Time seconds | ρ | 0.00002994T | $\frac{0.1258\,\rho}{T}$ | η centipoises | φ absolute |
|---|---|---|---|---|---|---|
| 100.00 | 344.5 | 1.5046 | 1.0314 | 0.0561 | 0.9753 | 102.53 |
| 79.6 | 692.0 | 1.4358 | 2.0718 | 0.0267 | 2.0451 | 48.90 |
| 78.6 | 705.0 | —— | 2.1108 | 0.0261 | 2.0847 | 47.97 |
| 76.9 | 712.0 | —— | 2.1317 | 0.0258 | 2.1059 | 47.49 |
| 71.5 | 725.0 | —— | 2.1707 | 0.0248 | 2.1459 | 46.60 |
| 70.0 | 732.0 | —— | 2.1916 | 0.0245 | 2.1671 | 46.14 |
| 66.7 | 728.5 | 1.3816 | 2.1811 | 0.0244 | 2.1567 | 46.37 |
| 64.5 | 718.0 | —— | 2.1497 | 0.0245 | 2.1252 | 47.05 |
| 63.6 | 712.0 | —— | 2.1317 | 0.0246 | 2.1071 | 47.46 |
| 62.5 | 709.5 | 1.3598 | 2.1242 | 0.0246 | 2.1071 | 47.46 |
| 58.8 | 683.0 | 1.3407 | 2.0449 | 0.0252 | 2.0197 | 49.51 |
| 55.5 | 661.0 | 1.3239 | 1.9790 | 0.0257 | 1.9534 | 51.19 |
| 52.6 | 635.5 | —— | 1.9027 | 0.0266 | 1.8761 | 53.30 |
| 50.0 | 593.0 | 1.2943 | 1.7754 | 0.0280 | 1.7474 | 57.23 |
| 33.3 | 472.0 | —— | 1.4132 | 0.0339 | 1.3793 | 72.50 |

[1] Poiseuille: Ann. Chim. Phys., **21**, 76 (1847).
[2] Bousfield: Jour. Chem. Soc., **107**, 1781 (1915).
[3] Graham: "Physical and Chemical Researches;" Phil. Trans., **153**, 373 (1861).

nitric acid the fluidity is raised above that of water. On further addition of acid the fluidity drops to a minimum value. The maximum deviation from a linear fluidity-volume concentration relationship[1] occurs for 40°, 20°, and 10° at 55.5%, 59.0%, and 60.0% nitric acid by volume, respectively, or at 65.0%, 68.5%, and 69.5% by weight. As the composition of the mixture showing maximum deviation from a linear fluidity-volume concentration curve shifts with the temperature, it cannot in this case be used to determine the presence of a hydrate. This, however, is to be expected in view of the negative curvature and of the fact that the acid forms at least two hydrates in aqueous solution.

TABLE V

Fluidities of Mixtures of Sulfuric Acid and Water at 10°

| % $H_2SO_4$ from | | Mean | Vol. % | Po gr/cm² | P gr/cm² | Time seconds | $\rho^{10}/_4$ | $\eta$ cp. | $\varphi$ abs. |
|---|---|---|---|---|---|---|---|---|---|
| Analysis | Density | | | | | | | | |
| 97.70 | —— | 97.73 | 95.91 | 97.49 | 97.48 | 453.6 | 1.8472 | 35.17 | 2.843 |
| 97.77 | —— | —— | —— | 97.13 | 97.10 | 454.7 | —— | 35.12 | 2.847 |
| 87.62 | 87.92 | 87.76 | 79.63 | 75.67 | 75.66 | 650.4 | 1.8126 | 39.14 | 2.555 |
| 87.69 | —— | —— | —— | 75.31 | 75.31 | 653.9 | —— | 39.17 | 2.554 |
| 75.23 | 75.06 | 75.05 | 62.13 | 75.69 | 75.67 | 346.9 | 1.6796 | 20.88 | 4.789 |
| 74.83 | —— | —— | —— | 75.35 | 75.32 | 348.2 | —— | 20.86 | 4.794 |
| 62.67 | 62.65 | 62.67 | 47.80 | 66.22 | 66.13 | 165.0 | 1.5359 | 8.679 | 11.52 |
| 62.85 | —— | —— | —— | 66.22 | 66.13 | 165.4 | —— | 8.700 | 11.49 |
| —— | —— | —— | —— | 66.52 | 66.43 | 164.5 | —— | 8.692 | 11.50 |
| 50.03 | 49.80 | 49.98 | 35.27 | 212.96 | 212.88 | 1561.1 | 1.4010 | 4.895 | 20.43 |
| 50.07 | —— | —— | —— | 213.30 | 213.20 | 1558.1 | —— | 4.893 | 20.44 |
| 37.86 | 37.79 | 37.81 | 24.90 | 199.10 | 198.95 | 1085.2 | 1.2911 | 3.180 | 31.45 |
| 37.80 | —— | —— | —— | 199.14 | 199.28 | 1084.4 | —— | 3.183 | 31.42 |
| 25.10 | 25.15 | 25.11 | 15.46 | 199.05 | 198.69 | 777.7 | 1.1860 | 2.276 | 43.94 |
| 25.05 | —— | —— | —— | 199.35 | 198.99 | 776.5 | —— | 2.276 | 43.94 |
| 11.76 | 11.69 | 11.72 | 6.75 | 199.43 | 198.98 | 615.5 | 1.0823 | 1.804 | 55.43 |
| 11.75 | —— | —— | —— | 199.15 | 198.69 | 616.7 | —— | 1.805 | 55.40 |
| —— | —— | —— | —— | 199.43 | 198.98 | 615.5 | —— | 1.804 | 55.43 |

Although the correction for kinetic energy in Graham's determinations amounts to about five percent, his values

[1] "Fluidity and Plasticity," p. 172.

given in Table IV and plotted as black dots in Figure 2, agree fairly with ours, except for the pure acid. But as he took no precaution against the absorption of water by his highly concentrated acid, his value for the absolute nitric acid, which is stated to be as hygroscopic as sulfuric acid, is probably too low.

TABLE VI

Fluidities of Mixtures of Sulfuric Acid and Water at 20°

| % $H_2SO_4$ from | | Mean | Vol. % | Po gr/cm² | P gr/cm² | Time seconds | $\rho^{20}/_4$ | $\eta$ cp. | $\varphi$ abs. |
|---|---|---|---|---|---|---|---|---|---|
| Analysis | Density | | | | | | | | |
| 97.70 | —— | 97.73 | 95.91 | 97.48 | 97.47 | 312.4 | 1.8370 | 24.22 | 4.129 |
| 97.77 | —— | —— | —— | 97.13 | 97.10 | 314.1 | —— | 24.26 | 4.122 |
| 87.62 | 87.80 | 87.76 | 79.63 | 75.68 | 75.67 | 430.0 | 1.8008 | 25.88 | 3.864 |
| 87.69 | —— | —— | —— | 75.32 | 75.31 | 432.2 | —— | 25.89 | 3.863 |
| 75.23 | 75.06 | 75.05 | 62.13 | 75.70 | 75.67 | 246.4 | 1.6699 | 14.83 | 6.743 |
| 74.83 | —— | —— | —— | 75.36 | 75.33 | 247.5 | —— | 14.83 | 6.743 |
| 62.67 | 62.59 | 62.67 | 47.80 | 66.52 | 66.37 | 125.1 | 1.5265 | 6.604 | 15.14 |
| 62.85 | —— | —— | —— | 66.22 | 66.07 | 126.1 | —— | 6.627 | 15.09 |
| —— | —— | —— | —— | 66.52 | 66.37 | 125.4 | —— | 6.620 | 15.10 |
| —— | —— | —— | —— | 66.22 | 66.07 | 125.8 | —— | 6.611 | 15.13 |
| 50.03 | 50.00 | 49.98 | 35.27 | 212.95 | 212.80 | 1212.0 | 1.3951 | 3.779 | 26.32 |
| 50.07 | —— | —— | —— | 213.29 | 213.12 | 1210.5 | —— | 3.800 | 26.32 |
| 37.86 | 37.80 | 37.81 | 24.90 | 199.09 | 198.83 | 861.8 | 1.2837 | 2.524 | 39.62 |
| 37.80 | —— | —— | —— | 199.43 | 199.12 | 860.9 | —— | 2.525 | 39.60 |
| 25.10 | 25.14 | 25.11 | 15.46 | 198.98 | 198.40 | 598.5 | 1.1794 | 1.749 | 57.18 |
| 25.05 | —— | —— | —— | 199.31 | 198.76 | 597.4 | —— | 1.749 | 57.18 |
| 11.76 | 11.71 | 11.72 | 6.75 | 199.40 | 198.61 | 484.7 | 1.0782 | 1.418 | 70.52 |
| 11.75 | —— | —— | —— | 199.12 | 198.39 | 484.9 | —— | 1.417 | 70.57 |

### Mixtures of Sulfuric Acid and Water

Figure 3 gives the fluidity-weight concentration curve for mixtures of sulfuric acid and water. The black dots in Figure 3 represent the data of Dunstan and Wilson for 25°, which are given in Table VIII. The data for our curves are given in Tables V, VI, and VII.

The first addition of sulfuric acid sharply depresses the fluidity, due probably to the formation of a viscous hydrate. The fluidity of the water, on addition of 11% $H_2SO_4$, is depressed

27%, 29%, and 32% at 10°, 20°, and 40°, respectively. On further addition of sulfuric acid the fluidity drops steadily until a concentration of about 85 percent acid is reached, when further addition of acid has little effect.

Dunstan and Wilson's observations at 25° display the same characteristics as our curves, and show the same rapid decrease in fluidity on the first addition of acid. Their curve has a

TABLE VII

Fluidities of Mixtures of Sulfuric Acid and Water at 40°

| % $H_2SO_4$ from | | Mean | Vol. % | Po gr/cm² | P gr/cm² | Time sec. | $\rho^{40}/_4$ | $\eta$ cp. | $\varphi$ abs. |
|---|---|---|---|---|---|---|---|---|---|
| Analysis | Density | | | | | | | | |
| 97.70 | —— | 97.73 | 95.93 | 97.48 | 97.34 | 168.8 | 1.8170 | 13.07 | 7.651 |
| 97.77 | —— | —— | —— | 97.12 | 97.00 | 169.4 | —— | 13.07 | 7.651 |
| 87.62 | 87.75 | 87.76 | 79.71 | 75.67 | 75.62 | 219.8 | 1.7791 | 13.22 | 7.564 |
| 87.69 | —— | —— | —— | 75.31 | 75.27 | 220.8 | —— | 13.22 | 7.564 |
| 75.23 | 75.05 | 75.05 | 62.24 | 75.68 | 75.54 | 140.2 | 1.6509 | 8.424 | 11.87 |
| 74.83 | —— | —— | —— | 75.34 | 75.20 | 140.7 | —— | 8.416 | 11.88 |
| 62.67 | 62.61 | 62.67 | 47.92 | 54.29 | 54.04 | 98.4 | 1.5099 | 4.230 | 23.64 |
| 62.85 | —— | —— | —— | 54.59 | 54.34 | 97.7 | —— | 4.223 | 23.68 |
| —— | —— | —— | —— | 54.59 | 54.34 | 97.7 | —— | 4.223 | 23.68 |
| —— | —— | —— | —— | 54.29 | 54.04 | 98.4 | —— | 4.230 | 23.64 |
| 50.03 | 50.01 | 49.98 | 35.38 | 213.30 | 213.02 | 795.5 | 1.3796 | 2.496 | 40.06 |
| 50.07 | —— | —— | —— | 212.94 | 212.66 | 796.5 | —— | 2.495 | 40.08 |
| 37.86 | 37.81 | 37.81 | 24.99 | 199.06 | 198.37 | 564.7 | 1.2691 | 1.650 | 60.61 |
| 37.80 | —— | —— | —— | 199.38 | 198.78 | 563.2 | —— | 1.649 | 60.64 |
| 25.10 | 25.13 | 25.11 | 15.52 | 199.00 | 197.69 | 391.5 | 1.1663 | 1.140 | 87.72 |
| 25.05 | —— | —— | —— | 199.30 | 197.97 | 390.6 | —— | 1.139 | 87.80 |
| 11.76 | 11.71 | 11.72 | 6.78 | 199.36 | 197.65 | 332.5 | 1.0685 | 0.968 | 103.3 |
| 11.75 | —— | —— | —— | 199.37 | 197.80 | 331.9 | —— | 0.967 | 103.4 |

maximum at 93 percent of sulfuric acid by weight in a region where our observed values are too far apart to detect such a change.

### Mixtures of Nitric Acid and Sulfuric Acid

Figure 4 shows the fluidity-weight concentration curves for mixtures of nitric acid and sulfuric acid, for 40°, 20°, and 10°. The experimental data are scattered throughout Tables X to

TABLE VIII

Data of Dunstan and Wilson for Aqueous Solutions of Sulfuric Acid at 25°

| % $H_2SO_4$ | $\rho$ | $\eta$*cp. | $\varphi$ corrected + |
|---|---|---|---|
| 99.21 | 1.827 | 1.0616 | 4.05 |
| 97.51 | 1.832 | 0.85761 | 5.01 |
| 95.72 | 1.829 | 0.83255 | 5.17 |
| 93.41 | 1.823 | 0.84211 | 5.11 |
| 92.30 | 1.819 | 0.85088 | 5.05 |
| 91.36 | 1.815 | 0.87158 | 4.93 |
| 90.44 | 1.810 | 0.88508 | 4.86 |
| 89.57 | 1.805 | 0.95132 | 4.52 |
| 88.73 | 1.799 | 0.91588 | 4.70 |
| 88.00 | 1.795 | 0.92568 | 4.65 |
| 86.87 | 1.786 | 0.93366 | 4.61 |
| 86.98 | 1.787 | 0.93527 | 4.60 |
| 85.07 | 1.772 | 0.94794 | 4.54 |
| 84.97 | 1.770 | 0.92966 | 4.63 |
| 84.28 | 1.765 | 0.92529 | 4.63 |
| 83.98 | 1.761 | 0.91010 | 4.73 |
| 83.40 | 1.756 | 0.90866 | 4.73 |
| 82.58 | 1.747 | 0.89842 | 4.79 |
| 82.21 | 1.744 | 0.86571 | 4.97 |
| 81.54 | 1.737 | 0.83108 | 5.18 |
| 81.09 | 1.732 | 0.83452 | 5.15 |
| 80.24 | 1.723 | 0.78099 | 5.51 |
| 79.84 | 1.718 | 0.60272 | 7.14 |
| 79.53 | 1.715 | 0.74084 | 5.81 |
| 78.24 | 1.700 | 0.67228 | 6.40 |
| 76.27 | 1.677 | 0.57396 | 7.49 |
| 74.75 | 1.660 | 0.53603 | 8.02 |
| 70.52 | 1.610 | 0.40095 | 10.73 |
| 69.20 | 1.595 | 0.36450 | 11.80 |
| 67.21 | 1.572 | 0.32322 | 13.31 |
| 64.64 | 1.543 | 0.28042 | 15.34 |
| 58.36 | 1.475 | 0.20568 | 20.91 |
| 51.64 | 1.406 | 0.15370 | 27.98 |
| 49.86 | 1.388 | 0.14706 | 29.25 |
| 43.23 | 1.327 | 0.11293 | 38.09 |
| 36.43 | 1.267 | 0.09239 | 46.55 |
| 26.49 | 1.186 | 0.07119 | 60.42 |
| 15.70 | 1.104 | 0.05851 | 75.31 |
| 0.00 | 0.997 | 0.00891 | 112.2 |

* Dunstan and Wilson: Jour. Chem. Soc., **91**, 85 (1907).

+ Dunstan and Wilson: Proc. Chem. Soc., **30**, 104 (1914).

XII. Table IX gives the values obtained after allowing for the effect of the water present in the mixtures. The method of calculation is explained in the next section.

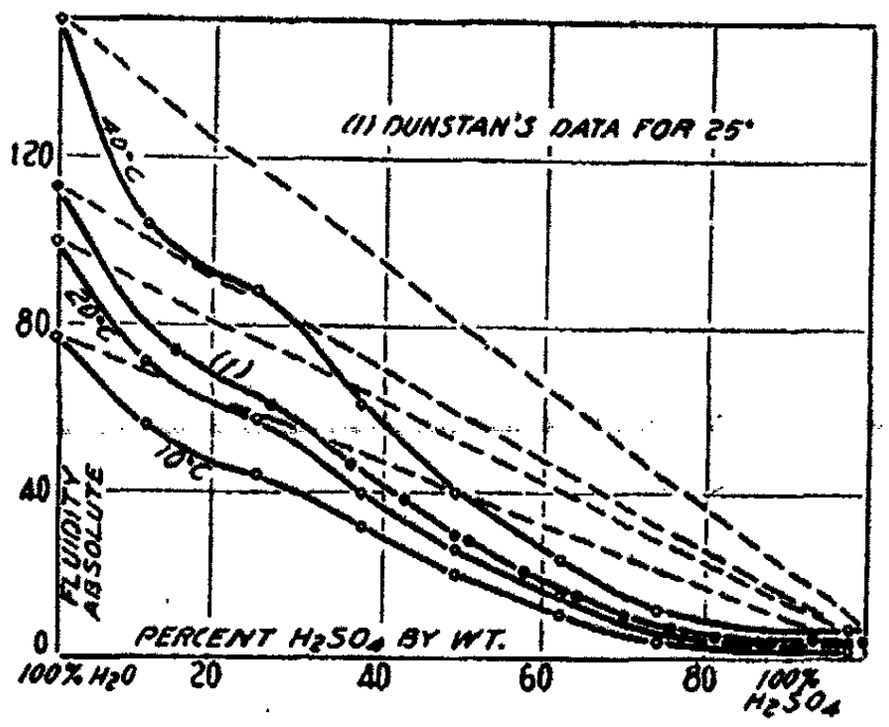



Fig. 3

Fluidity-Weight Concentration Curves for Aqueous Solutions of Sulfuric Acid

The first addition of nitric acid to the absolute sulfuric acid causes a slight decrease in fluidity, but the nitric acid has little effect on the fluidity until over 30 percent has been added,

TABLE IX

Fluidities of Mixtures of Sulfuric Acid and Nitric Acids

| % $HNO_3$ | % $H_2SO_4$ | Volume percent $HNO_3$ | 10° $\varphi$ abs. | Volume percent $HNO_3$ | 20° $\varphi$ abs. | Volume percent $HNO_3$ | 40° $\varphi$ abs. |
|---|---|---|---|---|---|---|---|
| 100.0 | 0.00 | 100.0 | 96.40 | 100.0 | 113.9 | 100.0 | 147.1 |
| 87.50 | 12.50 | 89.39 | 41.40 | 89.46 | 52.35 | 89.55 | 75.80 |
| 75.00 | 25.00 | 78.31 | 29.25 | 78.45 | 37.90 | 78.60 | 59.20 |
| 62.50 | 37.50 | 66.73 | 7.75 | 66.89 | 11.55 | 67.11 | 20.10 |
| 50.00 | 50.00 | 54.61 | 5.40 | 54.80 | 8.25 | 55.05 | 15.05 |
| 37.50 | 62.50 | 41.93 | 2.60 | 42.11 | 3.70 | 42.35 | 8.35 |
| 25.00 | 75.00 | 28.63 | 1.80 | 28.77 | 2.85 | 28.98 | 6.30 |
| 12.50 | 87.50 | 14.67 | 1.55 | 14.76 | 2.55 | 14.88 | 5.45 |
| 0.00 | 100.0 | 0.00 | 3.00 | 0.00 | 4.50 | 0.00 | 7.90 |

when further increases in the percentage of nitric acid rapidly increase the fluidity. In view of the wide difference in the fluidities of the components, the fact that the addition of 30

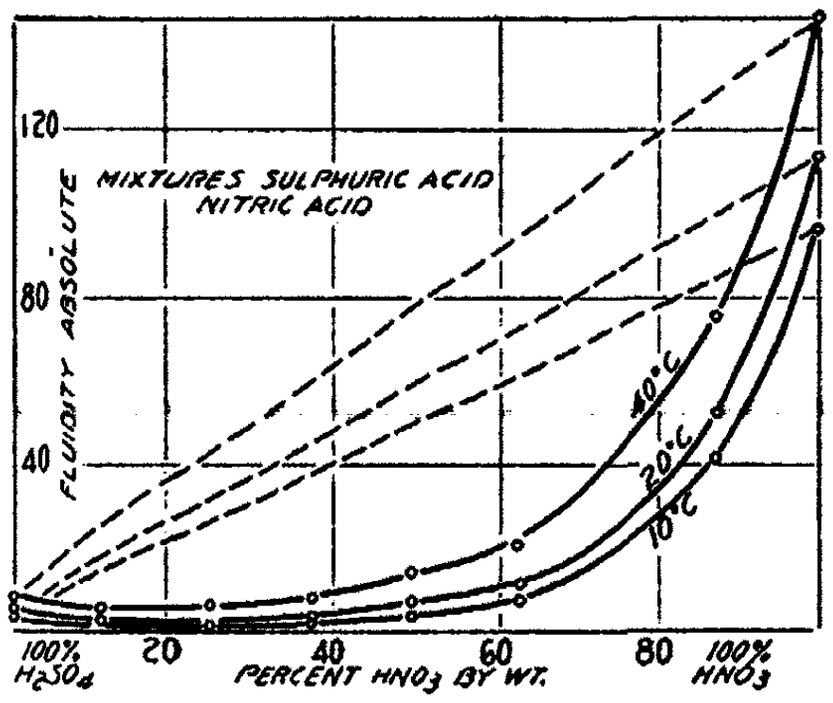



Fig. 4

Fluidity-Weight Concentration Curve for Mixtures of Nitric and Sulfuric Acids

TABLE X

Fluidities of Ternary Mixtures at 10°

| % $HNO_3$ | % $H_2SO_4$ | Mean % $HNO_3$ | % $H_2SO_4$ | Po gr/cm² | P gr/cm² | Time seconds | $\rho^{10}/_4$ | $\eta$ cp. | $\varphi$ abs. |
|---|---|---|---|---|---|---|---|---|---|
| 10.42 | 13.47 | 10.46 | 13.44 | 273.33 | 272.30 | 448.4 | 1.1623 | 1.7985 | 55.60 |
| 10.49 | 13.40 | —— | —— | 273.63 | 273.61 | 448.0 | —— | 1.7989 | 55.59 |
| 12.58 | —— | 12.56 | 21.41 | 273.52 | 272.97 | 607.6 | 1.2401 | 2.4430 | 40.93 |
| 12.53 | 21.41 | —— | —— | 273.52 | 272.99 | 607.2 | —— | 2.4414 | 40.96 |
| 12.97 | 40.41 | 12.97 | 40.40 | 273.39 | 272.36 | 1207.4 | 1.4126 | 3.7437 | 20.58 |
| 12.97 | 40.40 | —— | —— | 273.75 | 273.53 | 1206.6 | —— | 3.7446 | 20.57 |
| 12.62 | —— | 12.61 | 48.64 | 272.99 | 272.92 | 1811.6 | 1.4910 | 7.2827 | 13.73 |
| 12.60 | 48.64 | —— | —— | 273.77 | 273.70 | 1804.4 | —— | 7.2745 | 13.75 |
| 12.39 | 61.59 | 12.51 | 61.54 | 93.84 | 93.82 | 215.8 | 1.6365 | 16.098 | 6.212 |
| 12.62 | 61.48 | —— | —— | 93.52 | 93.46 | 216.2 | —— | 16.073 | 6.222 |
| 11.96 | 73.00 | 11.93 | 73.04 | 101.98 | 101.96 | 371.7 | 1.7456 | 30.144 | 3.317 |
| 11.89 | 73.08 | —— | —— | 101.64 | 101.62 | 373.0 | —— | 30.149 | 3.317 |
| 12.19 | 87.80 | 12.24 | 87.79 | 126.39 | 126.37 | 635.0 | 1.8931 | 6.383 | 1.567 |
| 12.18 | 87.78 | —— | —— | 126.06 | 126.00 | 635.9 | —— | 6.373 | 1.569 |

TABLE XI

Fluidities of Ternary Mixtures at 20°

| Mean % $HNO_3$ | % $H_2SO_4$ | Po | P | Time seconds | $\rho^{20}/_4$ | $\eta$ cp. | $\varphi$ abs. |
|---|---|---|---|---|---|---|---|
| 10.46 | 13.44 | 273.30 | 271.75 | 351.8 | 1.1560 | 1.4082 | 71.01 |
| —— | —— | 273.60 | 272.06 | 351.6 | —— | 1.4090 | 70.97 |
| 12.56 | 21.41 | 273.52 | 272.63 | 478.0 | 1.2326 | 1.9195 | 52.10 |
| —— | —— | 273.52 | 272.62 | 478.1 | —— | 1.9199 | 52.09 |
| 12.97 | 40.40 | 273.38 | 273.11 | 930.6 | 1.4035 | 3.7437 | 26.71 |
| —— | —— | 273.74 | 273.47 | 929.6 | —— | 3.7446 | 26.71 |
| 12.61 | 48.64 | 273.67 | 273.54 | 1363.7 | 1.4814 | 5.4946 | 18.20 |
| —— | —— | 273.29 | 273.16 | 1366.8 | —— | 5.4994 | 18.18 |
| 12.51 | 61.54 | 74.91 | 74.84 | 194.2 | —— | 11.560 | 8.650 |
| —— | —— | 74.59 | 74.52 | 195.2 | —— | 11.570 | 8.643 |
| 11.93 | 73.04 | 101.72 | 101.67 | 246.7 | 1.7341 | 19.950 | 5.012 |
| —— | —— | 102.07 | 102.01 | 246.0 | —— | 19.961 | 5.010 |
| 12.24 | 87.79 | 126.41 | 126.38 | 399.2 | 1.8778 | 40.13 | 2.492 |
| —— | —— | 126.03 | 126.00 | 400.1 | —— | 40.10 | 2.494 |

TABLE XII

Fluidities of Ternary Mixtures at 40°

| Mean % $HNO_3$ | % $H_2SO_4$ | Po gr/cm² | P gr/cm² | Time seconds | $\rho^{40}/_4$ | $\eta$ cp. | $\varphi$ abs. |
|---|---|---|---|---|---|---|---|
| 10.46 | 13.44 | 273.25 | 269.98 | 240.7 | 1.1433 | 0.9572 | 104.47 |
| —— | —— | 273.60 | 270.32 | 240.0 | —— | 0.9556 | 104.65 |
| 12.56 | 21.41 | 273.50 | 271.60 | 325.2 | 1.2179 | 1.3010 | 73.66 |
| —— | —— | 273.46 | 271.56 | 325.2 | —— | 1.3008 | 73.88 |
| 12.97 | 40.40 | 273.40 | 272.77 | 604.9 | 1.3854 | 2.4304 | 41.15 |
| —— | —— | 273.76 | 273.13 | 604.0 | —— | 2.4300 | 41.15 |
| 12.61 | 48.64 | 273.35 | 273.03 | 863.5 | 1.4628 | 3.4727 | 28.80 |
| —— | —— | 273.73 | 273.42 | 863.3 | —— | 3.4768 | 28.76 |
| 12.51 | 61.54 | 74.59 | 74.39 | 113.6 | 1.6052 | 6.7219 | 14.88 |
| —— | —— | 74.91 | 74.72 | 113.0 | —— | 6.7162 | 14.89 |
| —— | —— | 74.59 | 74.39 | 113.5 | —— | 6.7159 | 14.89 |
| 11.93 | 73.04 | 69.71 | 69.63 | 184.9 | —— | 10.241 | 9.765 |
| —— | —— | 69.38 | 69.28 | 186.0 | —— | 10.250 | 9.756 |
| 12.24 | 87.79 | 126.39 | 126.32 | 189.5 | 1.8557 | 19.04 | 5.252 |
| —— | —— | 126.01 | 125.92 | 190.1 | —— | 19.04 | 5.252 |

percent of nitric acid with its high fluidity to the highly viscous sulfuric acid has so little effect on the fluidity would seem to indicate some form of combination.

The maximum deviation of the fluidity-volume concentration curves from a linear relationship, which should[1] indicate

TABLE XIII

Fluidities of Ternary Mixtures at 10°

| % $HNO_3$ | % $H_2SO_4$ | Mean % $HNO_3$ | Mean % $H_2SO_4$ | Po gr/cm² | P gr/cm² | Time sec. | $\rho^{10}/_4$ | $\eta$ cp. | $\varphi$ abs. |
|---|---|---|---|---|---|---|---|---|---|
| 23.44 | 12.44 | 23.38 | 12.49 | 273.28 | 272.61 | 549.7 | 1.2430 | 2.207 | 45.30 |
| 23.32 | 12.54 | —— | —— | 273.28 | 270.15 | 555.0 | 2.2085 | 2.208 | 45.28 |
| 25.69 | 24.74 | 25.64 | 24.77 | 273.34 | 273.04 | 874.0 | 1.3644 | 3.515 | 28.45 |
| 25.58 | 24.80 | —— | —— | 273.70 | 273.46 | 873.4 | —— | 3.518 | 28.42 |
| 24.44 | 36.80 | 24.40 | 36.80 | 273.36 | 273.24 | 1504.7 | 1.4653 | 6.056 | 16.51 |
| 24.35 | 36.80 | —— | —— | 273.73 | 273.61 | 1503.9 | —— | 6.061 | 16.50 |
| 24.76 | 48.93 | 24.76 | 48.96 | 50.17 | 50.14 | 275.9 | 1.5851 | 11.003 | 9.088 |
| 24.77 | 48.99 | —— | —— | 49.85 | 49.74 | 278.1 | —— | 11.002 | 9.089 |
| —— | —— | —— | —— | 50.17 | 50.14 | 275.6 | —— | 10.991 | 9.098 |
| —— | —— | —— | —— | 49.86 | 49.83 | 278.1 | —— | 11.022 | 9.073 |
| 24.10 | 61.08 | 24.04 | 61.14 | 76.25 | 76.23 | 330.3 | 1.7003 | 20.027 | 4.993 |
| 23.98 | 61.19 | —— | —— | 75.92 | 75.91 | 332.0 | —— | 20.046 | 4.988 |
| 27.00 | 72.89 | 27.18 | 72.96 | 126.09 | 126.06 | 474.5 | 1.8513 | 47.58 | 2.102 |
| 27.35 | 73.03 | —— | —— | 125.71 | 125.69 | 475.3 | —— | 47.52 | 2.104 |

TABLE XIV

Fluidities of Ternary Mixtures at 20°

| Mean % $HNO_3$ | Mean % $H_2SO_4$ | Po gr/cm² | P gr/cm² | Time seconds | $\rho^{20}/_4$ | $\eta$ cp. | $\varphi$ abs. |
|---|---|---|---|---|---|---|---|
| 23.38 | 12.49 | 273.24 | 272.09 | 421.7 | 1.2348 | 1.6901 | 59.17 |
| —— | —— | 273.56 | 271.88 | 422.0 | —— | 1.6900 | 59.17 |
| 25.64 | 24.77 | 273.32 | 272.83 | 682.0 | 1.3546 | 2.7408 | 36.49 |
| —— | —— | 273.68 | 273.19 | 681.1 | —— | 2.7408 | 36.49 |
| 24.40 | 36.80 | 273.32 | 273.17 | 1137.0 | 1.4547 | 4.575 | 21.86 |
| —— | —— | 273.70 | 273.11 | 1134.1 | —— | 4.579 | 21.84 |
| —— | —— | 273.32 | 273.76 | 1135.8 | —— | 4.580 | 21.84 |
| 24.76 | 48.96 | 50.23 | 50.17 | 200.3 | 1.5738 | 7.993 | 12.51 |
| —— | —— | 49.91 | 49.85 | 201.8 | —— | 8.001 | 12.50 |
| —— | —— | 50.25 | 50.19 | 200.6 | —— | 8.008 | 12.49 |
| 24.04 | 61.14 | 59.12 | 59.09 | 293.0 | 1.6895 | 13.771 | 7.262 |
| —— | —— | 58.77 | 58.75 | 294.7 | —— | 13.771 | 7.262 |
| 27.18 | 72.96 | 126.12 | 126.08 | 298.3 | 1.8382 | 29.916 | 3.343 |
| —— | —— | 125.74 | 125.74 | 298.9 | —— | 29.886 | 3.346 |

[1] "Fluidity and Plasticity," p. 174.

the composition of any solvate present, occurs at volume concentrations corresponding to the weight concentrations of 68,

TABLE XV

Fluidities of Ternary Mixtures at 40°

| Mean % $HNO_3$ | Mean % $H_2SO_4$ | Po gr/cm² | P gr/cm² | Time seconds | $\rho^{40}/_4$ | $\eta$ cp. | $\varphi$ abs. |
|---|---|---|---|---|---|---|---|
| 23.38 | 12.49 | 273.23 | 270.83 | 290.0 | 1.2184 | 1.1569 | 86.44 |
| —— | —— | 273.55 | 271.16 | 289.8 | —— | 1.1575 | 86.39 |
| 25.64 | 24.77 | 273.30 | 272.22 | 451.4 | 1.3370 | 1.810 | 55.25 |
| —— | —— | 273.64 | 272.52 | 450.9 | —— | 1.810 | 55.24 |
| 24.40 | 36.80 | 273.29 | 272.86 | 730.0 | 1.4337 | 2.934 | 34.08 |
| —— | —— | 273.67 | 273.24 | 729.5 | —— | 2.936 | 34.06 |
| 24.76 | 48.96 | 50.34 | 50.15 | 120.0 | 1.5518 | 4.787 | 20.89 |
| —— | —— | 50.02 | 49.83 | 120.8 | —— | 4.788 | 20.89 |
| 24.04 | 61.14 | 58.85 | 58.75 | 160.0 | 1.6666 | 7.4763 | 13.38 |
| —— | —— | 59.19 | 59.08 | 159.0 | —— | 7.4725 | 13.38 |
| —— | —— | 58.85 | 58.75 | 160.0 | —— | 7.4763 | 13.38 |
| 27.18 | 72.96 | 126.16 | 126.02 | 142.7 | 1.8147 | 14.304 | 6.99 |
| —— | —— | 125.78 | 125.63 | 143.0 | —— | 14.290 | 6.998 |

TABLE XVI

Fluidities of Ternary Mixtures at 10°

| % $HNO_3$ | % $H_2SO_4$ | Mean % $HNO_3$ | Mean % $H_2SO_4$ | Po gr/cm² | P gr/cm² | Time seconds | $\rho^{10}/_4$ | $\eta$ cp. | $\varphi$ abs. |
|---|---|---|---|---|---|---|---|---|---|
| 38.92 | 12.11 | 38.77 | 12.20 | 273.30 | 272.87 | 713.8 | 1.3470 | 2.8690 | 34.86 |
| 38.63 | 12.29 | —— | —— | 273.64 | 273.21 | 712.6 | —— | 2.8677 | 34.87 |
| 33.43 | 23.90 | 34.42 | 23.89 | 273.19 | 273.06 | 1020.7 | 1.4119 | 4.1054 | 24.36 |
| 33.41 | 23.89 | —— | —— | 273.54 | 273.41 | 1018.4 | —— | 4.1014 | 24.38 |
| 35.21 | 38.44 | 35.21 | 38.44 | 51.80 | 51.74 | 198.1 | 1.5541 | 8.1522 | 12.27 |
| 35.21 | 38.42 | —— | —— | 51.64 | 51.64 | 198.6 | —— | 8.1575 | 12.26 |
| 35.20 | 47.65 | 35.25 | 47.65 | 60.57 | 60.50 | 266.2 | 1.6535 | 12.81 | 7.806 |
| 35.30 | —— | —— | —— | 60.23 | 60.18 | 267.2 | —— | 12.79 | 7.819 |
| 37.15 | 62.80 | 37.17 | 62.79 | 97.59 | 97.55 | 417.8 | 1.8127 | 32.42 | 3.084 |
| 37.19 | 62.79 | —— | —— | 97.23 | 97.21 | 418.6 | —— | 32.37 | 3.089 |

68, 68.5 percent for 40°, 20°, and 10°, respectively. This corresponds approximately to the compound $3HNO_3.H_2SO_4$ which contains 65.9 percent nitric acid.

TABLE XVII

**Fluidities of Ternary Mixtures at 20°**

| Mean % $HNO_3$ | Mean % $H_2SO_4$ | Po gr/cm² | P gr/cm² | Time seconds | $\rho^{20}/_4$ | $\eta$ cp. | $\varphi$ abs. |
|---|---|---|---|---|---|---|---|
| 38.77 | 12.20 | 273.28 | 272.59 | 560.9 | 1.3361 | 2.2521 | 40.40 |
| —— | —— | 273.62 | 272.92 | 559.8 | —— | 2.2504 | 44.44 |
| 33.42 | 23.89 | 273.22 | 272.85 | 784.9 | 1.3995 | 3.1545 | 31.70 |
| —— | —— | 273.62 | 273.25 | 784.1 | —— | 3.1559 | 31.69 |
| 35.21 | 38.44 | 52.02 | 51.88 | 145.6 | 1.5405 | 6.008 | 16.66 |
| —— | —— | 51.71 | 51.58 | 146.3 | —— | 6.002 | 16.64 |
| 35.25 | 47.65 | 60.24 | 60.17 | 191.6 | —— | 9.1697 | 10.91 |
| —— | —— | 60.56 | 60.49 | 190.6 | —— | 9.1703 | 10.90 |
| 35.17 | 62.79 | 97.83 | 97.79 | 268.5 | 1.8010 | 20.885 | 4.788 |
| —— | —— | 97.47 | 97.43 | 268.3 | —— | 20.870 | 4.792 |

TABLE XVIII

**Fluidities of Ternary Mixtures at 40°**

| Mean % $HNO_3$ | Mean % $H_2SO_4$ | Po gr/cm² | P gr/cm² | Time seconds | $\rho^{40}/_4$ | $\eta$ cp. | $\varphi$ abs. |
|---|---|---|---|---|---|---|---|
| 38.77 | 12.20 | 273.24 | 271.69 | 375.8 | —— | 1.5039 | 66.49 |
| —— | —— | 273.58 | 272.03 | 375.6 | —— | 1.5050 | 66.45 |
| 33.42 | 23.89 | 273.28 | 272.41 | 510.7 | 1.3784 | 2.0492 | 48.80 |
| —— | —— | 273.63 | 272.79 | 509.6 | —— | 2.0476 | 48.84 |
| 35.21 | 38.44 | 51.78 | 51.48 | 89.7 | 1.5168 | 3.6730 | 27.26 |
| —— | —— | 52.08 | 51.76 | 89.1 | —— | 3.6680 | 27.23 |
| 35.25 | 47.65 | 60.56 | 60.35 | 110.2 | 1.6107 | 5.290 | 18.90 |
| —— | —— | 60.56 | 60.35 | 110.2 | —— | 5.290 | 18.90 |
| —— | —— | 60.24 | 60.03 | 110.7 | —— | 5.286 | 18.92 |
| 37.17 | 62.79 | 97.93 | 97.77 | 133.7 | 1.7750 | 10.398 | 9.618 |
| —— | —— | 97.55 | 97.39 | 134.2 | —— | 10.396 | 9.619 |

### Ternary Mixtures

Forty-five mixtures were prepared so as to contain as nearly as possible some multiple of 12.5 percent of each of the three components. Since the composition of the mixtures as determined by analysis always differed somewhat from the desired concentrations, the fluidity values for mixtures of the desired compositions were obtained by the following method.

TABLE XIX

Fluidities of Ternary Mixtures at 10°

| Mean % $HNO_3$ | Mean % $H_2SO_4$ | Po gr/cm² | P gr/cm² | Time seconds | $\rho^{10}/_4$ | $\eta$ cp. | $\varphi$ abs. |
|---|---|---|---|---|---|---|---|
| 50.29 | 12.31 | 273.34 | 273.03 | 868.8 | 1.4192 | 3.4940 | 28.62 |
| 50.24 | 12.31 | 273.67 | 273.36 | 867.3 | —— | 3.4922 | 28.64 |
| 48.88 | —— | 273.10 | 272.96 | 1326.4 | 1.5147 | 5.3330 | 18.75 |
| 48.86 | 25.06 | 273.53 | 273.39 | 1324.4 | —— | 5.3333 | 18.75 |
| 50.90 | 36.90 | 44.31 | 44.25 | 206.4 | —— | 7.2643 | 13.77 |
| 50.95 | 36.90 | 44.63 | 44.57 | 204.9 | —— | 7.2637 | 13.77 |
| 47.10 | 52.63 | 78.82 | 78.79 | 332.3 | —— | 20.826 | 4.802 |
| 47.22 | 52.56 | 79.18 | 79.15 | 331.1 | —— | 20.846 | 4.797 |

Fluidities of Ternary Mixtures at 20°

| Mean % $HNO_3$ | Mean % $H_2SO_4$ | Po gr/cm² | P gr cm² | Time seconds | $\rho^{20}/_4$ | $\eta$ cp. | $\varphi$ abs. |
|---|---|---|---|---|---|---|---|
| 50.26 | 12.31 | 273.33 | 272.82 | 670.4 | 1.4064 | 2.6940 | 37.12 |
| —— | —— | 273.64 | 273.13 | 669.7 | —— | 2.6943 | 37.12 |
| 48.87 | 25.06 | 273.18 | 272.93 | 1000.2 | 1.5011 | 4.0210 | 24.87 |
| —— | —— | 273.58 | 273.33 | 998.6 | —— | 4.0205 | 24.87 |
| 50.93 | 36.90 | 44.33 | 44.22 | 151.3 | —— | 5.3214 | 18.79 |
| —— | —— | 44.33 | 44.22 | 151.6 | —— | 5.3320 | 18.76 |
| 47.16 | 52.60 | 78.91 | 78.85 | 222.1 | —— | 13.930 | 7.179 |
| —— | —— | 79.27 | 79.21 | 221.0 | —— | 13.924 | 7.182 |

Fluidities of Ternary Mixtures at 40°

| Mean % $HNO_3$ | Mean % $H_2SO_4$ | Po gr/cm² | P gr, cm² | Time seconds | $\rho^{40}/_4$ | $\eta$ cp. | $\varphi$ abs. |
|---|---|---|---|---|---|---|---|
| 50.26 | 12.31 | 273.28 | 272.09 | 437.0 | 1.3765 | 1.7514 | 57.10 |
| —— | —— | 273.24 | 272.06 | 437.0 | —— | 1.7512 | 57.10 |
| 48.87 | 25.06 | 273.11 | 272.51 | 630.8 | 1.4747 | 2.5320 | 39.49 |
| —— | —— | 273.48 | 272.88 | 629.8 | —— | 2.5314 | 39.50 |
| 50.93 | 36.90 | 44.35 | 44.07 | 94.3 | —— | 3.3055 | 30.25 |
| —— | —— | 44.35 | 44.07 | 94.2 | —— | 3.3019 | 30.29 |
| 47.16 | 52.60 | 59.61 | 59.49 | 156.9 | —— | 7.425 | 13.47 |
| —— | —— | 59.27 | 59.16 | 158.2 | —— | 7.444 | 13.43 |
| —— | —— | 59.61 | 59.50 | 156.7 | —— | 7.416 | 13.48 |
| —— | —— | 59.27 | 59.16 | 158.2 | —— | 7.444 | 13.43 |

TABLE XX

**Fluidities of Ternary Mixtures at 10°**

| % $HNO_3$ | % $H_2SO_4$ | Mean % $HNO_3$ | Mean % $H_2SO_4$ | Po gr/cm² | P gr/cm² | Time seconds | $\rho^{10}/_4$ | $\eta$ cp. | $\varphi$ abs. |
|---|---|---|---|---|---|---|---|---|---|
| 59.35 | 12.00 | 59.33 | 12.05 | 274.75 | 274.46 | 913.1 | 1.4760 | 3.6915 | 27.07 |
| 59.30 | 12.10 | —— | —— | 274.37 | 274.08 | 914.5 | —— | 3.6920 | 27.09 |
| 60.41 | 25.00 | 60.41 | 25.02 | 274.81 | 274.66 | 1287.0 | 1.5805 | 5.2067 | 19.21 |
| 60.40 | 25.05 | —— | —— | 274.39 | 274.24 | 1289.2 | —— | 5.2076 | 19.20 |
| 61.30 | 38.24 | 61.29 | 38.22 | 59.70 | 59.66 | 280.5 | 1.7394 | 13.312 | 7.512 |
| 61.27 | 38.20 | —— | —— | 59.36 | 59.33 | 282.4 | —— | 13.326 | 7.504 |

**Fluidities of Ternary Mixtures at 20°**

| Mean % $HNO_3$ | Mean % $H_2SO_4$ | Po gr/cm² | P gr/cm² | Time seconds | $\rho^{10}/_4$ | $\eta$ cp. | $\varphi$ abs. |
|---|---|---|---|---|---|---|---|
| 59.33 | 12.05 | 274.38 | 273.89 | 697.6 | 1.4616 | 2.8143 | 35.53 |
| —— | —— | 274.76 | 274.27 | 696.6 | —— | 2.8142 | 35.53 |
| 60.41 | 25.02 | 274.42 | 274.17 | 1002.6 | 1.5662 | 4.0489 | 24.70 |
| —— | —— | 274.82 | 274.57 | 1001.1 | —— | 4.0488 | 24.70 |
| 61.29 | 38.22 | 59.97 | 59.90 | 193.5 | 1.7249 | 9.2188 | 10.85 |
| —— | —— | 59.63 | 59.56 | 193.3 | —— | 9.2518 | 10.81 |

Fluidities of Ternary Mixtures at 40°

| Mean % $HNO_3$ | Mean % $H_2SO_4$ | Po gr/cm² | P gr/cm² | Time seconds | $\rho^{10}/_4$ | $\eta$ cp. | $\varphi$ abs. |
|---|---|---|---|---|---|---|---|
| 59.33 | 12.05 | 274.37 | 273.20 | 450.7 | 1.4323 | 1.8137 | 55.14 |
| —— | —— | 274.75 | 273.58 | 450.1 | —— | 1.8138 | 55.13 |
| 61.41 | 25.02 | 274.83 | 274.20 | 630.8 | 1.5371 | 2.5477 | 39.25 |
| —— | —— | 274.43 | 273.80 | 632.4 | —— | 2.5505 | 39.21 |
| 61.29 | 38.22 | 60.06 | 59.91 | 106.6 | 1.6901 | 5.080 | 19.69 |
| —— | —— | 59.72 | 59.57 | 107.3 | —— | 5.084 | 19.67 |
| —— | —— | 60.06 | 59.91 | 106.5 | —— | 5.075 | 19.70 |
| —— | —— | 59.72 | 59.69 | 107.4 | —— | 5.099 | 19.61 |

Using the data in Tables X, XI, and XII for mixtures containing approximately 12.5 percent nitric acid, curves were drawn plotting fluidity against percentage $H_2SO_4$. From these curves the fluidity values at intervals of exactly 12.5 percent

sulfuric acid were read off. The data in Table XIII, XIV, and XV for mixtures containing approximately 25.0% nitric acid were similarly treated, i. e., the fluidity values were plotted against the percentage of sulfuric acid and the fluidity values read off at intervals of 12.5% $H_2SO_4$. The data in Tables XVI, XVII, and XVIII for mixtures containing 37.5% nitric acid and in Tables XIX, XX, and XXI for mixtures containing approximately 50.0, 62.5, 75.0, and 87.5% nitric acid were treated in the same manner. In this way the fluidity values were corrected for the deviations of the percentages of sulfuric acid from the desired concentrations.

TABLE XXI

Fluidities of Ternary Mixtures at 10°

| % $HNO_3$ | % $H_2SO_4$ | Mean % $HNO_3$ | Mean % $H_2SO_4$ | P gr/cm² | P gr/cm² | Time sec. | $\rho t/\eta$ | $\eta$ cp. | $\varphi$ abs. |
|---|---|---|---|---|---|---|---|---|---|
| 73.25 | | 73.27 | 12.90 | 37.56 | 37.33 | 105.5 | 1.5973 | 3.1327 | 31.92 |
| 73.28 | 12.90 | —— | —— | 37.24 | 37.01 | 106.3 | —— | 3.1297 | 31.95 |
| 72.80 | 26.50 | 72.86 | 26.49 | 38.23 | 38.05 | 121.1 | 1.6334 | 3.6653 | 27.28 |
| 72.92 | 26.48 | —— | —— | 37.91 | 37.73 | 122.3 | —— | 3.6709 | 27.24 |
| 85.72 | 13.60 | 85.41 | 13.60 | 38.06 | 37.70 | 84.9 | 1.6098 | 2.5462 | 39.27 |
| 85.39 | 13.60 | —— | —— | 37.74 | 37.39 | 85.5 | —— | 2.5428 | 39.32 |

Fluidities of Ternary Mixtures at 20°

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 73 | —— | 73.27 | 12.90 | 37.64 | 37.26 | 82.9 | —— | 2.457 | 40.70 |
| —— | —— | —— | —— | 37.32 | 36.96 | 83.2 | —— | 2.446 | 40.88 |
| —— | —— | 72.86 | 26.49 | 38.21 | 37.92 | 94.3 | 1.6161 | 2.8443 | 35.16 |
| —— | —— | —— | —— | 37.79 | 37.51 | 95.4 | —— | 2.8462 | 35.13 |
| —— | —— | 85.41 | 13.60 | 38.05 | 37.50 | 68.1 | 1.5934 | 2.0314 | 49.23 |
| —— | —— | —— | —— | 37.73 | 37.19 | 68.7 | —— | 2.0324 | 49.20 |

Fluidities of Ternary Mixtures at 40°

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| —— | —— | 73.27 | 12.90 | 37.72 | 36.91 | 55.8 | —— | 1.6384 | 61.04 |
| —— | —— | —— | —— | 37.40 | 36.61 | 56.3 | —— | 1.6395 | 60.99 |
| —— | —— | 72.86 | 26.48 | 38.21 | 37.53 | 61.3 | 1.5839 | 1.8300 | 54.65 |
| —— | —— | —— | —— | 37.79 | 37.12 | 61.9 | —— | 1.8279 | 54.70 |
| —— | —— | 85.41 | 13.60 | 38.11 | 36.98 | 47.0 | —— | 1.3825 | 72.33 |
| —— | —— | —— | —— | 37.79 | 36.68 | 47.5 | —— | 1.3860 | 72.15 |

The same method was employed to correct the fluidity values for the deviations of the nitric acid concentrations from the desired compositions. All mixtures in Table XXII having 12.5% $HNO_3$ were taken, and the fluidity plotted against

TABLE XXII

Values Read from Curves

| % $HNO_3$ | % $H_2S_4O$ | Fluidity Absolute | | |
|---|---|---|---|---|
| | | 10° | 20° | 40° |
| 10.46 | 12.50 | 58.05 | 74.05 | 108.15 |
| 12.56 | 25.00 | 36.50 | 46.85 | 67.20 |
| 12.97 | 37.50 | 23.25 | 30.35 | 44.60 |
| 12.61 | 50.00 | 12.75 | 17.00 | 26.95 |
| 12.51 | 62.50 | 5.75 | 8.10 | 14.15 |
| 11.93 | 75.00 | 3.00 | 4.60 | 9.25 |
| 12.24 | 87.50 | 1.55 | 2.50 | 5.40 |
| 23.38 | 12.50 | 45.25 | 59.15 | 86.40 |
| 25.64 | 25.00 | 28.20 | 36.00 | 54.85 |
| 24.40 | 37.50 | 15.90 | 21.25 | 33.00 |
| 24.76 | 50.00 | 8.55 | 1.85 | 20.05 |
| 24.04 | 62.50 | 4.65 | 6.80 | 12.70 |
| 27.18 | 75.00 | 1.65 | 2.65 | 5.95 |
| 38.77 | 12.50 | 34.50 | 44.00 | 65.85 |
| 33.42 | 25.00 | 23.70 | 30.70 | 46.60 |
| 35.21 | 37.50 | 13.05 | 17.65 | 28.20 |
| 35.25 | 50.00 | 7.20 | 10.40 | 17.25 |
| 37.17 | 62.50 | 2.50 | 3.65 | 8.35 |
| 50.26 | 12.50 | 28.45 | 36.95 | 56.75 |
| 48.87 | 25.00 | 18.75 | 24.90 | 39.65 |
| 50.93 | 37.50 | 11.60 | 16.00 | 26.75 |
| 47.16 | 50.00 | 5.90 | 8.70 | 15.45 |
| 59.33 | 12.50 | 26.80 | 35.10 | 54.65 |
| 60.41 | 25.00 | 19.20 | 24.65 | 39.25 |
| 61.29 | 37.50 | 8.30 | 12.10 | 21.15 |
| 73.27 | 12.50 | 32.20 | 41.10 | 61.45 |
| 72.86 | 25.00 | 27.55 | 35.50 | 55.10 |
| 85.40 | 12.50 | 40.05 | 50.05 | 73.50 |

the percentage of nitric acid. The fluidity values at intervals of 12.5% $HNO_3$ were then read from the curves. All mixtures in Table XXII containing 25%, or 37.5% or 50.0%, etc., of sulfuric acid were similarly treated. The values obtained are

TABLE XXIII

Fluidity Values after Correction for the Deviations from the Desired Composition

| % $HNO_3$ | % $H_2SO_4$ | Fluidity Absolute | | |
|---|---|---|---|---|
| | | 10° | 20° | 40° |
| 0.00 | 12.50 | 54.35 | 69.40 | 102.3 |
| 12.50 | 12.50 | 57.50 | 72.95 | 106.6 |
| 25.00 | 12.50 | 42.90 | 56.85 | 83.55 |
| 37.50 | 12.50 | 34.85 | 45.00 | 67.25 |
| 50.00 | 12.50 | 28.65 | 37.00 | 57.00 |
| 62.50 | 12.50 | 27.15 | 35.60 | 55.00 |
| 75.00 | 12.50 | 33.25 | 42.25 | 63.10 |
| 87.50 | 12.50 | 41.40 | 52.35 | 75.80 |
| 0.00 | 25.00 | 43.95 | 57.15 | 87.80 |
| 12.50 | 25.00 | 36.50 | 46.90 | 67.35 |
| 25.00 | 25.00 | 28.60 | 36.60 | 55.50 |
| 37.50 | 25.00 | 22.00 | 28.50 | 43.55 |
| 50.00 | 25.00 | 18.55 | 24.60 | 39.40 |
| 62.50 | 25.00 | 20.10 | 25.75 | 40.30 |
| 75.00 | 25.00 | 29.25 | 37.90 | 59.20 |
| 0.00 | 37.50 | 31.85 | 40.05 | 61.50 |
| 12.50 | 37.50 | 23.55 | 30.85 | 45.10 |
| 25.00 | 37.50 | 15.70 | 20.95 | 32.65 |
| 37.50 | 37.50 | 12.70 | 17.10 | 27.65 |
| 50.00 | 37.50 | 11.85 | 16.10 | 26.90 |
| 62.50 | 37.50 | 7.75 | 11.55 | 20.10 |
| 0.00 | 50.00 | 20.45 | 27.20 | 39.90 |
| 12.50 | 50.00 | 12.85 | 17.10 | 27.00 |
| 25.00 | 50.00 | 8.40 | 11.85 | 20.00 |
| 37.50 | 50.00 | 6.90 | 10.15 | 16.80 |
| 50.00 | 50.00 | 5.40 | 8.25 | 15.05 |
| 0.00 | 62.50 | 11.60 | 15.30 | 23.90 |
| 12.50 | 62.50 | 5.75 | 8.10 | 14.50 |
| 25.00 | 62.50 | 2.40 | 4.20 | 9.45 |
| 37.50 | 62.50 | 2.60 | 3.70 | 8.35 |
| 0.00 | 75.00 | 4.85 | 6.95 | 12.00 |
| 12.50 | 75.00 | 2.95 | 4.50 | 9.05 |
| 25.00 | 75.00 | 1.80 | 2.85 | 6.30 |
| 0.00 | 87.50 | 2.50 | 3.90 | 7.60 |
| 12.50 | 87.50 | 1.55 | 2.55 | 5.45 |
| 0.00 | 100.00 | 3.00 | 4.50 | 7.90 |
| 100.00 | 0.00 | 96.40 | 113.9 | 147.1 |

given in Table XXIII where the original values have been corrected for the deviations of both the nitric and sulfuric acids from the desired concentrations.

The results are shown graphically in Figure 5 which represents the effect of replacing water by nitric acid in mixtures containing a constant percentage of sulfuric acid.

Curves 1, 1′ and 1″ in Figure 5 for 40°, 20°, and 10°, respectively, represent the effect of replacing water by nitric acid in a mixture containing 12.5 percent sulfuric acid, i. e., Curve 1 for 40° starts at (12.5% $H_2SO_4$, 87.5% $H_2O$), passes through the points (12.5% $H_2SO_4$, 12.5% $HNO_3$, 75.0% $H_2O$), (12.5% $H_2SO_4$, 25.0% $HNO_3$, 62.5% $H_2O$)..... and ends at the point (12.5% $H_2SO_4$, 87.5% $HNO_3$).

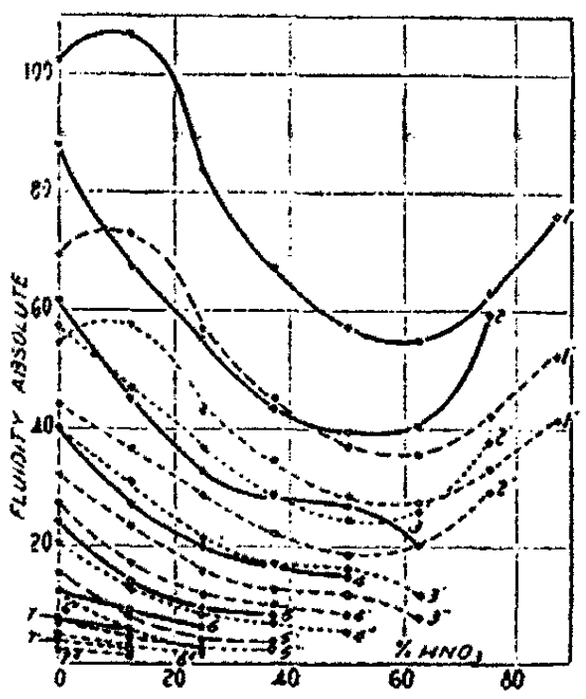



Fig. 5

Fluidity-Weight Concentration of Nitric Acid Curves for Ternary Mixtures Containing Constant Percentages of Sulfuric Acid

The first effect of replacing water by nitric acid is to increase the fluidity, producing a so-called "negative viscosity" effect which is equally well pronounced at all temperatures. This can only be ascribed partly to the action of the nitric acid on the associated water molecules as seen in Figure 2 and must be largely due to some other dissociating influence of the nitric acid. On further replacement of the water present by nitric acid the fluidity drops to a minimum and then increases. The decrease in fluidity is probably due to the nitric acid combining with a large portion of the water present in the mixture and thereby having its fluidity reduced. On further substitution of nitric acid by water the amount of unhydrated molecules of nitric acid increases and the fluidity is raised.

Curves 2, 2′ and 2″ for 40°, 20° and 10°, respectively, show the result of replacing water by nitric acid in a mixture containing 25 percent sulfuric acid, i. e., Curve 2 for 40° starts at the point (25% $H_2SO_4$, 75.0% $H_2O$), passes through the points (25.0% $H_2SO_4$, 12.5% $HNO_3$, 62.5% $H_2O$), (25.0% $H_2SO_4$, 25.0% $HNO_3$, 50.0% $H_2O$). . . . . and ends at the point (25.0% $H_2SO_4$, 75.0% $HNO_3$). The first replacement

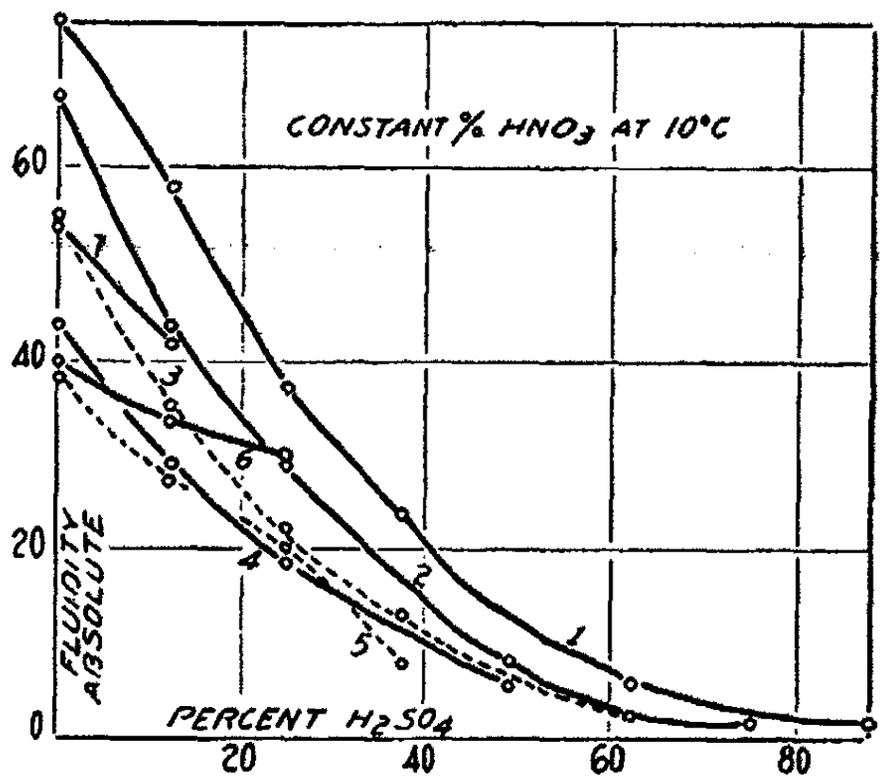



Fig. 6

*Fluidity-Weight Concentration of Sulfuric Acid Curves for Ternary Mixtures Containing Constant Percentages of Nitric Acid*

of water by nitric acid now produces no negative curvature. With Curves 2, 2′ and 2″ as with Curves 1, 1′ and 1″ the fluidity drops to a minimum and then increases. The decrease in fluidity is probably due as before to the nitric acid combining with the water present, and the increase in fluidity produced by replacement of most of the water present by nitric acid means an increase in the number of molecules of unhydrated nitric acid.

In Curves 3, 3′ and 3″ which show the effect of substituting nitric for water in a mixture containing 37.5 percent

sulfuric acid (the curve starting at the point 37.5% $H_2SO_4$, 62.5% $H_2O$ and ending at the point 37.5% $H_2SO_4$, 62.5% $HNO_3$) the first replacement of water by nitric acid lowers the fluidity. With further replacement of water the number of unhydrated nitric acid molecules increases which tends to raise the fluidity, and in the mixture having a high concentra-

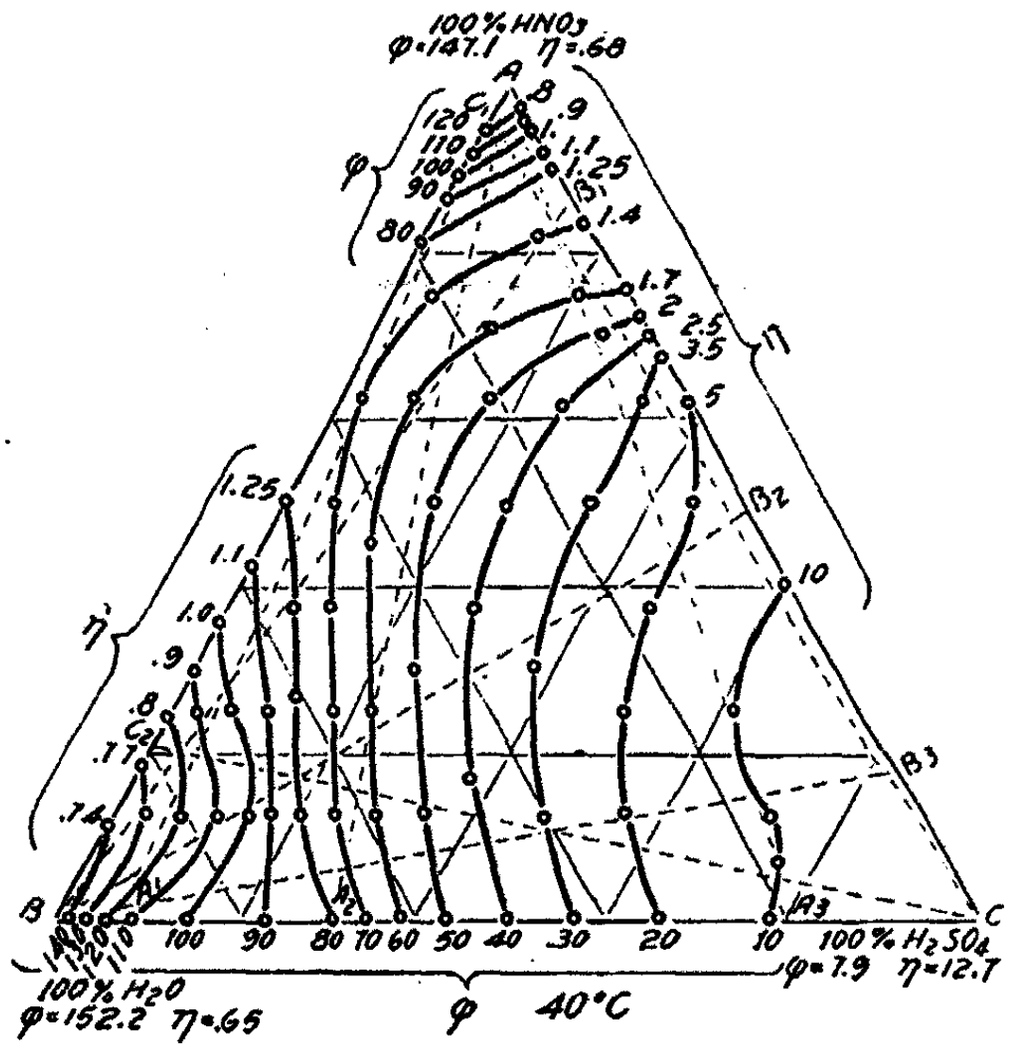



Fig. 7

Isorrhes for 40°

tion of acid a combination of the two acids probably takes place which tends to lower the fluidity. Where these opposite effects balance we have a region of nearly constant fluidity as in Curves 3, 3′ and 3″. In the curves previously discussed any combination of the two acids, taking place in the strongly acid mixtures, was not sufficient counteracted by the increase in fluidity due to the increasing concentration of free nitric

acid molecules, but in Curves 3, 3′ and 3″ the increase in the concentration of free nitric acid molecules no longer offsets the effect produced by the combination of the two acids and the curves no longer show a minimum.

In Curves (4, 4′, 4″), (5, 5′, 5″), (6, 6′, 6″), and (7, 7′, 7″), the replacement of water by nitric acid causes a gradual decrease in fluidity. Here again the combination of the two acids in the highly acid mixtures more than offsets the increase in

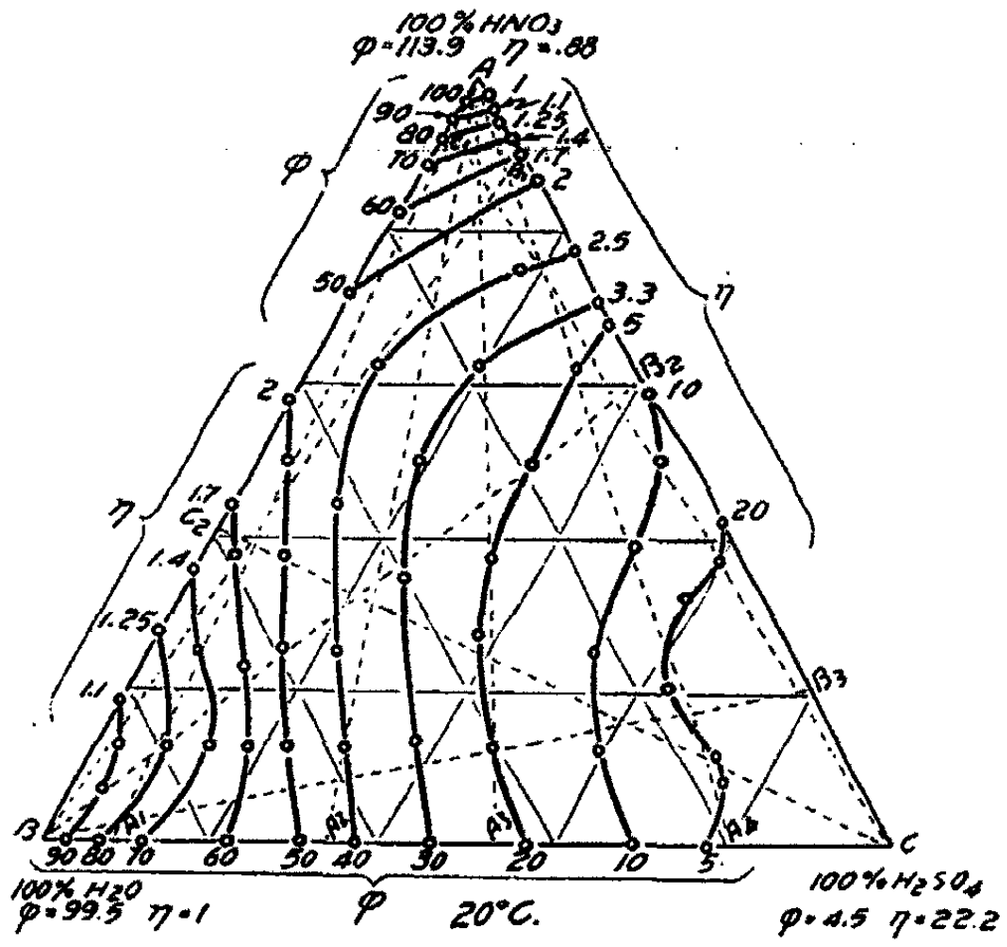



Fig. 8

Isorrhes for 20°

the concentration of unhydrated nitric acid molecules.

Figure 6 shows the effect of replacing water by sulfuric acid in a mixture containing a constant percentage of nitric acid. As no significant temperature variations were noted only the curves for 10° are given.

Curve 1 represents the effect of replacing water by sulfuric acid in a mixture containing 12.5 percent nitric acid, i. e.,

the curve starts at the point (12.5% $HNO_3$, 87.5% $H_2O$) and ends at the point (12.5% $HNO_3$, 87.5% $H_2O$). Because of the wide difference in fluidities of the water and of the sulfuric acid, which is substituted for it, the replacement of water rapidly increases the viscosity. With increasing concentration of sulfuric acid the combination between the two acids accounts for part of the increase in viscosity.

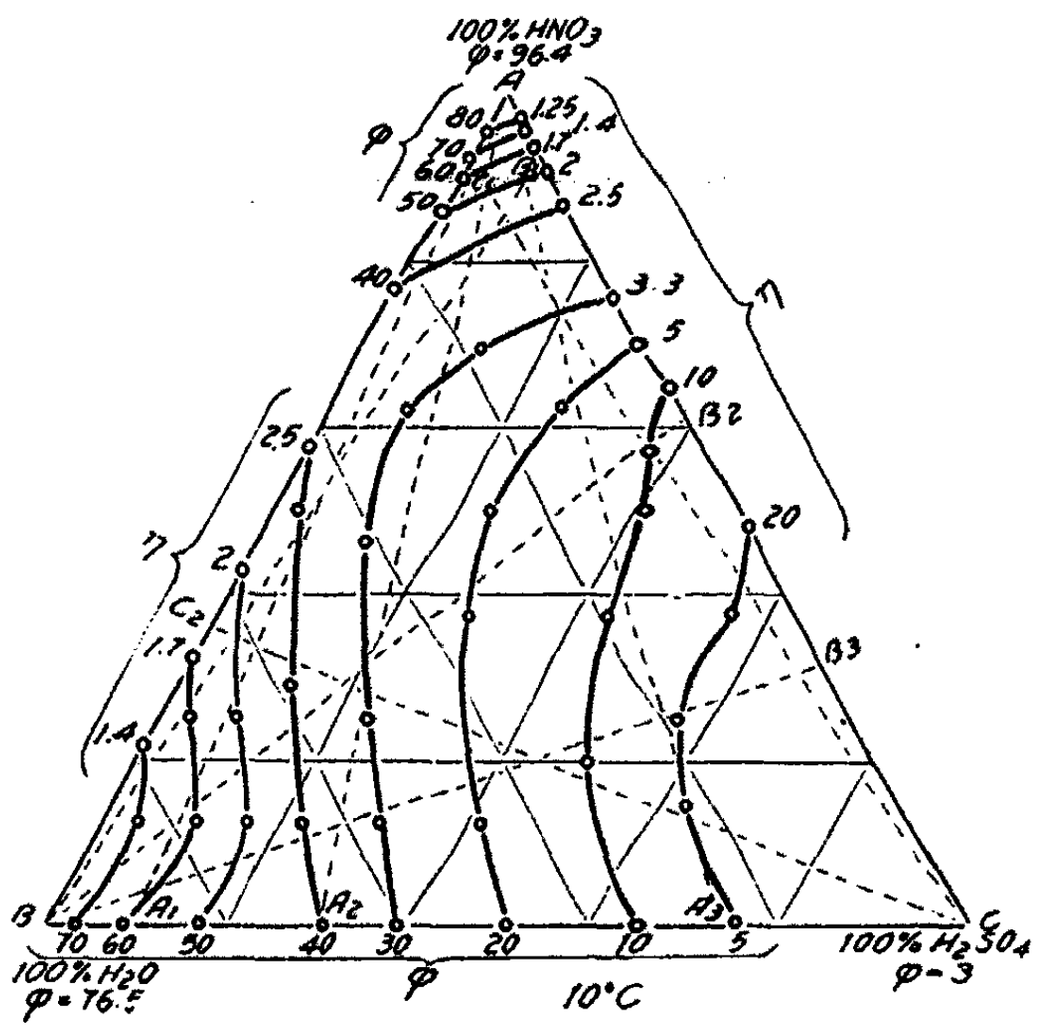



Fig. 9

Isorrhes for 10°

Curves 2, 3, 4, 5, 6 and 7 show the effect of replacing water by sulfuric acid in mixtures containing 25%, 37.5%, 50%, 62.5%, 75% and 87.5%, respectively. In all these curves the replacement of the highly fluid water by the highly viscous sulfuric acid causes a decrease in fluidity. Combination of the two acids, and a dehydration of the nitric acid as

suggested by Saposchnikow[1] probably are responsible for a part of the decrease in the more strongly acid mixtures.

## Isorrheic Mixtures

At the suggestion of Professor John R. Crawford the curves representing mixtures of equal fluidity will be referred

TABLE XXIV

Composition of Ternary Mixtures Having the Same Fluidities

| Fluidity | 10° | | 20° | | 40° | |
|---|---|---|---|---|---|---|
| | % $HNO_3$ | % $H_2SO_4$ | % $HNO_3$ | % $H_2SO_4$ | % $HNO_3$ | % $H_2SO_4$ |
| 5 | 12.50 | 65.25 | 12.50 | 72.50 | — | — |
| – | 25.00 | 56.30 | 25.00 | 60.40 | — | — |
| – | 37.50 | 55.50 | 37.50 | 59.90 | — | — |
| – | 14.70 | 62.50 | 20.75 | 62.50 | — | — |
| – | 0.00 | 74.65 | 0.00 | 77.25 | — | — |
| – | 48.00 | 52.00 | 42.15 | 57.85 | — | — |
| – | — | — | 9.15 | 75.00 | — | — |
| 10 | 12.50 | 54.20 | 12.50 | 59.15 | 12.50 | 72.30 |
| — | 25.00 | 47.00 | 25.00 | 52.50 | 25.00 | 61.55 |
| — | 37.50 | 43.00 | 37.50 | 50.10 | 37.50 | 60.05 |
| — | 50.00 | 41.10 | 50.00 | 47.00 | — | — |
| — | 62.50 | 35.50 | — | — | — | — |
| — | 3.00 | 62.50 | 8.60 | 62.50 | 22.35 | 62.50 |
| — | 19.70 | 50.00 | 39.20 | 50.00 | — | — |
| — | 57.10 | 37.50 | — | — | — | — |
| — | 0.00 | 65.00 | — | — | 0.00 | 78.40 |
| — | 64.65 | 35.35 | — | — | 40.75 | 59.25 |
| 20 | 12.50 | 41.30 | 12.50 | 47.10 | 12.50 | 55.60 |
| — | 25.00 | 33.00 | 25.00 | 38.60 | 25.00 | 50.00 |
| — | 37.50 | 27.35 | 37.50 | 33.90 | 37.50 | 46.20 |
| — | 50.00 | 23.50 | 50.00 | 31.75 | 50.00 | 44.65 |
| — | 62.50 | 25.30 | 62.50 | 30.70 | — | — |
| — | 0.70 | 50.00 | 8.30 | 50.00 | 4.50 | 62.50 |
| — | 17.70 | 37.50 | 27.35 | 37.50 | — | — |
| — | 43.40 | 25.00 | — | — | — | — |
| — | 62.00 | 25.00 | — | — | — | — |
| — | 0.00 | 50.60 | 0.00 | 56.90 | 0.00 | 66.05 |
| — | 70.00 | 30.00 | 67.60 | 32.40 | 62.10 | 37.90 |

[1] Saposchnikow: loc. cit.

| Fluidity | 10° | | 20° | | 40° | |
|---|---|---|---|---|---|---|
| | % $HNO_3$ | % $H_2SO_4$ | % $HNO_3$ | % $H_2SO_4$ | % $HNO_3$ | % $H_2SO_4$ |
| 30 | 12.50 | 30.90 | 12.50 | 38.25 | 12.50 | 47.75 |
| — | 25.00 | 23.60 | 25.00 | 29.95 | 25.00 | 40.00 |
| — | 37.50 | 16.70 | 37.50 | 23.60 | 37.50 | 35.40 |
| — | 50.00 | 11.30 | 50.00 | 19.00 | 50.00 | 34.30 |
| — | 62.50 | 8.75 | 62.50 | 19.50 | 62.50 | 32.80 |
| — | 75.00 | 22.45 | —— | —— | —— | —— |
| — | 3.25 | 75.00 | 13.35 | 37.35 | 30.50 | 37.50 |
| — | 22.80 | 25.00 | 34.80 | 25.00 | 9.10 | 50.00 |
| — | —— | —— | 68.20 | 25.00 | —— | —— |
| — | 46.45 | 12.50 | —— | —— | —— | —— |
| — | 69.40 | 12.50 | —— | —— | —— | —— |
| — | 0.00 | 39.00 | 0.00 | 45.90 | 0.00 | 57.40 |
| — | 75.60 | 24.40 | 70.70 | 29.30 | 67.70 | 32.30 |
| 40 | 12.50 | 22.30 | 12.50 | 29.95 | 12.50 | 40.80 |
| — | 25.00 | 14.90 | 25.00 | 22.30 | 25.00 | 32.85 |
| — | 37.50 | 8.80 | 37.50 | 15.70 | 37.50 | 27.45 |
| — | 50.00 | 2.65 | 50.00 | 10.25 | 50.00 | 24.40 |
| — | —— | —— | 62.50 | 8.00 | 62.50 | 25.25 |
| — | —— | —— | 75.00 | 17.70 | —— | —— |
| — | —— | —— | 0.15 | 37.50 | —— | —— |
| — | 6.75 | 25.00 | 20.75 | 25.00 | 47.10 | 25.00 |
| — | —— | —— | —— | —— | 61.80 | 25.00 |
| — | 28.75 | 12.50 | 44.25 | 12.50 | —— | —— |
| — | —— | —— | 71.65 | 12.50 | —— | —— |
| — | 0.00 | 30.60 | —— | —— | 0.00 | 49.95 |
| — | 57.70 | 0.00 | —— | —— | —— | —— |
| — | 76.65 | 0.00 | —— | —— | —— | —— |
| — | 86.50 | 13.50 | —— | —— | 70.15 | 29.85 |
| 50 | 12.50 | 16.35 | 12.50 | 23.10 | 12.50 | 34.65 |
| — | 25.00 | 8.20 | 25.00 | 16.30 | 25.00 | 27.80 |
| — | 37.50 | 2.75 | 37.50 | 9.60 | 37.50 | 21.30 |
| — | —— | —— | 50.00 | 3.80 | 50.00 | 17.10 |
| — | —— | —— | —— | —— | 62.50 | 16.60 |
| — | —— | —— | —— | —— | 8.60 | 37.50 |
| — | —— | —— | 8.70 | 25.00 | 29.75 | 25.00 |
| — | —— | —— | —— | —— | 70.20 | 25.00 |
| — | 19.60 | 12.50 | 31.60 | 12.50 | —— | —— |
| — | —— | —— | 84.75 | 12.50 | —— | —— |
| — | 42.80 | 0.00 | 57.70 | 0.00 | —— | —— |
| — | 85.75 | 0.00 | 71.65 | 0.00 | —— | —— |
| — | 0.00 | 16.70 | 0.00 | 30.90 | 0.00 | 43.60 |
| — | 90.85 | 9.15 | 86.10 | 13.90 | 72.30 | 27.70 |

| Fluidity | 10° | | 20° | | 40° | |
|---|---|---|---|---|---|---|
| | % $HNO_3$ | % $H_2SO_4$ | % $HNO_3$ | % $H_2SO_4$ | % $HNO_3$ | % $H_2SO_4$ |
| 60 | 12.50 | 10.75 | 12.50 | 18.20 | 12.50 | 29.00 |
| — | 25.00 | 3.20 | 25.00 | 10.75 | 25.00 | 23.00 |
| — | —— | —— | 37.50 | 3.85 | 37.50 | 15.95 |
| — | —— | —— | —— | —— | 50.00 | 10.75 |
| — | —— | —— | —— | —— | 62.50 | 8.80 |
| — | —— | —— | —— | —— | 75.00 | 20.95 |
| — | —— | —— | —— | —— | 1.10 | 37.50 |
| — | —— | —— | —— | —— | 20.25 | 25.00 |
| — | —— | —— | 22.75 | 12.50 | 45.10 | 12.50 |
| — | —— | —— | —— | —— | 71.05 | 12.50 |
| — | 32.10 | 0.00 | 43.90 | 0.00 | —— | —— |
| — | 89.90 | 0.00 | 82.25 | 0.00 | —— | —— |
| — | 0.00 | 8.65 | 0.00 | 22.05 | 0.00 | 38.20 |
| — | 93.60 | 6.40 | 89.80 | 10.20 | 75.60 | 24.40 |
| 70 | 12.50 | 4.30 | 12.50 | 13.90 | 12.50 | 23.95 |
| — | —— | —— | 25.00 | 5.95 | 25.00 | 18.60 |
| — | —— | —— | —— | —— | 37.50 | 11.40 |
| — | —— | —— | —— | —— | 50.00 | 5.10 |
| — | —— | —— | —— | —— | 62.50 | 2.10 |
| — | —— | —— | —— | —— | 75.00 | 4.30 |
| — | —— | —— | —— | —— | 10.25 | 25.00 |
| — | —— | —— | 0.65 | 12.50 | 34.95 | 12.50 |
| — | —— | —— | —— | —— | 82.00 | 12.50 |
| — | 21.60 | 0.00 | 35.35 | 0.00 | —— | —— |
| — | 93.00 | 0.00 | 88.80 | 0.00 | —— | —— |
| — | 0.00 | 3.00 | 0.00 | 12.50 | 0.00 | 34.50 |
| — | 95.25 | 4.75 | 92.00 | 8.00 | 83.45 | 16.55 |
| 80 | —— | —— | 12.50 | 8.95 | 12.50 | 20.40 |
| — | —— | —— | 25.00 | 1.30 | 25.00 | 14.10 |
| — | —— | —— | —— | —— | 37.50 | 7.30 |
| — | —— | —— | —— | —— | 50.00 | 0.15 |
| — | —— | —— | —— | —— | 4.20 | 25.00 |
| — | —— | —— | —— | —— | 27.20 | 12.50 |
| — | —— | —— | 27.80 | 0.00 | 50.20 | 0.00 |
| — | 95.50 | 0.00 | 91.75 | 0.00 | 81.10 | 0.00 |
| — | —— | —— | 0.00 | 6.75 | 0.00 | 30.20 |
| — | 97.00 | 3.00 | 93.80 | 6.20 | 90.10 | 9.90 |

| Fluidity | 10° | | 20° | | 40° | |
|---|---|---|---|---|---|---|
| | % $HNO_3$ | % $H_2SO_4$ | % $HNO_3$ | % $H_2SO_4$ | % $HNO_3$ | % $H_2SO_4$ |
| 90 | —— | —— | 12.50 | 3.10 | 12.50 | 17.15 |
| — | —— | —— | —— | —— | 25.00 | 9.90 |
| — | —— | —— | —— | —— | 37.50 | 3.20 |
| — | —— | —— | —— | —— | 22.50 | 12.50 |
| — | —— | —— | 18.30 | 0.00 | 42.40 | 0.00 |
| — | 98.25 | 0.00 | 94.35 | 0.00 | 86.50 | 0.00 |
| — | —— | —— | 0.00 | 3.05 | 0.00 | 22.80 |
| — | 98.80 | 1.20 | 95.40 | 4.60 | 92.05 | 7.95 |
| 100 | —— | —— | —— | —— | 12.50 | 14.40 |
| — | —— | —— | —— | —— | 25.00 | 6.25 |
| — | —— | —— | —— | —— | 18.35 | 12.50 |
| — | —— | —— | 87.50 | 9.30 | —— | —— |
| — | —— | —— | —— | —— | 35.75 | 0.00 |
| — | —— | —— | 96.85 | 0.00 | 89.20 | 0.00 |
| — | —— | —— | —— | —— | 0.00 | 14.15 |
| — | —— | —— | 97.20 | 2.80 | 94.45 | 5.55 |
| 110 | —— | —— | —— | —— | 12.50 | 11.15 |
| — | —— | —— | —— | —— | 25.00 | 2.65 |
| — | —— | —— | —— | —— | 29.80 | 0.00 |
| — | —— | —— | 99.30 | 0.00 | 91.80 | 0.00 |
| — | —— | —— | —— | —— | 0.00 | 8.45 |
| — | —— | —— | 99.15 | 0.85 | 96.10 | 3.90 |
| 120 | —— | —— | —— | —— | 12.50 | 7.20 |
| — | —— | —— | —— | —— | 24.10 | 0.00 |
| — | —— | —— | —— | —— | 94.25 | 0.00 |
| — | —— | —— | —— | —— | 0.00 | 5.30 |
| — | —— | —— | —— | —— | 97.50 | 2.50 |
| 130 | —— | —— | —— | —— | 12.50 | 3.45 |
| — | —— | —— | —— | —— | 18.05 | 0.00 |
| — | —— | —— | —— | —— | 96.60 | 0.00 |
| — | —— | —— | —— | —— | 0.00 | 3.00 |
| — | —— | —— | —— | —— | 98.55 | 1.45 |

| Fluidity | 10° | | 20° | | 40° | |
|---|---|---|---|---|---|---|
| | | | % $HNO_3$ | % $H_2SO_4$ | % $HNO_3$ | % $H_2SO_4$ |
| 140 | —— | —— | —— | —— | 11.10 | 0.00 |
| —— | —— | —— | —— | —— | 98.60 | 0.00 |
| —— | —— | —— | —— | —— | 0.00 | 1.50 |
| —— | —— | —— | —— | —— | 99.35 | 0.65 |
| 150 | —— | —— | —— | —— | 2.15 | 0.00 |
| —— | —— | —— | —— | —— | 0.00 | 0.30 |

to as isorrhes (or isorrheals). The data for the isorrheic mixtures were interpolated from Figures 2, 3, 4, 5, 6, and from the curves similar to those of Figure 6 for 20° and 40°. The data so obtained are given in Table XXIV and shown graphically in Figures 7, 8 and 9.

From these curves the same relationships plotted in Figures 5 and 6 can be read off. For example, if in Figure 7 we pass from left to right along the straight line which contains 10% $HNO_3$, we find that replacing water by sulfuric acid in a mixture which contains 10% $HNO_3$ lowers the fluidity in a regular manner until the mixture contains about 30% $H_2SO_4$ when further replacements of water by sulfuric acid decrease the fluidity much less rapidly. If we read from bottom to top on the line containing 10% $H_2SO_4$ we see that replacing water by nitric acid in a mixture containing 10% $H_2SO_4$ decreases the fluidity until a minimum is reached at around 40 to 50 fluidity units, after which further replacements of water by nitric acid increase the fluidity.

As any line drawn from one of the apices to the opposite side, such as $AA_1$, $AA_2$, $BB_1$, etc., indicates a constant ratio of the other two components, the effect of adding one component to any mixture of the other two can be readily seen.

By referring to the line $AA_1$, Figure 7, it is seen that the first effect of adding absolute nitric acid to a mixture containing 93% $H_2O$ and 7% $H_2SO_4$ is to increase the fluidity, giving negative curvature. On further addition of nitric acid the

fluidity decreases to a minimum, after which any addition of nitric acid raises the fluidity. When nitric acid is added to a mixture of water and sulfuric acid containing between 20 to 70% $H_2SO_4$, the fluidity steadily decreases to a minimum after which it is increased by further additions of nitric acid (line $AA_2$). As the amount of sulfuric acid in the original mixture is increased, the amount of nitric acid, which must be added in order to reach the point, of minimum fluidity, steadily decreases. When nitric acid is added to a mixture of sulfuric acid and water containing over 80% $H_2SO_4$, the fluidity is increased only slightly as is seen in line $AA_3$, Figure 7. It is interesting to note that negative curvature is found on adding absolute nitric acid to mixtures of sulfuric acid and water, which contain either a large excess of water (line $AA_1$) or a large excess of acid (line $AA_3$). This negative curvature cannot very well be ascribed to a decomposition of either the associated water molecules or the associated sulfuric acid molecules, for, as is seen in Figure 2, only an exceedingly slight negative curvature is exhibited on adding nitric acid to water, and no trace of negative curvature is found on adding nitric acid to sulfuric acid (Figure 4). Any attempt to explain the negative curvature as due to a dissociation of the sulfuric acid-water complexes by the nitric acid, meets with the objection that no negative curvature is found when nitric acid is added to mixtures of sulfuric acid and water containing between 20% and 80% $H_2SO_4$. As the concentration of the sulfuric acid-water complexes is greatest in such mixtures, the dissociation of the complexes and the negative curvature should be also most pronounced.

On adding sulfuric acid to mixtures of nitric acid and water as in lines $CC_1$ and $CC_2$ the fluidity steadily decreases. On adding sulfuric acid to mixtures of nitric which are rich in nitric acid (line $CC_1$) the fluidity drops much more rapidly, as seen by the closer spacing of the isorrhes, than when sulfuric acid is added to mixtures rich in water (line $CC_2$). As nitric acid and water have approximately the same fluidity,

this effect must be due either to a combination of the nitric acid and sulfuric acid or some other chemical change such as suggested by Saposchnikow.

On adding water to a mixture of nitric acid and sulfuric acid containing over 70% $HNO_3$ (line $BB_1$), the fluidity falls to a minimum and then increases, a behavior which resembles that of nitric acid on the addition of water. When water is added to mixtures of sulfuric acid and nitric acid containing over 30% $HNO_3$ (line $BB_2$), the result produced is similar to that of adding water to sulfuric acid, in that the fluidity steadily increases.

## Conclusions

1. The fluidities of forty-five binary and ternary mixtures of nitric acid, sulfuric acid, and water have been measured at the temperatures of 10°, 20°, and 40° C.

2. Several cases of both negative and positive curvature of the fluidity-volume concentration curves have been observed. The evidence favors the view that negative curvature is due to some form of dissociation while positive curvature is brought about by solvation.

3. The concentration of the mixture showing the maximum deviation from the linear fluidity-volume concentration curve is independent of the temperature, provided that only one solvate is formed, and in such favorable cases it is believed that this concentration may be utilized for finding the composition of the solvate.

4. Concentrations of equal fluidity (isorrhes), differing by intervals of ten absolute units, have been calculated for each of the three temperatures and plotted on triangular diagrams given herewith.

*Easton, Pa.*
*Jan. 29, 1923*

# CATALYTIC ACTIVITY OF TIN

BY O. W. BROWN AND C. O. HENKE

## Introduction

In our previous papers[1] we have given the results of some studies on the activity of several catalysts and have shown that several metals which were not known to be catalysts were excellent catalysts. In this paper we shall give the results of some studies with tin as catalyst and the effect of the physical condition of the tin on its activity. For this study nitrobenzene was used, a few experiments being carried out with ortho-nitro-toluene and ortho-nitro-anisole.

## Experimental Details

The apparatus used, method of work and analysis was the same as in our previous papers where it has been fully described. In all of the experiments in this paper unless otherwise noted the catalyst tube was a $^1/_2$ inch glass combustion tube.

The tin catalysts were prepared from C. P. Stannous Chloride crystals. Baker's Lot No. 2322 was used, which was labeled to contain 0.002% Fe and 0.001% $SO_3$. A test for iron indicated less than this amount. It was also tested for lead but none was detected. Previous experiments had indicated that iron was exceedingly poisonous to the tin catalyst while lead decreased its activity to a smaller extent.

Stannous hydroxide was prepared by precipitation from a solution of 300 grams $SnCl_2.2H_2O$ in 1350 cc water (the stannous chloride hydrolyzed to a certain extent) by a solution of sodium carbonate containing 150 gm $Na_2CO_3$ in 750 cc water. The sodium carbonate solution was added to the stannous chloride solution, both at room temperature (about 20° C). The precipitated hydroxide was washed by decantation five

[1] Brown and Henke: Jour. Phys. Chem., **26**, 161, 272, 324, 631, 636 (1922).

times using 3 to 4 liters of water each time. It was then filtered on a Buechner funnel and allowed to dry at room temperature. All the stannous hydroxide used for catalysts for this paper was prepared in this way. Unless otherwise stated the oxide was ground to pass through a 40 mesh sieve.

### Behavior of Stannous Hydroxide

Bury and Partington[1] state that when an excess of alkali is used to precipitate stannous hydroxide, the stannous hydroxide darkens and becomes almost black. We precipitated our stannous hydroxide in a tall cylinder, 12 cm diameter by 58 cm high, the capacity being a little over 6 liters. In preparing our stannous hydroxide we at first had no trouble, the precipitate being white when filtered and remaining white during drying. After drying, the cakes of stannous hydroxide were covered with a thin coating having a slight yellow color, the inside of the cake being practically white. After making several batches in this manner we tried to prepare some from a hydrochloric acid solution of stannous chloride which contained some iron and lead. The cakes of the hydroxide after drying were black on the inside. The outside of the cake was white with a thin coating of a slight yellow color but the inside was black. The thickness of the white part varied in different attempts. Sometimes there was but a narrow streak of black while at other times the white covering was very thin with a corresponding increase in the thickness of the black layer. Sometimes the black was noted before filtering.

After having this difficulty we tried to prepare more catalyst from stannous chloride as we had prepared it at first. But our dried cake very often contained black material. In repeated attempts to get a satisfactory product it was noted that around the bottom of the cylinder black streaks would form in the precipitated mixture. These small black streaks corresponded to scratches in the glass caused by rubbing the stirrer against the side of the cylinder. Also in pouring out the suspension of

[1] Bury and Partington: Jour. Chem. Soc., 121, 1998 (1922).

stannous hydroxide black particles were noticed in the last part of the suspension. The cylinder was cleaned with concentrated hydrochloric acid and appeared perfectly clean. However upon again precipitating another batch of stannous hydroxide the black streaks again appeared and the dried cakes contained a black core.

When a 10 cm Buechner funnel was used about 5 filter cakes would be secured from one batch. Sometimes all of these would turn black. Often only the last cake or the last two would turn black. In filtering it was noted that the black particles seemed to be in the last portion. That is the black particles would settle more rapidly than the other particles. Likewise the last cake was usually the worst. This indicated that the black particles acted as catalysts causing the white to change to the black form which is probably the anhydrous stannous oxide. The cakes would vary from practically white to coal-black, depending upon the relative number of black and white particles. When a 19 cm Buechner funnel was used the entire precipitate would be collected in one filter cake. Upon allowing the cake to dry on drying paper it would crack in two or more pieces. Quite frequently one piece would have a black core while the other piece would be practically white throughout.

The cylinder was then cleaned with a strong solution of sodium hydroxide and our difficulties disappeared. There were no black streaks around the lower part of the cylinder. The filter cake after drying would be almost perfectly white with the thin coating of a slight yellow color. These observations indicate that the black particles act as a catalyst causing the white to become black. Only an extremely small number of black particles are necessary for we have an autocatalytic process.

Bury and Partington have shown in their work that moist stannous hydroxide reacts with air only slightly if at all. From their work the dried stannous hydroxide corresponds approximately to the formula $3SnO.2H_2O$. Hence it might better be called a hydrated stannous oxide.

## Experimental Results

In Table I are given results with four different catalysts. Catalyst F45 was prepared as above described. Catalyst F35 was prepared by soaking cleaned pumice (through 10 on 20 mesh) in 50% $SnCl_2.2H_2O$ solution. This was placed in a vacuum desiccator and evacuated. This was for the purpose of removing the air from the pores of the pumice. Then upon admitting air the solution is forced into these pores. The pumice was then dropped into a 20% solution of sodium carbonate and filtered, washed and dried. Catalyst F15 was prepared by igniting pumice with stannous chloride at 386° C until fumes quit coming off. The catalyst consisted of 6 grams of the ignited tin compound. Catalyst F25 was made by precipitating a 40% solution of $SnCl_2.2H_2O$ with a 10% solution of $(NH_4)2C_2O_4.H_2O$. These catalysts were all treated alike. They were heated in hydrogen at 294° C for one hour and then used at this same temperature in two experiments after which one experiment was carried out at each of the other temperatures in the order in which they are given in the table. The first experiment with each catalyst was not titrated and is not given in the table.

TABLE I

Catalysts heated in hydrogen at 294° C for 1 hour.
Rate of flow of hydrogen—14 liters per hour.
Rate of flow of nitrobenzene—9.3 grams per hour.
Excess of hydrogen—170%.

| Temperature ° C | Catalyst no. F45 | Catalyst no. F35 | Catalyst no. F15 | Catalyst no. F25 |
|---|---|---|---|---|
| | Catalyst from 11 gm tin hydroxide | Catalyst from 3.5 gm tin hydroxide on 6 gm pumice | Catalyst from $SnCl_2$ ignited on pumice | Catalyst from 12 gm of $SnC2O_4$ |
| | Material yield of aniline in percent of theory | | | |
| 294 | 89.0 | 71.6 | 58.8 | 90.5 |
| 275 | 78.9 | 56.4 | 38.9 | 85.3 |
| 256 | 42.3 | 37.1 | 25.2 | 77.4 |
| 237 | 21.5 | 14.8 | 13.8 | 48.9 |

The results of Table I show that the catalyst from the oxalate is the best and the one from the hydroxide a close second. The stannous hydroxide on pumice catalyst (Catalyst F35) is decidedly inferior to these two while the catalyst from the ignited stannous chloride is still worse.

Catalysts similar to the two best catalysts of Table I were now tested at different rates of flow of nitrobenzene. These results are given in Table II in the order in which the experiments were carried out.

TABLE II

All catalysts air dried.
Catalyst heated in hydrogen at 294° C for 1 hour.
Rate of flow of hydrogen—14 liters per hour.
Rate of flow of nitrobenzene[1]—5.6 grams per hour.
Excess of hydrogen—360%.

| Temperature °C | Catalyst no. F27 | Catalyst no. F28 | Catalyst no. F37 |
|---|---|---|---|
| | Catalyst from 13 gm tin hydroxide | Catalyst from 11 gm of tin oxalate | Catalyst from 13 gm of tin hydroxide |
| | Material yield of aniline in percent of theory | | |
| 294 | 97.9 | 94.6 | 97.5 |
| 294 | 96.0 | 94.6 | 97.4 |
| 275 | 94.2 | 91.6 | 92.7 |
| 256 | 92.0 | 80.8 | 84.9 |
| 237 | 82.3 | 56.9 | 66.6 |

[1] Catalyst F37 was used with the rate of flow of nitrobenzene at 4 grams per hour making the excess of hydrogen 540%.

On comparing the results of Table II with those given in Table I it is seen that a decrease in the rate of flow of nitrobenzene from 9.3 grams per hour to 5.6 grams per hour increased the yield of aniline with both the catalyst from the hydroxide and the one from oxalate. However, the increase in yield was greater with the catalyst from the oxide than with the one from the oxalate. Thus with the rate of flow of nitrobenzene at 5.6 grams per hour the catalyst from the hydroxide is the better while with the rate at 9.3 grams per hour the catalyst from the oxalate was the better. Catalyst F37, which was like F27 and

F45, was used with the rate of flow of nitrobenzene at 4 grams per hour. When these results (of F37) are compared with those of the other two catalysts (F27 and F45) it will be seen that the highest yields were obtained with F27 where the nitrobenzene flow was 5.6 grams per hour. This would indicate that a catalyst made by heating stannous hydroxide in hydrogen is better than one made from the oxalate.

In order to compare catalysts made from stannous and stannic chlorides a solution of stannic chloride was precipitated by sodium carbonate. The precipitated hydroxide dried to a very hard mass. When this was heated in hydrogen and then used as a catalyst the yields of aniline secured were less than $^1/_3$ the yields secured (under the same conditions) with a catalyst made from the hydroxide which had been prepared by precipitation from stannous chloride by sodium carbonate.

Of all these catalysts the catalyst from the stannous hydroxide, with the rate of flow of nitrobenzene at 5.6 grams per hour, was the best. The effect of various conditions on the activity of catalysts from stannous hydroxide was next determined. The stannous hydroxide was in each case prepared as described above and allowed to dry at room temperature. After drying the filter cake, the hydroxide was white throughout with a thin outer coating of a slightly yellow color. As noted above the work of Bury and Partington indicates that the reaction, if any, is slight between the moist stannous hydroxide and the air, and the composition of the dried material is probably $3SnO.2H_2O$.

In Table III are given the results with three catalysts prepared from the hydroxide which had been ignited in different ways. Each was ignited in a small porcelain dish at 300° C in a muffle for one hour. For catalyst F16, the stannous hydroxide was in the form of lumps during the ignition and a current of air was drawn through the muffle. After ignition this was ground to pass a 40 mesh sieve. For catalyst F36, the lumps of stannous hydroxide in the evaporating dish were covered with a watch glass and no air was drawn through the muffle during ignition. In making catalyst F46, the stannous

hydroxide was powdered to pass a 40 mesh sieve before ignition. During ignition the dish was kept covered with a watch glass as in catalyst F46. Upon ignition the stannous hydroxide burns to the $SnO_2$ with an evolution of heat. This makes it difficult to regulate the temperature during the first part of the ignition. Also when the stannous hydroxide burns to $SnO_2$ it becomes incandescent for a moment at the point where the oxidation takes place. The experiments are given in the table in the order in which they were carried out. After heating in hydrogen at 294° C two experiments were carried out at this temperature and then one experiment at each of the other temperatures. The first experiment with each catalyst was not titrated and is not given in the table.

TABLE III

Catalyst ignited at 300° C for one hour.
Catalysts heated in hydrogen at 294° C for one hour.
Rate of flow of hydrogen—14 liters per hour.
Rate of flow of nitrobenzene—5.6 grams per hour.
Excess of hydrogen—360%.

| Temperature °C | Catalyst no. F16 | Catalyst no. F36 | Catalyst no. F46 |
|---|---|---|---|
| | Grams used 17.5 | Grams used 14 | Grams used 15 |
| | Material yield of aniline in percent of theory | | |
| 294 | 96.0 | 96.0 | 92.7 |
| 275 | 96.4 | 93.7 | 94.9 |
| 256 | 94.9 | 89.0 | 84.6 |
| 237 | 89.0 | 60.8 | 53.4 |

These results show that Catalyst F16 was the best. This was the one in which a current of air was drawn through the muffle during ignition. Also the stannous hydroxide in lump form was in an open dish. This would indicate that a catalyst prepared from $SnO_2$ made by oxidizing stannous hydroxide is better than one made from stannous hydroxide directly. In the succeeding tables all the ignited catalysts were ignited in this manner.

The effect of temperature of ignition was next studied. The method of ignition was that which gave the best results in Table III. The results with catalysts ignited at different temperatures are given in Table IV. For convenience in comparison the results of F16 of Table III and F27 of Table II are included. The first experiment with Catalysts F16 and F26 were not titrated. The experiments are given in the order in which they were carried out.

TABLE IV

Catalysts heated in hydrogen at 294° C for one hour.
Rate of flow of hydrogen—14 liters per hour.
Rate of flow of nitrobenzene—5.6 grams per hour.
Excess of hydrogen—360%.

| Temperature ° C | Catalyst no. F27 | Catalyst no. F26 | Catalyst no. F16 | Catalyst no. F17 |
|---|---|---|---|---|
| | Grams used 13 | Grams used 16.5 | Grams used 17.5 | Grams used 13 |
| | Ignited at air dried | Ignited at 150° C | Ignited at 300° C | Ignited at 450° C |
| | Material yield of aniline in percent of theory | | | |
| 294 | 97.9 | —— | —— | 94.5 |
| 294 | 96.0 | 97.1 | 96.0 | 95.2 |
| 275 | 94.2 | 96.0 | 96.4 | 96.4 |
| 256 | 92.0 | 94.2 | 94.9 | 92.4 |
| 237 | 82.3 | 90.5 | 89.0 | 86.8 |

On comparing the results of Table IV the differences are seen to be very small. The results for F26 and F16 are a little higher than for the other two Catalysts, F26 being a little higher than F16, although this latter difference is well within experimental error. These results show that the lower the temperature of ignition, within the limits studied, the better the resulting catalyst. However, within relatively wide limits the difference due to temperature of ignition is small. Catalyst F27 which was merely air dried and not ignited gave lower results than those that were ignited.

To determine the effect of temperature of reduction a temperature of ignition of 300° C was chosen. Each catalyst in

lump form in an open dish was ignited at this temperature for one hour with a current of air through the muffle. They were then reduced for one hour at the temperatures indicated in Table V. To show the effect of length of time of reduction Catalyst F310 was reduced at 350° C for $3^3/_4$ hours. Catalysts F39 and F48 are duplicates and show how different catalysts, when made in the same way and treated alike check. These two catalysts were even used in different sets of apparatus. Catalysts F38 and F49 are likewise duplicates. For convenience in comparison the results with Catalyst F16 of Table III are included. The experiments are given in the order in which they were carried out.

TABLE V

Catalysts ignited at 300° C for one hour.
Rate of flow of hydrogen—14 liters per hour.
Rate of flow of nitrobenzene—5.6 grams per hour.
Excess of hydrogen—360%.

| Temperature °C | Catalyst no. F29 | F16 | F38 | F49 | F310[1] | F39 | F48 |
|---|---|---|---|---|---|---|---|
| | Grams used | | | | | | |
| | 15.5 | 17.5 | 14 | 15.5 | 15.5 | 15.5 | 14.0 |
| | Reduced at C | | | | | | |
| | 237° | 294° | 350° | 350° | 350° | 420° | 420° |
| | Material yield of aniline in percent of theory | | | | | | |
| 294 | 97.1 | —— | 95.7 | 94.2 | 94.2 | 97.5 | 96.8 |
| 294 | 96.4 | 96.0 | 97.1 | 96.1 | 96.8 | 97.5 | 96.4 |
| 275 | 95.3 | 96.4 | 95.3 | 94.9 | 95.7 | 94.6 | 96.4 |
| 256 | 95.3 | 94.9 | —— | 92.7 | 88.7 | 92.4 | 92.7 |
| 237 | 92.0 | 89.0 | —— | 81.6 | 71.0 | 74.2 | 72.7 |

[1] Catalyst F310 was reduced for $3^1/_4$ hours instead of one hour.

The experiments of Table V show that the lower the temperature of reduction the better the catalyst (within the limits studied). However, this difference is not great and at the two higher temperatures the results are practically the same within experimental error. Also the length of time of reduction at 350° C has but a small effect upon the activity of the

catalyst. Thus Catalyst F310 gave practically the same yields as F49 at the higher temperatures, although at the lower temperatures the results with F310 are lower, indicating a slight loss in activity due to prolonged reduction at 350° C.

Catalyst F410 was used to determine the effect of length of time of ignition. The results with this catalyst are given in Table VI. It was ignited at 300° C for three hours while Catalyst F49 of Table V was ignited but for one hour at this temperature. The results with Catalyst F49 of Table V are included in Table VI for purposes of comparison.

TABLE VI

Catalysts ignited in air at 300° C.
Catalysts heated in hydrogen at 350° C for one hour.
Rate of flow of hydrogen—14 liters per hour.
Rate of flow of nitrobenzene—5.6 grams per hour.
Excess of hydrogen—360%.

| Temperature °C | Catalyst no. F410 | Catalyst no. F49 |
|---|---|---|
| | Grams used 15.5 | Grams used 15.5 |
| | Time of ignition 3 hours | Time of ignition 1 hour |
| | Material yield of aniline in percent of theory | |
| 294 | —— | 94.2 |
| 294 | 92.4 | 96.1 |
| 275 | 93.1 | 94.9 |
| 256 | 94.6 | 92.7 |
| 237 | 84.6 | 81.6 |

The results of Table VI show that the activity of a tin catalyst is reduced by prolonged ignition of the oxide at 300° C prior to reduction. Thus the highest yield obtained with catalyst F410 was 94.6 while Catalyst F49, which was ignited but one hour, gave a yield of 96.1% in the second experiment. However, at the lower temperatures F410 (ignited for 3 hours) gave the higher yields. Temperature does not have so large an effect on F410 as on F49. Thus with F410 the greatest difference in yield is 8.5% while with F49 the greatest difference is 14.5%.

In all the foregoing experiments the catalysts (except those on pumice) were put through a 40 mesh sieve. The effect of mesh size of the catalyst on its activity is shown in Table VII. The last column, F210X, shows the effect of oxidation and reduction. After using Catalyst F210, in the experiments given in the first column it was oxidized at 300° C for one hour by a current of air and then reduced at 294° C for one hour. It was then used in the experiments listed under F210X. The results with Catalyst F49 of Table V are included for convenience in comparison. The experiments are given in the order in which they were carried out.

TABLE VII

Catalysts ignited in air at 300° C for one hour.
Catalysts heated in hydrogen at 350° C for one hour.
Rate of flow of hydrogen—14 liters per hour.
Rate of flow of nitrobenzene—5.6 grams per hour.
Excess of hydrogen—360%.

| Temperature °C | Catalyst no. F210 | Catalyst no. F110 | Catalyst no. F49 | Catalyst no. F210X |
|---|---|---|---|---|
| | Grams used 15.5 | Grams used 15.5 | Grams used 15.5 | Grams used 15.5 |
| | Mesh size through 4 on 6 | Mesh size through 10 on 20 | Mesh size through 40 | |
| | Material yield of aniline in percent of theory | | | |
| 294 | 98.3 | 94.2 | 94.2 | —— |
| 294 | 95.7 | 95.7 | 96.1 | 96.8 |
| 275 | 96.1 | 94.6 | 94 9 | 94.6 |
| 256 | 94.9 | 95.3 | 92.7 | 93.4 |
| 237 | 90.9 | 91.2 | 81.6 | 81.6 |

On comparing the results of the first three columns of Table VII it will be seen that the results in the third column are lower than those in the other two columns, especially at the lower temperatures. That is the catalyst from the finest material was the poorest. Catalysts F210 and F110 gave practically the same results, the yields with Catalyst F210 averaging slightly higher although the difference is well within experimental error. These results show that a catalyst from

a rather coarse material is the better although the difference is not large.

The results of F210X compared with F210 show that oxidation and reduction decreased the yields somewhat, especially at the lowest temperature, indicating that after oxidation and reduction its activity is not quite as high as it originally was.

TABLE VIII

Catalysts ignited in air at 300° C for one hour.
Catalysts heated in hydrogen at 350° C for one hour.
Mesh size—through 40 mesh.
Rate of flow of hydrogen—14 liters per hour.
Rate of flow of nitrobenzene—5.6 grams per hour.
Excess of hydrogen—360%.

| Temperature ° C | Catalyst no. F49 | Catalyst no. F19 |
|---|---|---|
| | Grams used 15.5 | Grams used 15.5 |
| | Catalyst tube Glass | Catalyst tube Iron |
| | Material yield of aniline in percent of theory | |
| 294 | 94.2 | 83.1 |
| 294 | 96.1 | 84.2 |
| 275 | 94.9 | 87.2 |
| 256 | 92.7 | 90.1 |
| 237 | 81.6 | 91.6 |
| 294 | 99.0 | 87.2 |
| 312 | 99.4 | 85.0 |
| 331 | 98.3 | 79.3 |

All the foregoing experiments have been carried out with the catalyst in a glass combustion tube. In Table VIII are given comparative values for catalysts in glass and iron tubes. The two catalysts for Table VIII were prepared exactly alike and used under the same conditions. The stannous hydroxide was ignited in a current of air at 300° C for one hour. It was in the form of lumps in an open dish. After ignition it was ground to pass through a 40 mesh sieve.

The results of Table VIII are plotted in Figure 1. The average of the three results at 294° C for each catalyst is used

in plotting the curves. The experiments of Table VIII are given in the order in which they were carried out. It will be noted that this is first with decreasing temperature and then with increasing temperature. The curve with the catalyst in an iron tube is the opposite of that with the catalyst in a glass tube. Thus in an iron tube the highest yield was secured at the lowest temperature while with the glass tube the lowest yield was secured at this temperature. As the temperature was increased the yield with the catalyst in a glass tube increased while with the catalyst in an iron tube the yield decreased. We are unable to account for this difference in behavior in iron and glass.

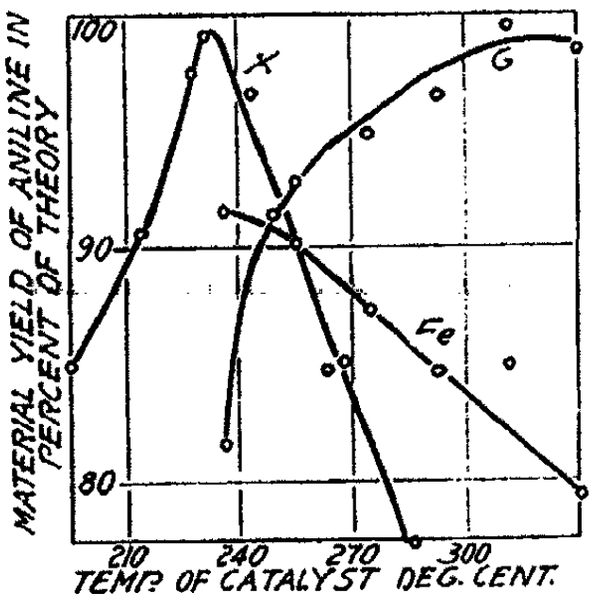



Fig. 1

In the foregoing tables it will be noted that each catalyst was first used in two experiments at 294° C and then in one experiment at 275°, 256° and 237° C, respectively.[1] This was the method that was chosen as a means of studying a catalyst. The catalyst giving the highest yields of aniline has been called the best catalyst. For convenience it has often been styled the most active.

The results of the first two tables show that of all the tin catalysts studied, the one prepared from the stannous hydroxide was the best. All the catalysts in the succeeding tables were then prepared from this material which had been precipitated and dried as described in the first part of this paper. Table III showed that the best way to ignite the stannous hydroxide was by placing it, in the form of lumps, in an open dish and drawing a current of air through the muffle during ignition. All

[1] Catalysts F19 and F49 were used further but were first used as outlined above.

of the subsequently ignited catalysts were ignited in this way. In Table IV it was found that temperature of ignition did not have, within the limits studied, a great importance. However, catalysts ignited at 150° and 300° C were slightly better than the other catalysts, the difference between these two catalysts being well within experimental error. The catalysts in the later tables were prepared from the oxide which had been ignited at 300° C by the method which gave the highest yields in Table III. Table B showed that the lower the temperature of reduction the better the catalyst, although within rather wide limits the difference was not great. Prolonged ignition, according to Table VI is injurious. In the later tables the ignition period was in each case one hour. Catalyst F310 of Table V had likewise shown that prolonged heating in hydrogen at 350° C was slightly injurious. So the catalysts in the later tables were heated in hydrogen for one hour. In Table VII it was seen that a catalyst in the lump form was somewhat better than when in the powdered state. However all the other catalysts were put through a 40 mesh sieve. Table VIII shows that a glass tube is better than an iron tube. In all the tables except Table VIII a glass tube was used. From these results the best tin catalyst is prepared by ignition of the stannous hydroxide at 150° to 300° C for one hour and heating the resulting oxide in hydrogen at a low temperature (237° C) for one hour. The lump form is preferable to the powdered condition and a glass catalyst tube is superior to an iron one.

In the previous tables no thorough study has been made of the effect of temperature although all of the catalysts have been used at several different temperatures, which was the method chosen of studying a particular catalyst. The effect of temperature was now studied with a catalyst prepared and used under the best conditions as outlined in the latter part of the last paragraph, with the exception that the catalyst was powdered instead of in the lump form. The results are given in Table IX. Catalyst F211 was prepared from an oxide ignited at 300° C for one hour. Results under F211X are with this same catalyst after it had been used in the experiments

listed in the first column. The experiments are given in the order in which they were carried out. Catalyst F413 was prepared like F211 and shows how different catalysts used in different apparatus check. Results with Catalyst F111 are also given. This catalyst was not ignited.

TABLE IX

Catalysts ignited in air at 300° C for one hour.
Catalysts heated in hydrogen at 237° C for one hour.
Mesh size—through 40 mesh.
Rate of flow of hydrogen—14 liters per hour.
Rate of flow of nitrobenzene—5.6 grams per hour.
Excess of hydrogen—360%.

| Temperature °C | Catalyst no. F211 | Catalyst no. F211X | Catalyst no. F413 | Catalyst no. F111[1] |
|---|---|---|---|---|
| | Grams used 16 | Grams used 16 | Grams used 16 | Grams used 15.5 |
| | Material yield of aniline in percent of theory | | | |
| 237 | 90.9 | 90.9 | 73.9 | 71.3 |
| 256 | 96.4 | 95.3 | 92.0 | 93.8 |
| 275 | 98.6 | 96.8 | 97.5 | 94.9 |
| 294 | 98.3 | 94.6 | 98.6 | 95.7 |
| 311 | 98.6 | 96.1 | 97.5 | —— |
| 330 | 98.3 | 96.8 | 97.9 | —— |
| 350 | 97.5 | 96.4 | 97.5 | —— |
| 368 | 90.5 | 87.5 | 95.7 | —— |

[1] Catalyst F111 was not ignited but was merely air dried.

The yields with the catalyst which was not ignited (F111) are much lower than with the other catalysts. This is in accord with the results of Table IV although the order of carrying out the experiments was different. The results with Catalyst F413 (except at the highest and lowest temperatures) compare very well with the results with Catalyst F211. The results under F211X are lower than under F211. This would indicate that use at the higher temperatures decreased to a small extent the activity of the catalyst.

The results with Catalyst F211 are shown graphically in curve Sn of Figure 2. It will be noted that high yields are

secured within a rather wide range of temperature. This will be especially noted upon comparing this curve with the curves for nickel and copper which have been redrawn from the data of a previous paper.[1] These high yields within the wide range of temperature would be distinctly advantageous commercially as it would not be necessary to control temperature within such narrow limits. The best temperature for carrying out the reaction in a glass tube is probably 275° to 294° C.

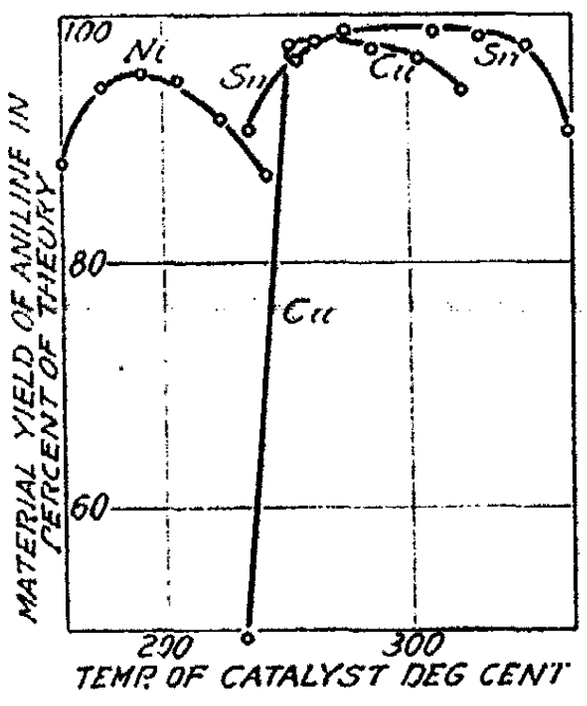



Fig. 2

The effect of rates of flow of hydrogen and nitrobenzene was now studied. In all the previous experiments except in Tables I and II the rate of flow of nitrobenzene was 5.6 grams per hour and the rate of flow of hydrogen was 14 liters per hour. The results with different rates of flow of nitrobenzene and the flow of hydrogen at 14

TABLE X

Catalysts ignited at 300° C for one hour.
Catalysts heated in hydrogen at 237° C for one hour.
Mesh size—through 40 mesh.
Temperature of catalyst—294° C.
Rate of flow of hydrogen—14 liters per hour.

| Rate of flow of nitrobenzene in grams per hour | Excess of hydrogen in percent | Material yield of aniline in percent of theory |
|---|---|---|
| 5.6 | 360 | 95.7 |
| 5.6 | 360 | 97.1 |
| 3.8 | 580 | 96.1 |
| 7.3 | 250 | 95.3 |
| 9.3 | 170 | 93.8 |
| 13.9 | 80 | 90.1 |
| 5.6 | 360 | 96.8 |

[1] Brown and Henke: Jour. Phys. Chem., 26, 161 (1922).

liters per hour are given in Table X. The catalyst for these experiments was prepared and used under the best conditions as previously determined with the exception that it was put through a 40-mesh sieve and not used in the lump form. It weighed 16 grams. The experiments are given in the table in the order in which they were carried out.

The results of Table X are plotted in Curve Sn of Figure 3. The first experiment is not used as this is frequently irregular. It will be noted that the last experiment was carried out under the same conditions as the first two. It checks well with the second showing that the catalyst did not change appreciably during use. In plotting, the average of the second and last experiments is used for that point. For purposes of comparison the curves for nickel and copper (from the precipitated oxide) are redrawn from the data of a previous paper.[1] Only at one point is the curve for tin below that for copper and here the difference is within experimental error. In fact in most places the values for tin are above those for copper. Tin is likewise superior to nickel at all but the highest rates while at the lower rates the yields with tin are far superior to those for nickel.

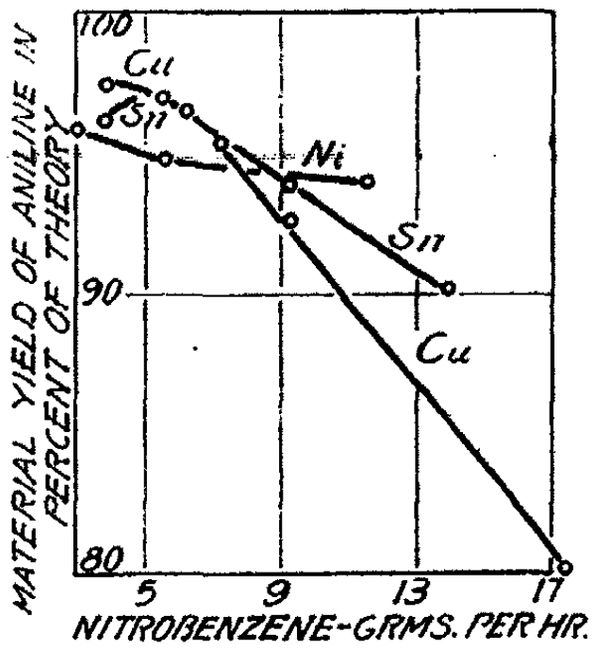



Fig. 3

The effect of flow of hydrogen with the rate of flow of nitrobenzene at 5.6 grams per hour is shown in Table XI. The catalyst for these experiments was prepared exactly like the catalyst for the experiments of Table X, 16 grams of catalyst being used.

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[1] Brown and Henke: Jour. Phys. Chem., 26, 161, 715 (1922).

The results of Table XI are shown graphically in Curve Sn of Figure 4. It will be noted that the last experiment was carried out under the same conditions as the first two. The average of the second and last experiments is used in plotting the curve, the first being, as usual, not considered. The curves for nickel and copper (from the precipitated oxide) are redrawn from the data of previous papers. The curve for tin has a different shape than the other two curves. Thus the decrease in yield with too much or too little hydrogen is more rapid than with the other two catalysts. However, the region within which high yields are secured is as wide or wider with tin than with the other catalysts.

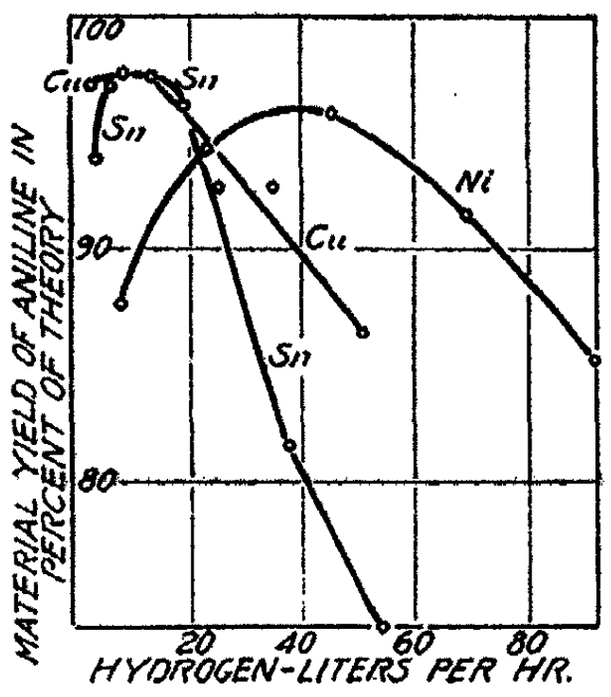



Fig. 4

On comparing the curves for tin with those for copper and

TABLE XI

Catalysts ignited in air at 300° C for one hour.
Catalysts heated in hydrogen at 237° for one hour.
Mesh size—through 40 mesh.
Temperature of catalysts 294° C.
Rate of flow of nitrobenzene—5.6 grams per hour.

| Rate of flow of hydrogen in liters per hour | Excess of hydrogen in percent | Material yield of anilline in percent of theory |
|---|---|---|
| 14 | 360 | 95.7 |
| 14 | 360 | 96.8 |
| 24 | 700 | 96.1 |
| 38 | 1160 | 81.6 |
| 55 | 1730 | 73.9 |
| 9 | 200 | 97.5 |
| 4.5 | 50 | 93.8 |
| 14 | 360 | 97.9 |

nickel (in Figures 2, 3 and 4) one is led to believe that for producing aniline a tin catalyst from stannous hydroxide would be better than one from precipitated copper oxide or ignited nickel oxide. Thus in Figure 2 the curves show that tin will give high yields over a wider range of temperature than either nickel or copper. As a result a tin catalyst would not necessitate such close temperature control as copper or nickel, which would be a distinct advantage commercially. In Figure 3 the curves for tin and copper are very close together, both being higher than nickel except at extremely high rates. In Figure 4 tin and copper are again close together both being higher than nickel. But here again tin gives high yields over a little wider range in rate of hydrogen flow than copper.

In using tin as a catalyst quite frequently small amounts of a white solid was observed at the exit end of the catalyst tube. Not enough of the material was secured to determine what it was. It was only slightly volatile as it would condense in the catalyst tube before reaching the condenser. We never secured more than a small amount of it and do not know what conditions are the most favorable for its preparation.

When ortho-nitro-toluene was used instead of nitrobenzene a 94.1% yield of ortho-toluidine was secured. The rate of flow of ortho-nitro-toluene was 5.6 grams per hour, and of the hydrogen 7 liters per hour. The temperature of the catalyst was 275° C. The catalyst had been prepared under the best conditions as determined above except it was in the powdered form instead of in lumps. When ortho-nitro-anisole was used under the same conditions that the ortho-nitro-toluene was used, a 93% yield of anisidine was secured.

A few experiments were carried out in an iron tube with a catalyst of stannous hydroxide which had been dried at 100° C. Twenty-three grams of catalyst was used which is about 50% more than was used in the previous experiments of this paper. This catalyst was heated in hydrogen at 288° C for 1½ hours and then used at this temperature. The results are given in Table XII. The experiments are given in the order in which they were carried out.

TABLE XII

Rate of flow of hydrogen—14 liters per hour.
Rate of flow of nitrobenzene—4 grams per hour.
Excess of hydrogen—640%.

| Temperature ° C | Material yield of aniline in percent of theory |
|---|---|
| 287 | 77.3 |
| 269 | 85.1 |
| 264 | 84.8 |
| 245 | 96.5 |
| 227 | 97.5 |
| 215 | 90.6 |
| 196 | 85.0 |
| 232 | 99.1 |
| 251 | 91.3 |

The results of Table XII are plotted in Curve X of Figure 1. It will be noted that this curve is similar to the Curve Fe. The highest yield on Curve X is at 232° C, while in Curve Fe the highest yield is at 237° C which was the lowest temperature used. The shape of Curve Fe indicates that a still lower temperature would have increased the yield but slightly if at all. However, much higher yields are secured in Curve X than in Curve Fe. The higher yields cannot be due to the difference in the method of preparing the catalysts. Thus the catalyst for Curve Fe was ignited while the one for Curve X was not, which would make the catalyst of Curve Fe the better instead of the worse. The difference in reduction temperatures would not have much effect. However, 50% more catalyst was used for Curve X than for Curve Fe which probably is the cause for the higher yields of Curve X. Also the rate of flow of nitrobenzene was lower in Curve X than in Curve Fe. At 287° C, Curve X is lower than Curve Fe. The low yield at 287° C is due to the reduction being carried too far, the odor of ammonia being pronounced. These results show that the best temperature for the reaction with tin as catalyst in an iron tube is 232° to 237° C. Also a greater amount of catalyst in a given space (within the above limits) increased the yield of amine.

Tin was then tried in furnaces of larger capacity and different design. Using a catalyst from 100 grams of the oxide in a vertical furnace (iron catalyst tube), 99% yields of aniline were secured at 232° C with the rate of flow of nitrobenzene at 29 grams per hour, and the rate of flow of hydrogen at 19 liters per hour. In this experiment excess of hydrogen was only 20%. Larger excesses of hydrogen gave similar high yields. After carrying out several experiments with nitrobenzene ortho-nitro-toluene was used. With the rate of flow of ortho-nitro-toluene at 20 grams per hour and that of the hydrogen at 14 liters per hour (40% excess hydrogen) 98 to 99% yields of ortho-toluidine were secured with the catalyst at 250° C. With the hydrogen flow at 23 liters per hour (130% excess hydrogen) similar high yields of ortho-toluidine were secured. This indicates that the process may have commercial possibilities.

## Summary of Results

1. Tin has been shown to be an excellent catalyst for the reduction of nitrobenzene to aniline by hydrogen.

2. Of all the tin catalysts studied the one made from the hydroxide, prepared by precipitation with sodium carbonate from a stannous chloride solution, was the best.

3. Oxidation of the hydroxide, prior to reduction, increased the efficiency of the resulting catalyst, the lower the temperature of oxidation, within the limits studied, the better the resulting catalyst.

4. The lower the temperature of reduction of the oxide within the limits studied, the better the resulting catalyst.

5. A tin catalyst in the form of rather coarse lumps is better than in the powdered form.

6. The behavior of a catalyst in glass and iron catalyst tubes is very different, a higher temperature being necessary in glass than in iron.

7. A larger temperature variation is permissible with tin than with many other catalysts. Probably 275° to 294° C

is the best temperature for the production of aniline when a glass catalyst tube is used.

8. The best rates of flow of nitrobenzene and hydrogen with the tin catalyst compare rather closely with those for copper.

9. When ortho-nitro-toluene and ortho-nitro-anisole were used instead of nitrobenzene, 94.1 and 93% yields were secured of ortho-toluidine and ortho-anisidine, respectively.

10. Experiments carried out in apparatus of larger capacity and different design gave yields of 99% aniline and 98 to 99% yields of ortho-toluidine, indicating that the process may have commercial possibilities.

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# FLUOSILICIC ACID. II

BY C. A. JACOBSON

1086

It has generally been considered as an accepted fact that fluosilicic acid may occur undecomposed in the vapor state as well as in solution. This assumption received apparent verification in the results of experiments by E. Baur and A. Glaessner [Ber., 36, page 4215 (1903)]. These experimenters conclude, however, that at a temperature over 100° more than two-thirds of the fluosilicic acid present will be decomposed.

Examining their results it is seen that the mean molecular weight of the gas obtained from $BaSiF_6$ and $H_2SO_4$ at 23° was 82.7 while that at 31.5° was 81.9. If the $H_2SiF_6$ had come over undecomposed a vapor density of 144.31, on the basis of $O_2 = 32$, would have been obtained. According to the results of Thorpe and Hamby[1] the density of hydrogen fluoride on the same basis, was 51.59 at 26.4°, 49.8 at 27.8°, 45.9 at 29.2°, 40.06 at 32°, and 20.75 at 88.1°. These values when extrapolated will show a vapor density of 59 at 23°, which is the temperature at which Baur and Glaessner (loc. cit.) obtained a vapor density of 82.3 for the gas mixture from fluosilicic acid at a pressure of 764 mm. When the vapor density of hydrogen fluoride is 60 its molecular composition must be $H_3F_3$.

At the temperatures in question it is more than likely that hydrogen fluoride is present both as $H_2F_2$ and $H_3F_3$ with a preponderance of $H_3F_3$ since this is the stabler form at 23°. When the decomposition of fluosilicic acid takes place in two ways simultaneously as shown in reactions (1) and (2),

$$H_2SiF_6 = H_2F_2 + SiF_4 \qquad (1)$$

$$3H_2SiF_6 = 2H_3F_3 + 3SiF_4 \qquad (2)$$

31.1% going according to (1) and 68.9% according to (2) the vapor density of the mixture or mean molecular weight

[1] Jour. Chem. Soc., **55**, 163 (1899).

will be 82.1, which is very close to the values of Baur and Glaessner. On this basis no molecules of $H_2SiF_6$ are present. In the previous paper it is seen that upon distilling fluosilicic acid a distillate was obtained yielding a concentration of 49.61% of this acid, and therefore it might be contended that the acid exists in the vapor phase.

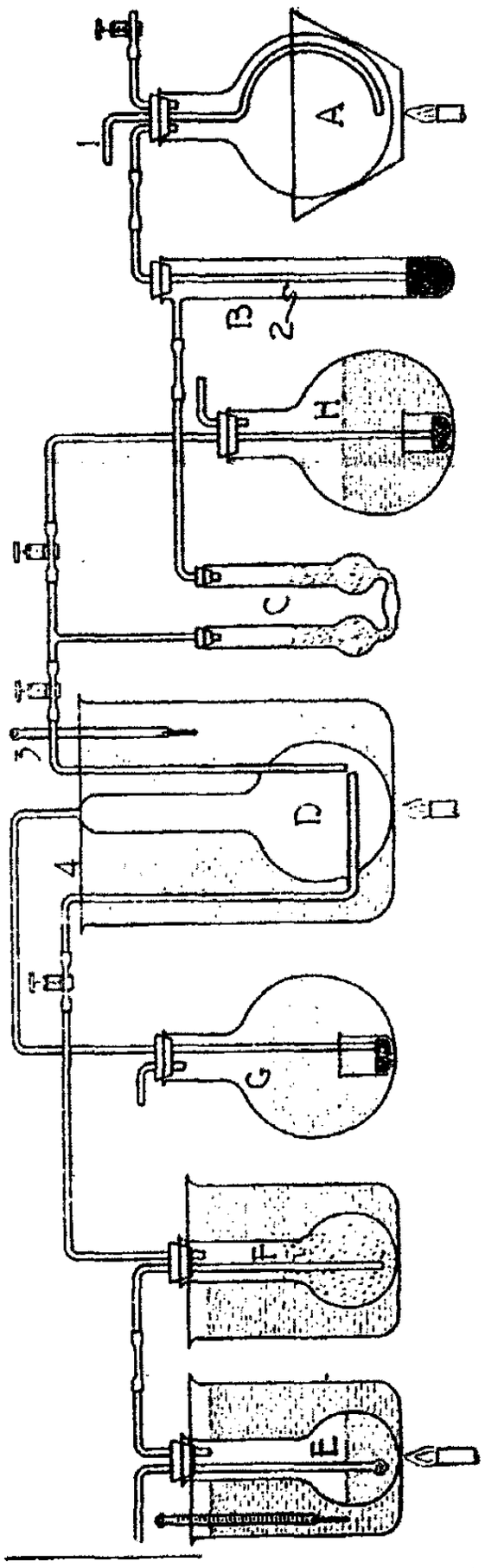


Fig. 1

Four series of experiments have been undertaken, bearing upon the state of this acid. Three of these depend upon the coexistence of water vapor and $SiF_4$ in the vapor phase without precipitating silica. It became necessary, therefore, to determine with great care if the following reaction, suggested by Hudleston and Bassett,[1] could take place in the vapor state.

$$SiF_4 + 2H_2O = SiO_2 + 4HF \quad (3)$$

An apparatus as shown in Figure 1 was assembled, the right hand side of which served for the generation of silicon-tetrafluoride and the left hand side for water vapor. A mixture of fluorspar, precipitated silica, and six to seven parts of conc. $H_2SO_4$ were introduced into flask A, which was con-

[1] Jour. Chem. Soc., **119**, 412 (1921).

nected with B by means of a glass tube ending below mercury in the bottom of this tube. This arrangement was to permit a better control of the flow of gas. B was in turn connected with a Peligot tube C containing glass wool, to remove any traces of HF that might get over. Bulb D was especially constructed of glass so as to permit the two vapors to enter it simultaneously, and then pass out through an opening at the top. D had a capacity of about 150 cc. $SiF_4$ was admitted through Tube 3, and water vapor through Tube 4. The two gases were then aspirated out through G, containing water.

E was a 100 cc round bottom flask fitted with a two hole rubber stopper holding a glass bubbler. Through the other hole in the stopper passed a glass tube connecting with flask F, which contained glass wool, to intercept any particles of liquid water which might be carried over from E. About 50 cc of water was put in E, and air aspirated through the same into D, by means of a filter pump connected with G. This flask had a capacity of two liters and was half full of water. In the bottom of G was a small beaker containing mercury, into which the glass tube connected with D dipped. H was another two liter flask half full of water, connected with C by means of a T tube and a glass tube bent at right angle, as shown in the cut. This flask was also provided with a small beaker of mercury like G, and served to absorb the excess of silicon tetrafluoride.

With this apparatus experiments were run at three different temperatures, but a different tube at D was used for each temperature, in order that the slightest deposit of silica in the same might be detected. Tube D was supported in a beaker of water, the water extending to within an inch of the top. Flasks E and F were also immersed in water contained in beakers.

For the first experiment the water in the beaker surrounding bulb D was held at 35°, while that surrounding E and F remained at room temperature. Air was aspirated through these flasks in a slow but constant stream. The generation of $SiF_4$ was started in flask A, with the screw clamp on the tube

connecting with H open, while that on the tube connecting with 3 closed. As soon as the air had been driven out of C, the latter clamp was opened gradually, while the former was screwed up little by little, until a slow stream of $SiF_4$ was admitted into D, where it met the moist air from E. The two gases were allowed to pass in together for about twenty minutes, after which D was taken out and examined. A very light deposit of silica was observed on the glass near the confluence of the two gases, but toward the top of the tube there was no deposit visible. The second and third experiments were performed exactly like the first, except that a new tube was used at D in each case, and the bath containing this tube was held at 80° in the second experiment, and 95–96° in the third, while flasks E and F were kept at 40° for the second, and 45° for the third experiment. At the end of these experiments a scarcely visible trace of deposited silica was found in D from the second experiment, while in the third D remained perfectly clean, without a trace of deposited silica. In all these experiments that portion of D which was above the bath liquid condensed water and held a very heavy deposit of silica. A fourth experiment was performed, admitting live steam together with $SiF_4$ into a tube of different construction corresponding to D, which was kept at a temperature of 120–125° in a bath of paraffin. At the end of twenty minutes no trace of deposited silica could be observed in the tube except where a few drops of water fell into it from the connecting tube.

These experiments establish the fact that reaction (1) does not take place in the gaseous phase between 95° and 125°, and in all probability does not take place at higher temperatures. The experiments also show that silicon tetrafluoride and water vapor do not react with each other between 30° and 80° C, except to a very insignificant degree.

The first method arranged for throwing light upon the state of $H_2SiF_6$ consisted of a gas flow meter constructed of glass, having a capacity of about 100 cc per minute under a pressure of 10 cm of water. This flow meter was accurately calibrated, and a curve drawn for the same. The flow of air in cc per

minute could thus be read directly from the curve for any given pressure maintained during the experiments.

Three 100 cc flasks were clamped in a water bath, immersed to the neck in water. Two of the flasks contained 50 cc each of the $H_2SiF_6$ solution to be examined, and the third flask 50 cc of water. Two hole rubber stoppers were fitted into these, each holding two glass tubes, one ending just below the stopper, and the other drawn to a narrow opening and ending below the surface of the liquid. A fourth flask containing water for absorption was clamped outside of the bath and connected with the second flask containing the acid solution. The flasks were all connected with one another by means of glass tubing and very short rubber connections, in such a manner that the measured air first bubbled through the water and then through the acid solutions. This was done in order to minimize concentration of the acid solutions due to evaporation of water into the stream of air. The results of the nine experiments performed with this apparatus are summarized in the following table.

TABLE I

| Concentration of $H_2SiF_6$ % | Temp. °C | Pressure in mm of $H_2O$ | Time in minutes | No. of cc passed | Gm $H_2SiF_6$ found in absorption $H_2O$ |
|---|---|---|---|---|---|
| 9.75 | 50 | 155 | 180 | 24,300 | 0.00126 |
| 9.75 | 70 | 155 | 180 | 24,300 | 0.00202 |
| 9.75 | 88 | 160 | 174 | 24,306 | 0.01210 |
| 15.00 | 50 | 165.5 | 155 | 22,382 | 0.00076 |
| 15.00 | 70 | 168 | 166 | 24,528 | 0.00760 |
| 15.00 | 88 | 170 | 164 | 24,420 | 0.02922 |
| 23.98 | 50 | 185 | 151 | 24,235 | 0.00479 |
| 23.23 | 70 | 166 | 168 | 24,276 | 0.01335 |
| 21.75 | 88 | 176 | 159 | 24,327 | 0.08692 |

These results show in a striking manner, that a rising temperature accelerates the decomposition of $H_2SiF_6$ much more rapidly than the increase in concentration up to 24%. If negative results had been obtained in these experiments they would have been fairly conclusive in establishing that, up to the

temperature and concentration employed the acid does not exist in the vapor phase.

For the second method the apparatus shown in the foregoing paper was employed. For Experiment 1, a strong solution of $H_2SiF_6$ was put into A. Then a large porcelain boat, nearly filled with recently boiled concentrated sulfuric acid, was placed in C, the receiver B connected up and packed in an ice-salt mixture, and the apparatus evacuated to 8 mm. At the end of 24 hrs. the receiver was taken out and examined. There was no trace of a liquid of any sort in it. A duplicate experiment was run with fresh $H_2SO_4$, yielding the same result.

Experiments 3, 4, and 5 were carried out in the same manner as the first two, except that anhydrous copper sulfate, calcium chloride, and phosphorus pentoxide were used respectively as desiccating agents, and held in two porcelain boats instead of one. Negative results were obtained in every case except when calcium chloride was used. Here a fine dew like deposit had formed on the sides of the flask. After the silicon tetrafluoride vapors had been removed from the receiver, this liquid deposit was washed out with water and titrated, showing that a small amount of $H_2SiF_6$ was present.

The third method is a modification of the second in that it provides for the removal of silicon tetrafluoride, one of the gaseous products of decomposition of the acid, which would accumulate and interfere with the passage of the fluosilicic acid vapors if they were present. The apparatus as arranged for the experiment is depicted in Figure 2.

Flask A had a capacity of 300 cc and was connected with flask B by a glass tube ending just below the rubber stopper. This tube was bent at two right angles, and the other end inserted in B, ending just above the surface of the liquid in B. This flask was similarly connected with C, the latter being connected with a long narrow side neck glass tube D, which was surrounded with ice in the tall four inch glass cylinder, as shown in the cut. A small glass tube was drawn out to a fine point, but not sealed, and inserted in D so that the apparatus could

be exhausted by means of it through the filter flask E. Another glass tube was drawn out to a fine point and fitted into A, so that the pin point opening was below the surface of the liquid. A rubber tube with screw cock being fitted on its upper end, so as to permit air to be drawn through in a very fine stream.

The three flasks were mounted in an air bath G, and about 100 cc of the 60% solution of fluosilicic acid, obtained as explained in the foregoing paper, were introduced into A, and connected up with B, C, and D in the manner just described. For the preliminary experiments, B and C were empty. The

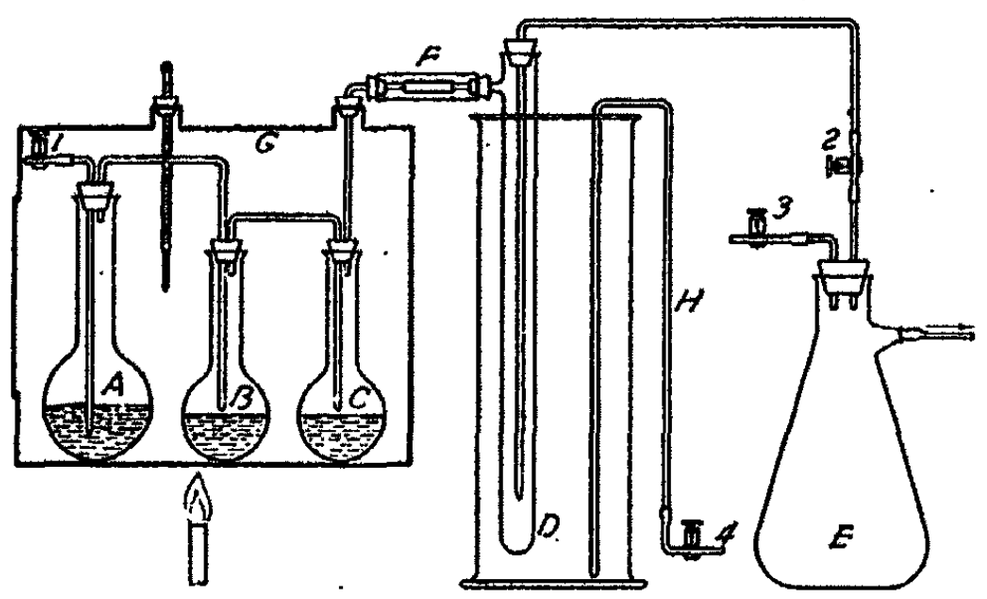



Fig. 2

system was exhausted through E, by means of a water filter pump, and the temperature of the air bath raised to about 90°, when the acid solution in A began to boil briskly. The temperature was dropped to 83°, and a slow ebullition continued for twenty minutes, while an exceedingly fine stream of air was admitted to A through the glass tube. The experiment was then stopped, all $SiF_4$ removed from D, and the condensed liquid in this tube washed out and titrated, showing that 0.039833 g $H_2SiF_6$ had been formed, which would have amounted to 0.119499 g if the experiment had been continued for one hour.

For the second experiment the apparatus remained exactly as in the first, but in flask B were introduced 100 cc of recently boiled concentrated sulfuric acid. This time the acid in A was kept at 85°, and therefore boiled a little more strongly than before, and the boiling continued for exactly one hour. After blowing out the $SiF_4$ from D its liquid contents were titrated, showing the presence of 0.008840 g $H_2SiF_6$. Experiment 3 was identical with the preceding with the exception that 100 cc $H_2SO_4$ were kept in each of the flasks B and C. The temperature of the air bath was 85°, and the boiling continued for one hour. This time the contents of D yielded 0.002201 g $H_2SiF_6$. These results are to each other as 54:4:1, which would indicate, that with perfect desiccation of the stream of vapor, no $H_2SiF_6$ would be found in the receiver D. The results of this method as well as those of the second point strongly toward the assumption that fluosilicic acid is non-volatile.

The apparatus for the fourth method was that used for the concentration of the acid, shown in the foregoing paper. 27.6 g pure dry sodium fluosilicate were introduced into A and in this powder was put a short specimen tube of conc. $H_2SO_4$, placed in an upright position. The receiver B, was packed in ice and salt, and surrounded with mohair packing. After exhausting the apparatus it was tilted so that the sulfuric acid ran into the salt. A slow effervescence began immediately and continued for several hours. Bulb A was kept at room temperature, and the pressure inside the apparatus was watched by means of an attached manometer. At the end of twenty-four hours the apparatus was demounted and examined. In the receiver B was not a drop of liquid of any kind, not even a sign of a deposited mist. Water was then added to B, whereupon a voluminous precipitate resulted, suggesting that $SiF_4$ had been present. $H_2SiF_6$ was identified in the filtrate.

The following observation should receive mention here since it throws light upon the chemical properties of this acid. Bulb A, Figure 1 in the foregoing paper, was employed as

the distillation flask and B as the receiver. After continued use A became etched but B remained clear, except for a cloudiness near the bottom. The etching in A was most pronounced at the surface line of the liquid, but was etched to a considerable extent all over the surface covered by the liquid. The etching faded about an inch above the water line and the glass remaining clear throughout the entire length of the tubes C and D. Undoubtedly the phenomenon can be explained as follows:

$$H_2SiF_6 = H_2F_2 + SiF_4 \quad (4)$$

the $H_2F_2$ dissolved in the water and attacked the glass, yielding more $SiF_4$ and water as shown below:

$$SiO_2 + 2H_2F_2 = SiF_4 + 2H_2O \quad (5)$$

The $SiF_4$ and water vapor passed through the tubes uncombined until $H_2O$ condensed in the receiver B and immediately reacted with $SiF_4$ to form $H_2SiF_6$ and $H_4SiO_4$ according to the reaction:

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + H_4SiO_4 \quad (6)$$

No free HF was present in the connecting tubes or receiver, and therefore remained unetched, but when the concentration of $H_2SiF_6$ in B mounted up there would be some decomposition of the acid, especially at such times when the cooling mixture was used up and the temperature rose.

## Conclusion

The results of four different types of experiments have been recorded. In the first case air was passed through dilute solutions of fluosilicic acid at different temperatures and the resulting products passed through water for absorption. In the second and third cases strong solutions of $H_2SiF_6$ were distilled, first at room temperature and then by boiling, with various desiccating agents introduced in the stream of vapor. In every experiment where the water was removed from the vapor mixture no trace of $H_2SiF_6$ was obtained in the receivers. In the fourth case an attempt was made to liberate $H_2SiF_6$ from sodium fluosilicate by means of conc. $H_2SO_4$ and con-

dense the acid in a receiver cooled in a freezing mixture of ice and salt. No liquid condensed, however, because $H_2SO_4$ removed the water from the gas mixture, leaving the apparatus filled with silicon tetrafluoride.

The observation of the etching of the glass flasks is shown to be in perfect harmony with the theory that undecomposed $H_2SiF_6$ does not pass into the vapor state. Lastly, it has been pointed out that the vapor density measurements, made by Baur and Glaessner (loc. cit.) upon the gas resulting when barium fluosilicate is treated with concentrated sulfuric acid, indicate the complete decomposition of $H_2SiF_6$ into the products $H_2F_2$, $H_3F_3$, and $SiF_4$.

Summarizing all the foregoing we are entitled to conclude, with a reasonable degree of certainty, that fluosilicic acid is a nonvolatile acid, like $H_2CO_3$ and $H_2SO_3$, and cannot exist under ordinary conditions in the vapor state.

*University of West Virginia*

# THE PHYSICO-CHEMICAL PROPERTIES OF STRONG AND WEAK FLOURS. VI. THE RELATION BETWEEN THE MAXIMUM VISCOSITY OBTAINABLE BY THE ADDITION OF LACTIC ACID AND THE CONCENTRATION OF FLOUR-IN-WATER SUSPENSIONS*

BY PAUL FRANCIS SHARP AND ROSS AIKEN GORTNER**

In the preceding papers we have determined the effect of various acids in increasing imbibition of 20 percent flour-in-water suspensions,[1] and of various acids in increasing imbibition of flour, from which the electrolytes had been largely removed, the residue suspended in water and made up to a total volume of 100 cc.[2]

We have shown[3] that in all probability glutenin is the protein primarily responsible for the desirable properties of a strong flour gluten. It therefore seemed desirable to ascertain to what extent the glutenin content of a series of flours was correlated with viscosity and loaf volume. At the time this work was in progress there was available a series of eleven flours which was being subjected to a joint investigation by Rumsey, Collatz and ourselves. The investigations of

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[1] R. A. Gortner and P. F. Sharp: "The Physico-Chemical Properties of Strong and Weak Flours. III." Jour. Phys. Chem., 27, 481 (1923).

[2] R. A. Gortner and P. F. Sharp: "The Physico-Chemical Properties of Strong and Weak Flours. IV." Jour. Phys. Chem., 27, 567 (1923).

[3] P. F. Sharp and R. A. Gortner: "The Physico-Chemical Properties of Strong and Weak Flours. V." Jour. Phys. Chem., 27, 674 (1923).

Rumsey[4] and of Collatz[5] have already been published. We have accordingly used these flours in the present investigation. A description of the flours has been given by both Rumsey and Collatz.

The accurate determination of the quantity of the various proteins present in wheat flour offers unusual difficulties, due to overlapping solubilities and the effects of the reagents upon the proteins remaining in the residue. These difficulties have been encountered by many investigators. We have utilized the following methods:

The nitrogen in the various fractions was determined by the Kjeldahl method and was converted into protein by the use of the factor 5.7.

*Total Protein.*—The values for the total protein are the average of independent determinations carried out in this laboratory by both Mr. Andrew Dingwall and by ourselves.

*Potassium Sulfate-Soluble Protein* was determined according to the A.O.A.C. method.[6]

*Alcohol-Soluble Protein* was determined according to the A.O.A.C. method.

*Potassium Sulfate-Soluble Protein, Centrifuged.*—The only difference between this and the A.O.A.C. method was that the material was centrifuged after digestion and before filtering.

*Alcohol-Soluble Protein in the Residue after Extraction with Potassium Sulfate.*—Enough alcohol was added to the residue after the removal of the potassium sulfate extract to make 150 cc of 70 percent alcohol by weight, corrections being made for the water remaining in the residue. The mixture was agitated in a mechanical shaker for 1 hour, at the end of this time the material was allowed to settle and was filtered clear

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[4] L. A. Rumsey: "The Diastatic Enzymes of Wheat Flour and Their Relation to Flour Strength." Am. Inst. Baking Bull., 8, 86 pp. (1922).

[5] F. A. Collatz: "Flour Strength as Influenced by the Addition of Diastatic Ferments." Ibid., 9, 74 pp. (1922).

[6] "Methods of Analysis," Association of Official Agricultural Chemists. Washington, 1920, pp. 167–168.

through a fluted filter and the nitrogen in a 50 cc aliquot of the filtrate determined.

All determinations were carried out in duplicate and if the duplicates did not show close agreement the determination was repeated. The results, expressed in percentage of the moisture free flour are given in Table I.

It is believed that the glutenin content is represented most accurately by subtracting from the total protein content of the flour, the sum of the amounts of protein extracted by 5 percent potassium sulfate solution followed by extraction with 70 percent alcohol. The A.O.A.C. method for determining the glutenin content is to subtract from the total protein content of the flour, the sum of the potassium sulfate- and alcohol-soluble proteins as determined on separate portions of flour. Due to the overlapping solubilities of the proteins in these two solvents the glutenin results obtained by this method are much too low.

The results for the potassium sulfate-soluble protein by the two methods do not agree. This may be due to the fact that, in the case of filtration without centrifuging, the starch and suspended matter have not settled out completely and the filters therefore clog and ultra filter out some of the protein material, while this suspended matter is thrown down in the centrifuge thus preventing the clogging of the filter paper pores. The difference in the rates of filtration in the two instances was very marked. The gliadin represented in Column 6 more or less parallels the glutenin represented in Column 9. No relationship between the various protein fractions and the loaf volume is apparent.

In order to determine the effect of concentration on the maximum viscosity produced by the addition of various amounts of lactic acid, 12, 15, 18, 21, and in some instances 24 grams of flour on the dry basis were suspended in water and made up to a total volume of 100 cc, and imbibition as effected by concentrated (syrupy) lactic acid determined. The concentrated acid was used in this instance because 2.0 cc was

sufficient to produce maximum viscosity (i. e., to bring the flour-in-water suspension to approximately pH=3.0) and the change due to dilution was slight. *It was found that if the logarithms of the maximum viscosity readings were plotted against the logarithms of the flour concentration the points fell in a straight*

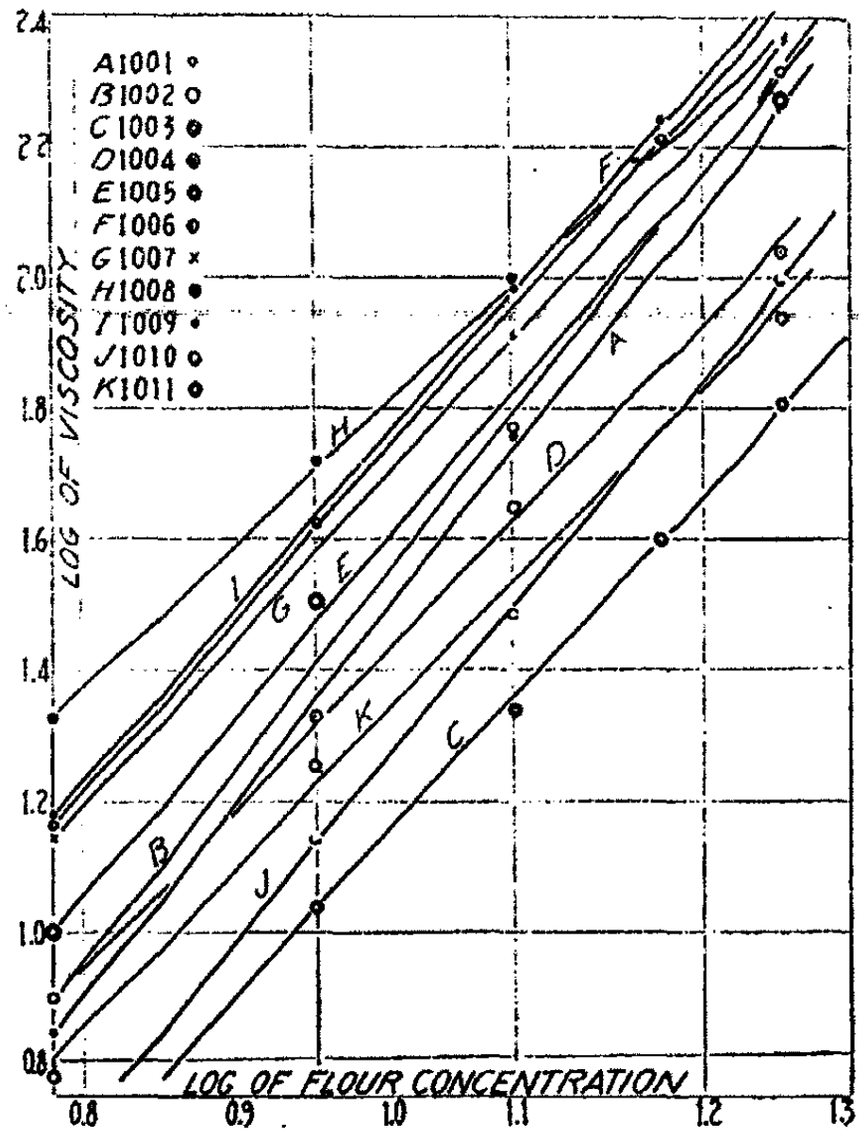



Fig. 1*a*

Logarithms of highest viscosity reading produced with lactic acid plotted against the logarithms of the flour concentration.

*line*. The results are expressed graphically in Figs. 1a–c. The logarithms of the viscosity are also plotted against the logarithms of the protein content, and of the glutenin content of the suspension.

The equation of the logarithmic curve is

Log of viscosity = $a + b$ (log of concentration)

where $a$ is the logarithm of the viscosity reading when the logarithm of the concentration is zero and $b$ is the tangent of the angle made by the logarithmic curve with the axis of abscissa. These constants for the above expression were calculated by the method of least squares and are given in Table II.

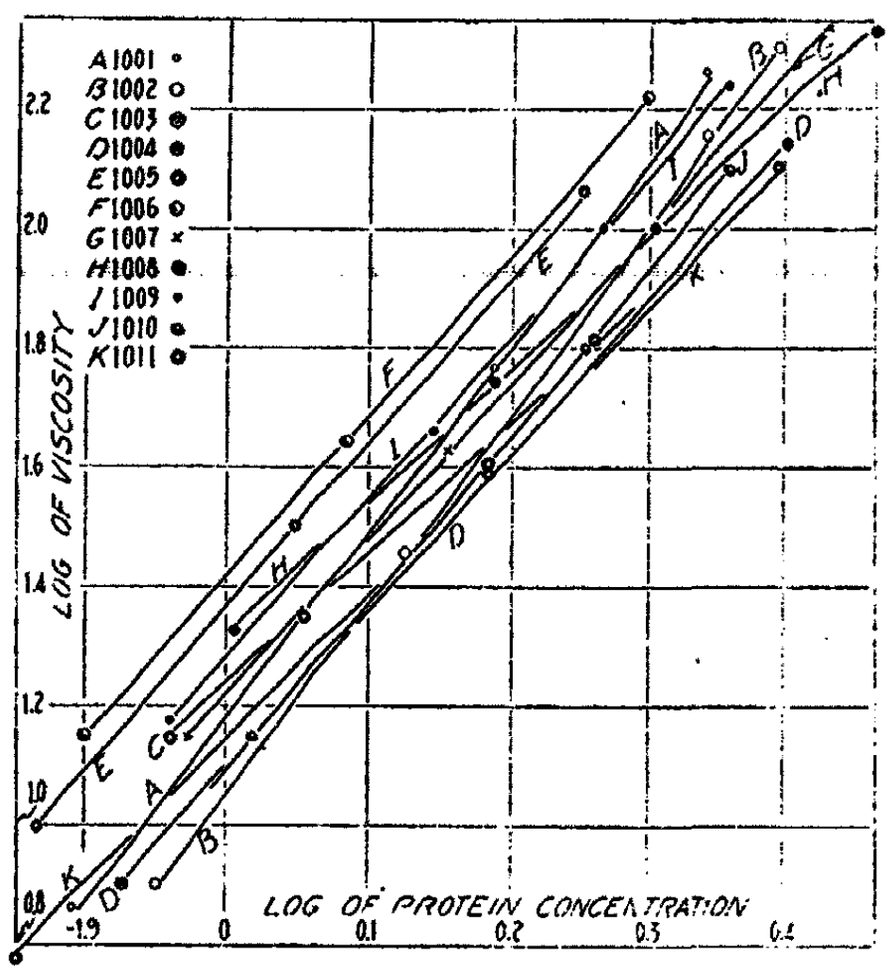



Fig. 1*b*

Logarithms of highest viscosity reading produced with lactic acid plotted against the logarithms of the protein concentration of the unextracted flour.

In a similar manner the maximum viscosity produced by normal lactic acid was determined after electrolytes present in the natural flours had been partially removed. In the removal of the "soluble ash" the weighed amount of flour was treated with 1 liter of distilled water and the mixture shaken at various intervals for 45 minutes, the flour was then allowed to settle, the supernatant liquid decanted, the residue treated with an additional 500 cc of distilled water, shaken as

before, allowed to settle and decanted; the residue was then made up to a volume of 100 cc with distilled water. For this determination 6, 9, 12, 15, 18, and in some instances 21 grams of flour, computed on a moisture-free basis, were used. The logarithms of the maximum viscosity which was reached were plotted against the logarithms of the flour concentration, of the

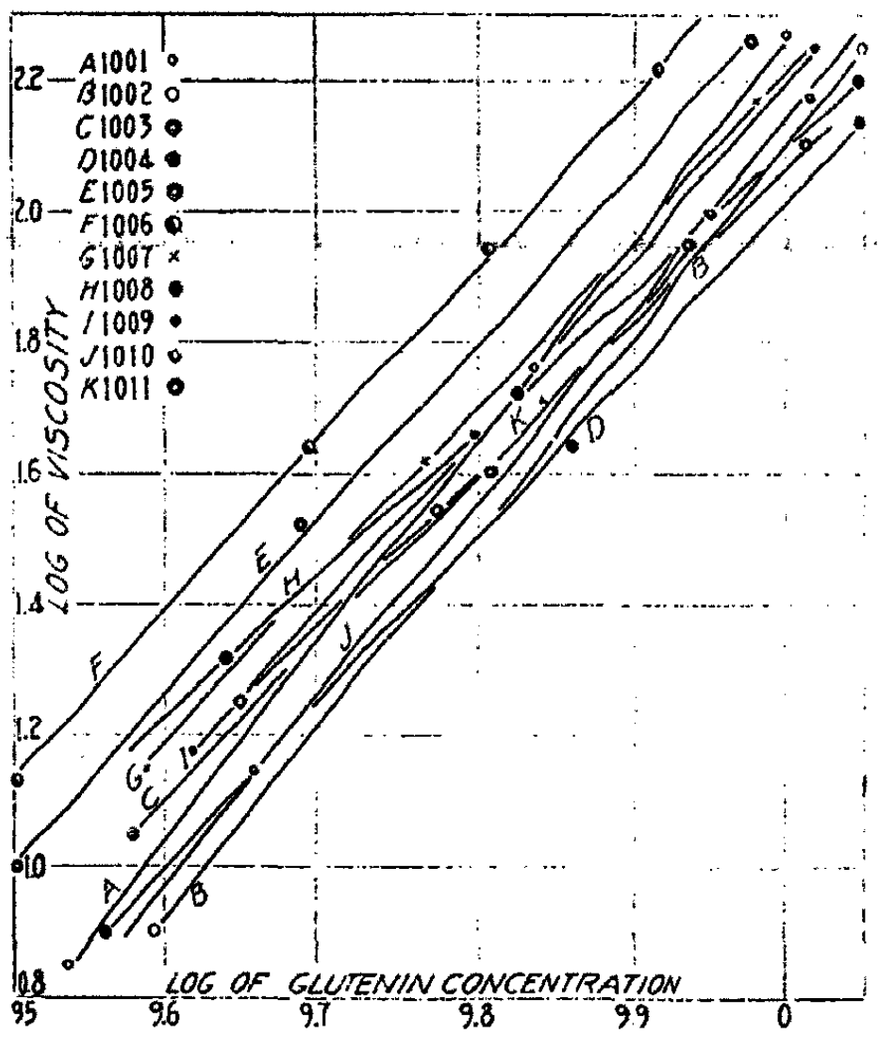



Fig. 1*c*

Logarithms of highest viscosity reading produced with lactic acid plotted against the logarithms of the glutenin concentration of the unextracted flour.

protein concentration and of the glutenin concentration as shown in Figs. 2a-c.

The constants for the logarithmic equation for the curves given in Figure 2 were calculated by the method of least squares and are given in Table III.

Suspensions of various concentrations of flour untreated

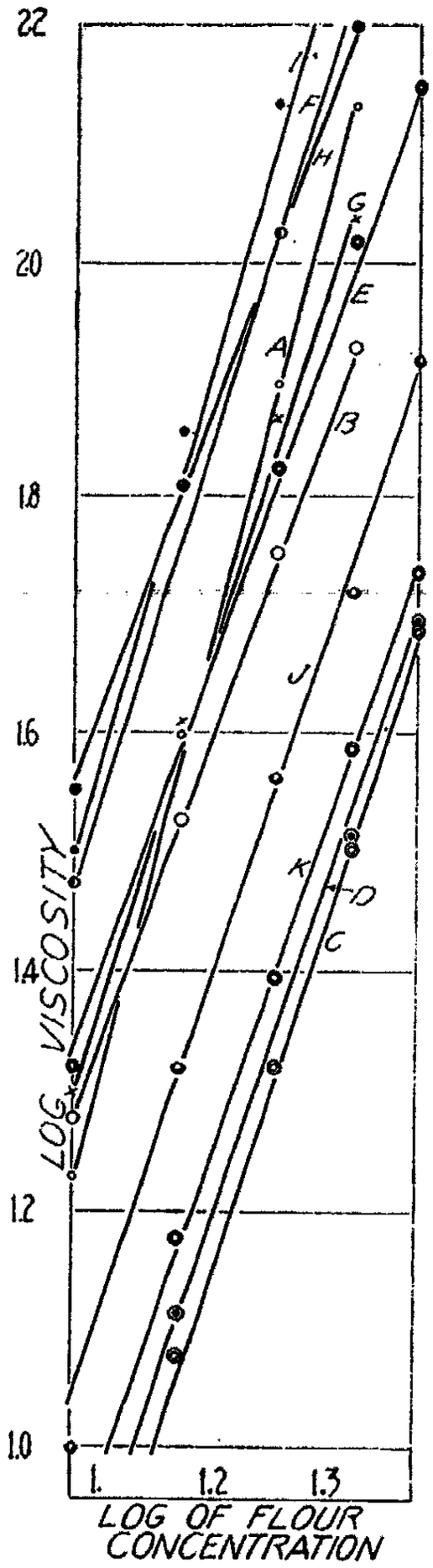



Fig. 2*a*

Logarithms of the highest viscosity reading produced with lactic acid plotted against the logarithms of the flour concentration.

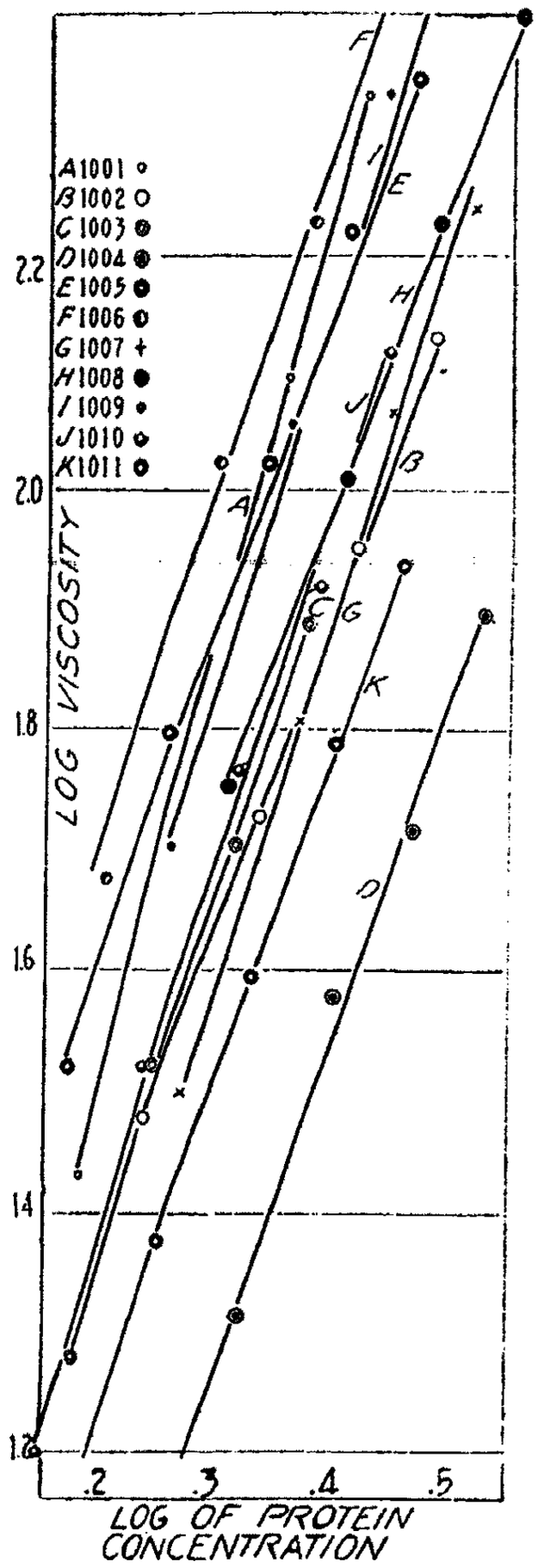



Fig. 2*b*

Logarithms of highest viscosity reading produced with lactic acid plotted against the logarithms of the protein concentration of the unextracted flour.

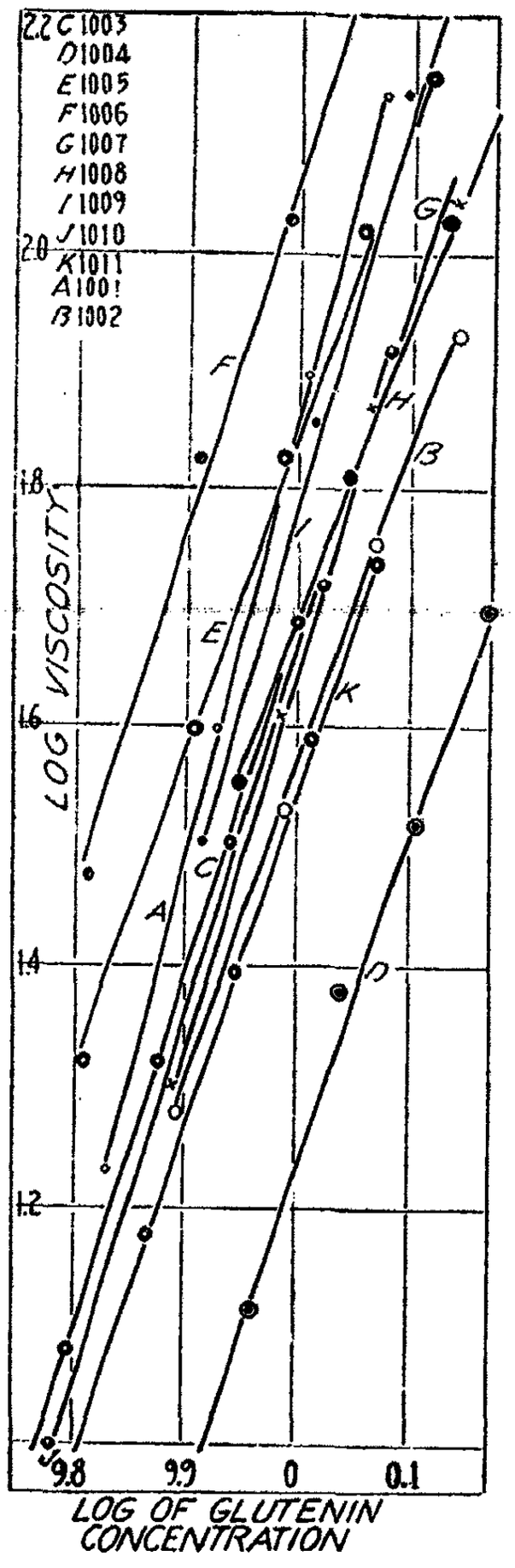



Fig. 2c

Logarithms of highest viscosity reading produced with lactic acid plotted against the logarithms of the glutenin concentration of the unextracted flour.

with acids would doubtless follow the logarithmic relationship and would probably give an angle somewhat similar to the ones obtained from Figures 1 and 2. Unfortunately the supply of the flours used in this study became exhausted so it was impossible to compare the curves produced with the untreated flours with those given in Figures 1 and 2. The attempt was made to introduce the relationship between the initial reading of the flour-in-water suspension and the maximum reading after the treatment with lactic acid, but the initial viscosity reading was so low that it could only be approximately determined with the torsion wire which it was necessary to use in the viscosimeter set for the higher viscosity, the experimental error on the untreated suspension being in some cases nearly 50 percent. It would seem desirable to investigate this point under conditions where the lower readings could be determined with sufficient accuracy to subject this relationship to a more exact quantitative study. Like-

wise the subtraction of the initial viscosity from the maximum viscosity was tried, but in some cases this produced relatively large values for the constant $b$ due to the fact that some of the flours with low baking strength yielded simple flour-in-water suspensions which gave relatively high viscosity readings and these suspensions increased only slightly in viscosity on the addition of acids. With such flours the practice of subtracting the initial viscosity from the maximum viscosity and plotting this difference gave relatively large, and apparently incorrect, values for the constant $b$.

It will be noted from Figures 1 and 2 that the curves do not all lie at the same angle with respect to the axis of abscissa, that is the viscosity increases more rapidly with concentration in some flours than in others. *It is probable that the tangent of the angle of this curve made with the abscissa represents more accurately than any other value thus far obtained, the imbibitional strength of the colloidal properties of the protein of the wheat. If the tangent of this angle is small the colloidal properties will be less marked, on the other hand if the tangent of the angle has a large value the colloidal properties will be very pronounced.*

Bearing in mind that the tangent $b$ of the angle thus obtained might be considered as the value indicating most accurately the colloidal strength of the flour, and that the imbibition of wheat flour as induced by acids is due mainly to the glutenin, it would be expected that a relationship might exist between these two factors. *Thus the colloidal strength of the flour would be the product of the quality factor as indicated by the constant b in the logarithmic equation, and the quantity factor as indicated by the quantity of glutenin.* In order to see if this product was actually related to the baking strength of the flour as indicated by loaf volume, the glutenin $\times$ $b$ was divided by the loaf volume. The results of this calculation are given in Table IV.

The values for the constant $b$ are higher for the series with the electrolytes present than they are for the series with the electrolytes removed. The wires used in the two series both

gave a reading of 29.2° M with a 60 percent sucrose solution, whose absolute viscosity is 43.86 centipoise at 25° C, the temperature at which all observations were made. Unfortunately the wire of the viscosimeter broke after one series had been completed and a new wire was used for the other series. The breaking of the wire was a great misfortune because it leaves the question of the effect of the salts present in the original flour on the slope of the curve still unanswered. The results do show, however, that the salts present in the flour exert an effect which differs from flour to flour, indicating that the various electrolytes occurring in the various flours are present in different proportions. This conclusion is also indicated in a previous paper[7] and aids in explaining the different order of the acids when arranged in the order of their power to produce maximum imbibition. The order of the acids was found to be more nearly the same when the electrolytes were removed.[8]

The effect of the actual quantity of electrolytes from the same wheat is shown in a comparison of the patent and clear flours from the same wheat as given in Table V. The greatest deviation between the constants *b* is found in the experiments where the electrolytes were not removed. Patent flour, 1001, gave a constant of 3.705 and the clear flour from the same wheat 1002, gave a constant of 2.689. In the other two cases the agreement is better. When the electrolytes were removed the patent flour in each case gave a slightly higher constant than the clear flour indicating that the *quality* of the protein in the patent flour was only slightly, if at all, better than the protein in the clear flour. This agreement is also an indication that the influence of the electrolytes present in the flour was largely eliminated, in so far as their effect on the evaluation of the imbibitional properties of the gluten was concerned, by the method which we used for their removal.

[7] R. A. Gortner and P. F. Sharp: The "Physico-Chemical Properties of Strong and Weak Flours. III." Jour. Phys. Chem., 27, 481 (1923).

[8] R. A. Gortner and P. F. Sharp: "The Physico-Chemical Properties of Strong and Weak Flours. IV." Ibid., 27, 567 (1923).

The constant K, obtained by dividing the product of the glutenin concentration and the constant *b*, by the loaf volume shows considerable fluctuation in the series obtained with the electrolytes present. When the electrolytes are removed we find that the constants fall into three groups. With the exception of flour 1010, tine first group contains patent or straight flours which would be used for bread making. Group two contains flours which, if used by themselves, would be considered pastry flours and would be used commercially for bread making only when blended with other flours of considerable baking strength. Group three contains the clear flours. The average of the constants K in the first group is 0.00829, the average deviation from this value is 1.99 percent while the maximum deviation is 4.1 percent. In the second group the average is 0.00661 while the average and maximum deviation is 3.93 percent. In the third group the avearge is 0.01089, the average deviation is 2.91 percent and the maximum deviation is 4.41 percent. The greatest experimental error is believed to be in the determination of the glutenin content of the flours. These results indicate a rather definite relation between the glutenin content, the constant *b* of the logarithmic equation, and the loaf volume. It is generally accepted that the actual volume of the loaf depends on many factors and it could hardly be expected that the measurement of one factor would determine the loaf volume. Our experiments indicate that within each group there is a definite relation between the glutenin content, the quality constant *b*, and the loaf volume. The groups of different constants are probably produced by other factors. Just what factors may be operative has not been determined other than the relation expressed in Table IV between the class and grade of wheat and the grade of flour.

Rumsey[9] and Collatz[10] have made a study of these flours in order to ascertain whether or not their baking value could be correlated with the diastatic activity of the doughs.

[9] L. A. Rumsey: loc. cit.
[10] F. A. Collatz: Ibid.

Collatz found that by the addition of malt flour and malt extracts, the loaf volume of flours 1002 and 1007 could be increased about 16 percent. Increasing the loaf volumes used for these flours in Table IV by 16 percent, we obtain the constant 0.00833 for flour 1002 and 0.00922 for flour 1007. The loaf volume of flour 1001 was increased 10 percent by the addition of malt which gives a constant of 0.00779 instead of 0.00857. Flour 1008 showed no increase in loaf volume on the addition of malt flour or extract. Flour 1003 showed an increase of 12 percent which changes the constant to 0.00566. It is undoubtedly unfair to take the increase in the case of this flour as 12 percent for this increase was obtained with only one loaf and was apparently much too high, the average increase in 14 experiments being only 3.73 percent.

Rumsey has shown that flour 1004 is intermediate in diastatic power between flours 1002 and 1007. It is probable that an increase in loaf volume might have been obtained with this flour by the addition of diastase. Table VI gives the relative diastatic powers of the flours as determined by Rumsey. The hydrogen ion concentration of the flour and of the fermented dough at the time of going into the oven are taken from the paper by Collatz.

Table VI shows that only two flours, namely the clear flours 1004 and 1007, did not reach approximately a pH of 5.0 which the work of Jessen-Hansen[11] indicates to be the general optimum for bread making.

Rumsey shows that these two flours are the most highly buffered of the flour samples under consideration. Thus one reason for the low volumes of the loaves resulting from these flours may have been that the optimum hydrogen ion concentration had not been reached. The clear flour 1002 did reach this optimum pH and making the correction for the increased loaf volume produced by added diastase yields a constant which agrees with those in group one. This indi-

[11] H. Jessen-Hansen: Comptes rendus Trav. Lab. Carlsburg, 10, 170–206 (1911).

cates that the factor causing the low loaf volume was probably insufficient diastase and not the buffer effect of the higher ash content. Flour 1007 is improved by added diastase yet it still gives a constant which is too high for group one. It may be that the low loaf volume in this case is caused by two factors, i. e., the low diastatic power and the failure of the dough to reach the optimum hydrogen ion concentration for baking due to the presence of excessive quantities of buffering salts.

If we take the first group of flours for comparison, then the second group yield larger loaf volumes than their glutenin content and its imbibitional properties would indicate. It is useless to theorize as to the factors operative in the formation of group two. The flours in group two are especially low in diastase; however, an increase in diastatic power should have a tendency to increase the loaf volume and yield a still lower constant.

While eleven flours with such meager data are by far too few a number upon which to base final conclusions, we believe that the glutenin content and its imbibitional properties may be used as a measurement of one of the main factors concerned with baking strength. The data presented in the present paper indicate three groups of flours as shown by imbibitional studies, later work may show more than three groups. In the method used all of the factors which go to make up viscosity and plasticity were probably operative. A study of the plasticity of flour suspensions is being carried out by one of us (S.) and may yield information which will give a better insight into the relation of imbibition to flour strength. The initial viscosity of the flour-in-water suspension untreated with acid should also be investigated.

## Summary

1. The A.O.A.C. method of determining glutenin by subtracting from the total protein content, the sum of the alcohol soluble protein and the potassium sulfate soluble

TABLE I

Protein Fractions of Various Flours in Terms of Percent of Total Flour on Dry Basis. Arranged in Order of Their Loaf Volume

| (1) Laboratory no. | (2) Loaf volume | (3) 5% $K_2SO_4$ soluble | (4) 5% $K_2SO_4$ soluble centrifuged filtered | (5) Alcohol soluble protein | (6) Alcohol soluble after $K_2SO_4$ extraction | (7) Total protein content | (8) Dry hand washed gluten | (9) Glutenin (7) − [(4) + (6)] |
|---|---|---|---|---|---|---|---|---|
| | cc | percent | percent | percent | percent | percent | percen | percent |
| 1009 | 2160 | 1.59 | 1.69 | 9.04 | 6.80 | 15.41 | 15.9 | 6.92 |
| 1001 | 2010 | 1.36 | 1.55 | 6.81 | 5.46 | 12.71 | 11.7 | 5.70 |
| 1008 | 2000 | 1.95 | 2.11 | 10.09 | 7.55 | 17.11 | 16.6 | 7.45 |
| 1002 | 1880 | 1.74 | 1.99 | 7.99 | 6.03 | 14.57 | 14.2 | 6.55 |
| 1005 | 1820 | 1.54 | 1.74 | 7.41 | 5.12 | 12.29 | 11.5 | 5.43 |
| 1010 | 1760 | 1.63 | 1.76 | 6.96 | 4.84 | 11.65 | 11.5 | 5.05 |
| 1006 | 1735 | 1.54 | 1.71 | 7.98 | 6.20 | 13.39 | 12.7 | 5.48 |
| 1011 | 1720 | 1.70 | 1.91 | 7.33 | 5.15 | 12.00 | 11.7 | 4.94 |
| 1003 | 1650 | 1.21 | 1.37 | 5.75 | 4.42 | 9.98 | 9.7 | 4.19 |
| 1007 | 1460 | 2.20 | 2.35 | 8.98 | 6.86 | 15.68 | 15.6 | 6.47 |
| 1004 | 1415 | 2.46 | 2.74 | 7.55 | 5.20 | 14.05 | 12.9 | 6.11 |

TABLE II

The constants for the logarithmic expression,
log viscosity = $a + b$ (log concentration),
with the flour ash present. The calculated values were obtained by the method of least squares, the values for $a$ are given on the basis of flour concentration, crude protein concentration, and glutenin concentration. The measured values for $b$ obtained by the graphical method are also given

| Flour laby. no. | Measured value of $b$ | Calculated values | | | |
|---|---|---|---|---|---|
| | | $b$ | Flour conc. $a$ | Protein conc. $a$ | Glutenin conc. $a$ |
| 1001 | 3.647 | 3.705 | −2.671 | +0.558 | +1.848 |
| 1002 | 2.662 | 2.689 | 1.799 | 0.570 | 1.555 |
| 1003 | 2.980 | 3.013 | 2.469 | 0.547 | 1.685 |
| 1004 | 2.852 | 2.829 | 2.184 | 0.207 | 1.232 |
| 1005 | 2.691 | 2.766 | 1.654 | 0.864 | 1.845 |
| 1006 | 2.955 | 2.996 | 1.731 | 0.883 | 2.048 |
| 1007 | 3.043 | 3.052 | 1.982 | 0.473 | 1.646 |
| 1008 | 2.620 | 2.643 | 1.295 | 0.732 | 1.686 |
| 1009 | 3.341 | 3.291 | 2.028 | 0.645 | 1.791 |
| 1010 | 2.858 | 3.005 | 2.227 | 0.578 | 1.669 |
| 1011 | 2.729 | 2.797 | 2.114 | 0.461 | 1.542 |

TABLE III

The constants for the logarithmic expression,
log viscosity = $a + b$ (log concentration),
with the salts removed. The calculated values were obtained by the method of least squares, the values for $a$ are given on the basis of flour concentration, crude protein concentration, and glutenin concentration. The measured values for $b$ obtained by the graphical method are also given

| Flour laby. no. | Measured value of $b$ | Calculated values | | | |
|---|---|---|---|---|---|
| | | $b$ | Flour conc. $a$ | Protein conc. $a$ | Glutenin conc. $a$ |
| 1001 | 3.048 | 3.023 | −1.515 | +1.193 | +2.244 |
| 1002 | 2.954 | 2.926 | 1.365 | 1.083 | 2.099 |
| 1003 | 2.492 | 2.499 | 1.352 | 1.157 | 2.099 |
| 1004 | 2.551 | 2.552 | 1.085 | 1.092 | 2.011 |
| 1005 | 2.631 | 2.666 | 1.048 | 1.378 | 2.325 |
| 1006 | 2.654 | 2.610 | 0.861 | 1.418 | 2.431 |
| 1007 | 2.565 | 2.568 | 0.840 | 1.226 | 2.213 |
| 1008 | 2.206 | 2.212 | 0.396 | 1.306 | 2.107 |
| 1009 | 2.678 | 2.622 | 0.848 | 1.281 | 1.195 |
| 1010 | 2.893 | 2.909 | 1.645 | 1.071 | 2.127 |
| 1011 | 2.304 | 2.398 | 1.062 | 1.148 | 2.073 |

TABLE IV

The Relation between Loaf Volume, Glutenin Content, and the Imbibitional Strength of the Glutenin as Represented by the Constant $b$ of the Logarithmic Equation

| Lab. no. | Loaf volume | Glutenin content | Electrolytes present | | Electrolytes removed | | Class of wheat | Flour grade |
|---|---|---|---|---|---|---|---|---|
| | | | Constant $b$ | $\frac{(\text{Glutenin}) \times (b)}{(\text{Loaf volume})} = K$ | Constant $b$ | $\frac{(\text{Glutenin}) \times (b)}{(\text{Loaf volume})} = K$ | | |
| 1009 | 2160 | 6.92 | 3.291 | 0.01054 | 2.622 | 0.00840 | Hd. Rd. Spr. | Patent |
| 1001 | 2010 | 5.70 | 3.705 | 0.01051 | 3.023 | 0.00857 | Hd. Rd. W'ter | Patent |
| 1008 | 2000 | 7.45 | 2.643 | 0.00985 | 2.212 | 0.00824 | Hd. Rd. Spr. | Patent |
| 1005 | 1820 | 5.45 | 2.766 | 0.00828 | 2.666 | 0.00795 | Hd. Rd. Spr. | Patent |
| 1010 | 1760 | 5.05 | 3.005 | 0.00862 | 2.909 | 0.00834 | Kofod* | Straight |
| 1006 | 1735 | 5.48 | 2.996 | 0.00946 | 2.610 | 0.00823 | Hd. Rd. Spr. | Patent |
| 1011 | 1720 | 4.93 | 2.797 | 0.00801 | 2.398 | 0.00687 | S'f't Rd. W'ter | Patent |
| 1003 | 1650 | 4.19 | 3.013 | 0.00765 | 2.499 | 0.00635 | White Club | Straight |
| 1002 | 1880 | 6.55 | 2.689 | 0.00936 | 2.926 | 0.01060 | Hd. Rd. W'ter | 1st Clear |
| 1007 | 1460 | 6.47 | 3.052 | 0.01352 | 2.568 | 0.01137 | Hd. Rd. Spr. | 1st Clear |
| 1004 | 1415 | 6.11 | 2.829 | 0.01221 | 2.552 | 0.01071 | Hd. Rd. Spr. | 2nd Clear |

NOTE:

1001 is a patent and 1002 is a clear from the same wheat.

1005 is a patent and 1004 is a clear from the same wheat.

1006 is a patent and 1007 is a clear from the same wheat.

* Identified by J. Allen Clark, of the U. S. Department of Agriculture as "probably Kofod." Rumsey (loc. cit.) and Collatz (loc. cit.) have recorded this sample as "like Sonora." Their classification is undoubtedly incorrect.

TABLE V

Relation between the patent and clear flours milled from the same wheat and the constant *b* of the logarithmic equation

| Laby. no. | Constant *b*. Electrolytes present | Constant *b*. Electrolytes removed | Flour grade |
|---|---|---|---|
| 1001 | 3.705 | 3.023 | Patent |
| 1002 | 2.689 | 2.926 | 1st clear |
| 1005 | 2.766 | 2.666 | Patent |
| 1004 | 2.829 | 2.552 | 2nd clear |
| 1006 | 2.996 | 2.610 | Patent |
| 1007 | 2.829 | 2.568 | 1st clear |

TABLE VI

Maltose produced in one hour by 10 grams of flour in 100 cc of water at 27° C. The pH value of a 1 to 5 flour-in-water suspension and of the fermented dough at the time of going into the oven

| Laby. no. | Maltose produced* | Flour** | Fermented dough** |
|---|---|---|---|
| | mgms | pH | pH |
| 1009 | 211.8 | —— | —— |
| 1001 | 248.2 | 5.81 | 4.79 |
| 1008 | 304.1 | 5.98 | 5.19(?) |
| 1005 | 131.9 | 5.84 | 5.17 |
| 1010 | 92.6 | —— | —— |
| 1006 | 105.7 | 5.78 | 5.03 |
| 1011 | 51.7 | 6.15 | 4.92 |
| 1003 | 34.8 | 6.00 | 5.05 |
| 1002 | 186.5 | 6.05 | 5.05 |
| 1007 | 123.6 | 6.10 | 5.53 |
| 1004 | 145.0 | 6.17 | 5.80 |

* Determinations by Rumsey: loc. cit.
** Determinations by Collatz: ibid.

protein determined on separate samples of flour gives too low results, due to overlapping solubilities.

2. It is believed that the glutenin content is represented most accurately by subtracting from the total protein (N × 5.7) content of the flour, the sum of the amounts of protein (N × 5.7) extracted by 5 percent potassium sulfate solution followed by an extraction with 70 percent alcohol.

3. Our data indicate that gliadin and glutenin are present in wheat flour in approximately equal amounts.

4. The concentration-viscosity curve of the maximum imbibition produced by lactic acid in flour-in-water suspensions is shown to be logarithmic.

5. The inorganic electrolytes present in the natural flours are shown to effect the constants of the logarithmic equation,

$$\text{Log viscosity} = a + b \text{ (log concentration)}.$$

6. Glutenin or protein concentration if used as abscissa for the logarithmic curves tend to bring the curves more closely together. This is also shown in the tables by the values for the constant $a$ becoming more nearly the same.

7. A relation between the quantity of glutenin, the quality of the glutenin as indicated by the constant $b$ of the logarithmic equation, and the loaf volume, is indicated for the flours studied.

8. Flour strength, in so far as the colloidal properties of the gluten are concerned, is apparently dependent upon the *quality* of the glutenin. A numerical value for glutenin quality is given in the constant $b$ of the logarithmic equation.

# BASIC COPPER SULPHATE

BY F. S. WILLIAMSON

Three hundred and twenty grams of crystallized copper sulphate, $CuSO_4.5H_2O$ were dissolved in distilled water and diluted to four liters. The solution was divided into four portions of one liter each. To these portions were added definite amounts of standard sodium hydroxide corresponding to 0.5, 1.0, 1.5, and 2.0 mols per mol of copper sulphate. Since all the copper was precipitated on adding two mols of sodium hydroxide, there was no point in adding more.

The treatment of the precipitate and the method of analysis for sulphate was the same as in the preceding two papers.[1] The copper was determined electrolytically. Approximately one gram of the sample was dissolved in 200 cc of distilled water containing 3 cc of concentrated nitric acid. The copper was then precipitated on a rotating copper cathode, using a platinum anode. Before the electrolysis the copper cathode was cleaned by dipping it momentarily into 1:1 nitric acid and rinsing it with distilled water. It was then dipped in 95% alcohol and 'flamed' by burning of the adhering alcohol. The cathode was 'flamed' again after the electrolysis.

The results of the analyses are given in Table I.

TABLE I

| Mols NaOH added | Average % Cu | Average % CuO | Average % $SO_3$ |
|---|---|---|---|
| 0.5 | 54.28 | 67.9 | 17.67 |
| 1.0 | 54.30 | 67.9 | 17.85 |
| 1.5 | 57.45 | 71.9 | 14.89 |
| 2.0 | 76.08 | 95.2 | 0.00 |

The first two precipitates agree in composition within the limit of experimental error and indicate the existence of a

[1] Williamson: Jour. Phys. Chem., 27, 380, 480 (1923).

basic salt. The fourth precipitate is evidently hydrous copper oxide, while the third is presumably a mixture. This conclusion is confirmed by the appearance of the precipitates. The first two were a light green, the third a gray-green, and the fourth a brown.

The data can be represented rather unsatisfactorily by the formula $(CuO)_4.SO_3.4H_2O$ and more accurately by the improbable formula, $(CuO)_{19}.(SO_3)_5.18H_2O$, as is shown in Table II.

TABLE II

| | CuO | $SO_3$ | $H_2O$ |
|---|---|---|---|
| Calculated for $(CuO)_4.SO_3.4H_2O$ | 67.7 | 17.0 | 15.3 |
| Calculated for $(CuO)_{19}.(SO_3)_5.18H_2O$ | 67.6 | 17.9 | 14.5 |
| Found by analysis | 67.9 | 17.8 | 14.3 |

These results do not agree well with those obtained by Stearn and Young[1] by another method. They allowed "copper sulphate in solution in water to combine with finely divided copper oxide. Preliminary results showed that this reaction was sufficiently rapid to be made use of. If copper oxide is allowed to stand at rest for three or four days in contact with a moderately strong solution of copper sulphate, it becomes thoroughly set into a hard cake of greenish gray, owing to the formation of basic salt. This cake is very hard and very difficultly soluble in strong acids and ammonia."

When copper sulphate solution was heated with copper oxide, the time necessary to reach equilibrium was 88 days at 25°, 22 days at 37.5°, and 15 days at 50°. "These figures show how unreliable must be the conclusions of previous investigators, who have allowed only a few minutes, or at most a few hours (often at room temperature) for the preparation of their salts." An examination of the solids showed them to be of two sorts. "Those prepared by using the smaller amounts of oxide, up to two molecules to one of sulphate, were clear, light grayish green. Those containing

[1] Jour. Am. Chem. Soc., 38, 1947 (1916).

larger amounts of oxide were darker in color and showed a tendency toward stratified settlement. This was taken as an indication of an excess of uncombined copper oxide, a conclusion which received confirmation upon a microscopic examination which showed the light green crystals of basic salt and black particles of oxide side by side. The examinations failed to yield any evidence of crystals of basic salt of more than one sort. The crystals were very minute and the evidence of the microscopic examination is of itself perhaps of little importance; but offers some support to conclusions to be drawn later from the results of analysis."

When discussing the results Stearn and Young say that "the first fact of importance to be noted is the negligible effect of temperature on the composition of the salts formed under otherwise like conditions. So closely do the analyses of the salts produced at the three temperatures check with one another, that it is safe to conclude that, within the limits investigated, the composition of the salts is independent of the temperature.

"In the second place, it is to be noticed that the amount of copper oxide in the salt increases with the amount added, as is to be expected. The amount of copper oxide which can be assimilated by one molecule of copper sulphate seems to be limited to about two molecules. The evidence furnished by the experiments is not sufficient to fix this limit beyond doubt, since the next higher amount of copper oxide used was four molecules to one of copper sulphate. Since, however, the salt produced in these cases contained large admixtures of unattacked copper oxide, and since the copper oxide in the solution was reduced practically to zero in all cases where two molecules of copper oxide to one of copper sulphate were used, and not where less than this amount was used, the presumption is very strong that this amount represents very closely the limit assimilable under the conditions of these experiments.

"Another conspicuous fact shown by the tabulated re-

sults is that in all cases the amount of water decreases as the amount of copper oxide increases, and that as a limit the molecules of oxide and water to one of sulphate approach equality in the most basic salt at the approximate value of two. In so far as is deducible from the evidence obtained in this investigation, the most basic salt which could be prepared by the method used would have approximately the formula $CuSO_4.2CuO.2H_2O$. Whether there is a lower limit to the amount of copper oxide which may be contained in a basic salt is not determinable from the evidence in hand, and remains a subject for further investigation."

In their summary Stearn and Young say that "the evidence obtained by a study of these salts [prepared by the direct action of copper oxide on solutions of copper sulphate] makes it seem probable that they are not definite compounds, but rather are to be regarded as a three-component system in which all three components, $CuSO_4$, CuO, and $H_2O$ (or if one prefers CuO, $SO_3$, $H_2O$) are continuously variable within limits. The evidence indicates that the maximum number of molecules that are capable of being taken up by one of copper sulphate is two, and that the formula for the most basic salt is probably quite close to $CuSO_4.2CuO.2H_2O$."

Such a salt would have the composition: CuO, 67.3; $SO_3$, 22.6; and $H_2O$, 10.1. There seems to be some question whether Stearn and Young washed their precipitates sufficiently in case there was any adsorption. There is also nothing in their experiments to disprove the possibility of a salt of a formula approximating $CuSO_4.3CuO.4H_2O$. It must be remembered, however, that the conditions are quite different. The salt obtained by Stearn and Young presumably represents equilibrium conditions and is apparently crystalline. The salt obtained by precipitation may be merely a case of adsorption. The constancy of composition in the basic sulphates of aluminum, chromium, and copper is not a certain proof of a definite compound, because the precipitation takes place under fairly comparable conditions. All it proves is

that we are not dealing with two phases in the ordinary sense of the term. It would be interesting to heat the precipitates with caustic soda at 50–25° for 15–88 days before washing them and then to analyze them. Unfortunately, that was not possible at the present time.

There is a good deal of evidence that the product obtained by the action of alkalies on copper sulphate solution has the composition $CuSO_4.3CuO.4H_2O$. By washing copper sulphate containing ammonia of crystallization with water, Kane[1] obtained the data given in Table III, using his atomic weights.

TABLE III

| | CuO by difference | $SO_3$ | $H_2O$ |
|---|---|---|---|
| Calculated for $CuSO_4.3CuO.4H_2O$ | 67.5 | 17.1 | 15.4 |
| Found by analysis | 67.3 | 16.4 | 16.3 |
| Found by analysis | 67.5 | 17.3 | 15.2 |

This same substance was obtained by adding an insufficient amount of caustic potash to a copper sulphate solution. On adding just enough to precipitate all the copper Kane obtained a precipitate which analyzed for $CuSO_4.7CuO.12H_2O$; but of course there is no evidence that this was not a mixture. Denham Smith[2] was unable to make this latter salt. Smith confirms Kane, however, as to the existence of $CuSO_4.3CuO.4H_2O$, p. 498. "This salt is obtainable in a great variety of ways. It is precipitated when a cold solution of sulphate of copper is mixed with an insufficient quantity of carbonate or of caustic soda, or potash, to decompose it completely. It may be prepared by digesting together cold,—equivalents of sulphate of copper, and of well-washed precipitated oxide of copper; by adding a solution of potash to a warm solution of sulphate of copper until a greenish blue precipitate falls, and no copper remains in solution; by treating a cold solution

[1] Ann. Chim. Phys., [2] 72, 270 (1839).
[2] Phil. Mag., [3] 23, 501 (1845).

in the same manner; by acting on the ammoniacal sulphate by a large quantity of water, etc. Numerous analyses of this salt, prepared by the various processes above-mentioned, have only served to confirm the correctness of the formula $CuSO_4.3CuO.4H_2O$, assigned to it by Professor Graham and Dr. Kane; it is therefore useless to quote any of these results."

Field[1] says that "no difficulty was experienced in obtaining the artificial salt of definite composition, by the addition of a small quantity of caustic potash to a great excess of sulphate of copper, and boiling for some time. On filtering off the excess of sulphate, and washing for many days until no trace of sulphuric acid or copper could be detected in the filtrate, the bright green powder, after drying at 212° until it ceased to lose weight, gave on analysis "figures agreeing very closely with the formula $CuSO_4.3CuO.4H_2O$, Table IV.

TABLE IV

| | CuO | $SO_3$ | $H_2O$ |
|---|---|---|---|
| Calculated for $CuSO_4.3CuO.4H_2O$ | 67.6 | 17.0 | 15.4 |
| Found by analysis | 67.5 | 17.0 | 15.5 |

The results obtained by Pickering[2] agree very closely with those obtained by myself. In the analyses given in Table V, the data refer to the anhydrous salt.

Up to 1.4 mols KOH the composition of the precipitate is practically constant. The percentage of copper oxide in Table I is 79.2 which is higher than all except one figure obtained by Pickering. This is quite a little below the 79.9 calculated for $CuSO_4.3CuO$; but Pickering thinks that this is due to insufficient washing. In another experiment in which the precipitate was washed a good deal more, the percentage of copper oxide rose to 79.7. If we assume that the sulphate determinations are about half a percent high through inadequate washing, occluded barium chloride, or both, then

[1] Phil. Mag., [4] **24**, 124 (1862).
[2] Chem. News, **47**, 181 (1883).

TABLE V

| Mol KOH added | % Total Cu precipitated | % CuO in anhydrous salt | Remarks |
|---|---|---|---|
| 0.16 | 10.8 | 78.1 | Light blue |
| 0.24 | 16.3 | 77.9 | " " |
| 0.35 | 24.3 | 77.9 | " " |
| 0.47 | 33.9 | 78.5 | " " |
| 0.47 | .... | 78.5 | " " |
| 0.67 | 46.6 | 77.0 | " " |
| 0.67 | .... | 79.2 | " " |
| 0.71 | .... | 78.2 | " " |
| 0.71 | .... | 78.6 | " " |
| 0.93 | .... | 79.2 | " " |
| 0.93 | .... | 79.0 | " " |
| 0.93 | 69.8 | 78.7 | " " |
| 0.93 | 68.1 | 78.3 | " " |
| 1.40 | 98.1 | 78.6 | " " |
| 1.72 | .... | .... | Dark blue |
| 1.97 | 100.0 | 99.5 | " " |
| 4.00 | 100.0 | 100.0 | " " |

the formula of the salt is undoubtedly $CuSO_4.3CuO.4H_2O$; but this cannot be considered as established conclusively.

Stearn and Young rather imply that they are the only ones who have allowed the precipitates to reach equilibrium; but they cannot really mean this because Denham Smith[1] reports that "by boiling at various intervals during ten weeks, equivalents of sulphate and oxide, I obtained the trisulphate of copper, $SO_3.3CuO.2H_2O$." This is the salt $CuSO_4.2CuO.2H_2O$, which Stearn and Young considered to be the limiting case. Smith goes on to say that "by digesting an equivalent of each for thirteen weeks the tetra sulphate, $CuSO_4.3CuO.4H_2O$ was produced." If this experiment is confirmed, it means that the results of Stearn and Young go by the board, because they did not reach equilibrium. On the other hand, the assumption of $CuSO_4.3CuO.4H_2O$ as the basic salt is not supported by adequate analyses as yet and nobody knows whether there is a time factor or not. In other words, the whole question of basic copper sulphates is still up in the air.

[1] Phil. Mag., [3] 23, 501 (1843).

Stearn and Young[1] claim that Pickering is wrong in saying that a definite basic copper sulphate can be prepared by heating copper sulphate and water in varying relative amounts. They may be right; but both their reasoning and their experiments are bad. They say that "it is a well-known fact that ordinary solutions of copper sulphate are in general supersaturated with respect to basic sulphate, even though unsaturated with the normal sulphate. This is evidenced by the fact that prolonged standing or short boiling of such solutions results in the deposition of certain amounts of basic sulphates." It is really a case of peptization and not of supersaturation. The experiments to show the varying composition of the precipitates are not conclusive because they did not wash enough to remove the adsorbed copper sulphate satisfactorily. On the other hand, if we are dealing, as we certainly are, with adsorption, the constancy of the ratio of copper to sulphate means absolutely nothing.

This work was done under the direction of Professor Bancroft and was made possible by a grant from the Chemical Foundation.

The general results of this paper are:

1. The results of Pickering have been confirmed that the precipitate obtained by adding varying amounts of caustic soda, not to exceed 1.5 mols per mol of copper sulphate, is practically constant in composition.

2. The bulk of the evidence favors the view that the precipitate obtained by adding less than 1.5 mols of NaOH to one mol of copper sulphate, has the composition $CuSO_4.3CuO.4H_2O$, which may also be written $(CuO_2H_2)_3.CuSO_4.H_2O$. All the analyses for sulphate comes a little high, however, which may be due to inadequate washing, as Pickering assumes; to errors in the analytical method; or to the substance being something else. The matter cannot be considered as settled.

3. By precipitation with alkali, as has been done hitherto,

[1] Jour. Am. Chem. Soc., **38**, 1952 (1916).

one does not get the substance, $CuSO_4.2CuO.2H_2O$ postulated by Stearn and Young. There is no evidence as to what the alkali treatment would give if the product were digested until equilibrium had been reached.

4. Denham Smith obtained the same compound that Stearn and Young did by working in much the same way; but he claims to have obtained the substance $CuSO_4.3CuO.4H_2O$ by continuing the operation for thirteen weeks. If this is confirmed, the experiments of Stearn and Young do not represent equilibrium conditions.

5. Since copper sulphate will peptize hydrous copper oxide and will be carried down by it, there is no certainty that we may not be dealing with a basic salt containing adsorbed copper sulphate.

6. The whole question of the basic sulphates needs careful revision.

*Cornell University*

# NEW BOOKS

**The Riddle of the Rhine.** *By Victor Lefebure. 21 × 15 c; pp. 282. New York: E. P. Dutton and Co., 1923. Price: $2.00.*—This is an American edition of a book first published in England nearly three years ago. At the time the book was written, its chief interest was in its description of chemical warfare and of the way in which the big chemical factories along the Rhine were converted into plants making poison gas. Today the interest centers more in the prophetic part and in the question whether Germany will ever use those plants again for the same purpose.

"The great ease and rapidity with which the German dye factories mobilised for poison gas production on a super-industrial scale has already been demonstrated. It took forty years and more to develop those factories. Yet forty days saw many of their plants producing huge tonnages of poison gas, and as many hours were sufficient for others. In some cases, indeed, they were already producing eventual munitions long before the outbreak of war. We must not remain insensible to the double-edged nature of this industrial weapon. When with one hand Germany withdrew life-giving drugs from America, with the other she poured upon us an endless stream of deadly poison made in the same factories. Even when our textile industries were threatened through lack of indigo, from the very plants on which we had depended there issued a steady stream of mustard gas, each ounce of which threatened Allied limb and life."

"The League of Nations may succeed in rooting out the means of production of certain munitions. But organic chemical factories must survive for the sake of their material contribution to the welfare of humanity. They cannot be inspected and controlled, as we have shown, and there is only one sound solution. The obstacle to peace must be removed by decentralising the organic chemical factories. We cannot leave this monopoly in the hands of any country. It now lies a weapon ready to the hands of those who created and wielded it with such success. Redistributed, this dangerous productive grouping will create a source of stability and strength to a League of Nations, and will invite a national sense of security, so essential to peace and disarmament under the present régime. This has only one meaning, the establishment of dye industries in Allied countries. This may clash with certain political schools of thought developed before the war without a due realisation of the organic way in which production links up with national defense. But let there be no misunderstanding. The refusal to support this critical industry is a definite sacrifice of vital national issues. Political principles responsible for such opposition no longer merit the name; they have become a fetish."

"Each nation and any League of nations must seriously face the question of the establishment of elaborate and complex chemical warfare organisations. It seems to me that the logical course of thought and action is as follows. If guarantees are forthcoming, internationally, removing this grave German chemical warfare threat through her manufacturing monopoly, then the need for a definite chemical striking force and organisation will be greatly reduced. National safety is itself a corollary of world disarmament. But if satisfactory guarantees

were forthcoming it would be consistent with national safety to limit the chemical warfare equipment of each nation to what would actually represent a scientific military brain. So long as national ministries for war or defense exist, they must possess even under the most stringent disarmament conditions, fully accredited within their regular staffs, an individual or individuals with scientific and military training, who represent knowledge, vision, and the power to expand in chemical warfare. What would be said of a great nation not equipped to think for the future on naval or artillery questions? Technical naval and military minds have evolved for these purposes. We are not slow to judge and act on the value of a new ship, tank, or machine-gun. The chemical arm is even more specialised and demands the same combination of scientific and military thinking and training. Whatever international disarmament decisions may be forthcoming, unless they seriously dismember the Defense Ministries, we should ensure that the pre-war position is corrected and that our staff conception and organisation covers the chemical weapon."

The author considers that the United States has seen the dangers more clearly than the other countries because we have "an independent peace Chemical Warfare Service, as sister service to the Infantry and Artillery," p. 274. This was written before the suit of the Government against the Chemical Foundation. He would hardly praise us now for our "clear and unprejudiced vision."

*Wilder D. Bancroft*

**Coal-Tar Colours in the Decorative Industries.** *By A. Clarke. 19 × 13 cm; pp. xiii + 166. New York: D. Van Nostrand Company, 1922. Price: $2.00.*—In the preface the author says: "It is obvious even to the casual observer that the general utility of coal-tar dyestuffs and their future possibilities in the decorative industries have not been realised to the full even by the workers engaged in those industries. Perhaps the greater part of the reason for such a state of affairs is that coal-tar colours have retained, as part of the legacy of early experience of these products, the stigma of being fugitive to light and weather conditions. Their lakes, for example, have from time to time been stated to be of insufficient covering power and liable to bleed into the vehicles employed along with them. These complaints could undoubtedly be levelled against the earlier dyestuffs and their lakes, and even at the present time cheap dyes and lakes do not always pay, but it is now possible to obtain dyes of excellent fastness and perfectly insoluble lake-pigments of satisfactory covering power in almost endless varieties of shades. In fact, it is the abounding variety of coal-tar dye products which constitutes one of the greatest stumbling-blocks to any but the expert colourist, since the selection of dyestuffs, suitable in each and every respect for the purposes for which they are to be employed, requires the greatest discrimination. There is, however, a very great future before coal-tar dyes as far as their use for decorative purposes is concerned, not only in lake-making, but in the staining of wood, in varnish-making and the manufacture of colours suitable for water-paint, distempers, artists' colours, etc., as well as in the tinting of such materials as paper, linoleum, leather, furs, ivory, horn, etc."

"The object of the book is to deal, in so far as is possible, in not too technical language with the use of coal-tar dyestuffs in lake-making, and in leather, fur, wood, paper, etc., colouring. Every effort has been made to include the latest

information on each subject. In many cases such information is only to be obtained by recourse to the manufacturers of the various products. Dyestuff manufacturers in particular are always well to the fore with developments in the uses of their products. The author desires to thank the numerous manufacturing houses which have placed their specialised information at his disposal."

The subject is presented under the following headings: introduction; dyes, dyeing and dye-testing; mordants; the manufacture of lakes and pigments; the testing and application of lake pigments; the staining and dyeing of wood; dyestuffs in oil and spirit varnishes; paper dyeing and staining; the dyeing and staining of leather, furs, etc.; miscellaneous applications of coal-tar colours.

"It was unfortunate from the standpoint of the decorative industries that the first coal-tar dyestuffs to be discovered, examined, and applied to technical uses were those of a comparatively fugitive character, namely, basic colours of the type of mauveine, magenta, Hofmann's violet, etc., since because of the fugitive nature of these early colours coal-tar dyes have always had to combat the onus of non-fastness, whereas there have been since 1870 an ever-increasing number of really fast colours suitable for all manner of technical uses," p. 1.

The book contains a large amount of empirical information. The author has taken pains not to touch on any theoretical points. *Wilder D. Bancroft*

**Dissoziation der Gaze.** *By A. Schelest. 24 × 17 cm; pp. 63. Berlin: Kniga, 1922.*—This is really only a pamphlet in which the author gives the results of some work on the dissociation of water, carbon dioxide, and the combustion products of naphtha. The pamphlet is written in a rather sloppy style, there being nothing definite in the section on the dissociation of carbon dioxide to show how it is assumed to dissociate. In another portion of the book, p. 50, it is evidently assumed that it dissociates into carbon and oxygen, which everybody else will deny.

The author considers that earthquakes are due to the explosion of the oxygen of the air with combustibles, presumably petroleum. The volcano is also an oil-burning furnace.

Another interesting conclusion, p. 61, is that "in nature there is no entropy but the specific heat of all natural substances varies with the pressure."

*Wilder D. Bancroft*

# SECOND REPORT OF THE COMMITTEE ON CONTACT CATALYSIS[1]

BY WILDER D. BANCROFT

1-1946

The first report was devoted chiefly to outlining the general situation in regard to contact catalysis. The present report will deal primarily with the experimental work done during the last two years.

## Adsorption and Catalysis

Taylor and Burns[2] say that "theories of catalytic activity have been based frequently upon the assumptions of adsorptive power on the part of the catalytic agent. Experimental investigation of such theories is possible in many cases; but, hitherto, a systematic attempt to apply such a test has not been undertaken. The selective action of catalytic agents suggests a starting point in such investigative work, and it is believed that a solution of the general problem of contact catalysis may be attained more readily when such a study has been accomplished. . . .

"It is, perhaps, natural that most observations of adsorption have been made with the platinum metals, since these were among the earliest recognized catalysts. On the other hand, since the development of the hydrogenation processes by Sabatier and his co-workers, the use of other elements, notably nickel, for catalytic agents has suggested the importance of extending an investigation to include these. Indeed, the apparent simplicity of certain hydrogenation re-

[1] Report of the Committee on Contact Catalysis of the Division of Chemistry and Chemical Technology of the National Research Council. Written by the Chairman in collaboration with the other members of the committee: Messrs. H. Adkins, W. C. Bray, R. F. Chambers, C. G. Fink, E. P. Kohler, A. B. Lamb, E. E. Reid, and H. S. Taylor. It is hoped that the third report will be written by H. S. Taylor in collaboration with the committee.

[2] Jour. Am. Chem. Soc., 43, 1273 (1921).

actions has invited the present attempt to study the relation of adsorption to catalytic activity, and more particularly to cases of specific hydrogenation action.

"From among reactions suitable for investigation, the following were chosen:

$$CO + 3\,H_2 = CH_4 + H_2O$$

$$CO_2 + 4\,H_2 = CH_4 + 2\,H_2O$$

$$C_2H_4 + H_2 = C_2H_6.$$

The metals used were nickel, cobalt, palladium, platinum, iron, and copper. All six of these catalyze the hydrogenation of ethylene; but, according to Sabatier, the methanation reactions can be accomplished only with the first three, nickel, cobalt, and palladium.

"A knowledge, then, of the adsorptions of hydrogen, carbon monoxide, carbon dioxide, and ethylene by these metals might be expected to give some insight into the function of catalytic agents and the mechanism of their action. Such a study of adsorptions should, moreover, contribute to the general theory of adsorption by solids. Most observations hitherto have been made upon porous, inert materials where capillarity and ease of liquefaction were important factors. In contrast to this, the present study has been confined to metals, substances which are chemically active, and which should therefore display adsorptions of a specific nature."

Nickel reduced from the oxide at 300° was found to take up about four volumes of hydrogen at 25°–218°, about 3.5 volumes CO at 184°, about 1.15–0.4 volumes $CO_2$ at 25°–218°, about 4.1–2.5 volumes $C_2H_4$ at 25°–218°, and no measurable amount of nitrogen. When the same nickel is heated in hydrogen to 600°–700°, it loses its catalytic power and the corresponding adsorptions drop to 0.3 for hydrogen, 0.75 for carbon monoxide, 0.2–0.05 for $CO_2$, and 0.35–0.15 for $C_2H_4$. There is, therefore, a striking parallelism between adsorption and catalytic activity.

Copper adsorbs no nitrogen at 25° and only negligible

quantities of hydrogen, carbon dioxide, and oxygen. It takes up about 0.6 volumes of carbon monoxide or of ethylene at 25°; but the adsorption of these two gases becomes negligible at 218°. Copper shows similar variability to nickel in adsorptive power with variation in mode of preparation. Samples of copper obtained by Dr. R. N. Pease in Princeton shows hydrogen adsorption amounting to as much as 3 cc per 100 gram sample. Mr. W. A. Dew has recently obtained a 30 g sample showing 5 cc adsorption at 100° C. This latter was obtained by slow reduction of granular copper oxide below 200° C followed by adsorption measurements with ammonia. The catalytic activity of such copper is high. It causes rapid combination of hydrogen and ethylene and of carbon monoxide and oxygen at 0° C. The carbon monoxide and ethylene adsorptions are correspondingly high. This reactivity with ethylene and hydrogen is occurring at 150° C, below hitherto recorded reaction temperatures.

Cobalt adsorbs carbon monoxide strongly at low temperatures, carbon dioxide to some extent and ethylene slightly less. An appreciable adsorption of hydrogen was obtained only with cobalt formed on a porous brick. The adsorptions by iron were small and only at 25° were measurable values obtained for hydrogen, carbon dioxide, and ethylene. At 25° iron took up 0.7 volumes CO, possibly because of the formation of carbonyl compounds. Stoffel[1] has shown that the iron pentacarbonyl, formed by the action of iron on carbon monoxide, is adsorbed by the iron and forms a protective film over the surface of the metal.

"Palladium took up large quantities of hydrogen, 753 volumes at 25° and over 540 volumes at 110°. It is interesting to note that the presence of less than 0.5% of water vapor in the hydrogen had the effect of diminishing markedly the rate at which the hydrogen was adsorbed by the palladium, although it did not affect the total amount taken up.[2]

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[1] Zeit. anorg. Chem., **84**, 56 (1913–14).

[2] Cf. Taylor: Trans. Am. Electrochem. Soc., **36**, 152 (1919).

"Palladium was found to take up large quantities of carbon monoxide and of oxygen. It was impossible to pump off either of these substances at 110°, and it was, therefore, necessary to wash the metal with hydrogen after each successive determination. Mond, Ramsay and Shields[1] believe that palladium forms a definite oxide and that this is dissociated suddenly at higher temperatures.

"Platinum black takes up considerably larger quantities of gases than does the spongy form. It is, too, the more active catalyst. There is evidently some inherent difference between these two forms of platinum since the ratio of adsorptions of the different gases by platinum black does not follow that shown by platinum sponge. For instance, while the adsorption of hydrogen by the former is only one-third more than by platinum sponge, the amount of oxygen taken up is from ten to fifteen times greater. Confirming Gutbier and Maisch,[2] we have found that the quantity of hydrogen taken up by spongy platinum increases slightly with the temperature, whereas the reverse is true for platinum black. Finally, the hydrogen value is greater than that for carbon monoxide in the case of the sponge but less than that of carbon monoxide for platinum black." Lemoine[3] has also come to the conclusion that the difference between spongy platinum black as catalytic agents is greater than can be accounted for by the difference in the surfaces.

Taylor and Burns[4] say that "carbon monoxide was found to adhere tenaciously to platinum, and it was necessary to burn off with oxygen and then remove the excess of oxygen with hydrogen. The hydrogen could then be removed by heating in a vacuum. We regard these results with carbon monoxide as a most significant fact, especially when contrasted with the behavior of palladium, from which carbon monoxide can be removed readily by hydrogen at ordinary temperatures.

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[1] Phil. Trans., **191A**, 105 (1989).
[2] Ber. deutsch. chem. Ges., **52B**, 1368 (1919).
[3] Comptes rendus, **173**, 7 (1921).
[4] Jour. Am. Chem. Soc., **43**, 1283 (1921).

When it is remembered that palladium is a good methanation catalyst at ordinary temperatures and that platinum even in its most active form cannot be used to effect this reaction,[1] the importance of this factor will readily be realized. When platinum black was not subjected to treatment with oxygen after having been exposed to carbon monoxide, but was merely evacuated, a subsequent measurement of hydrogen adsorptions showed 3 volumes at 25° and 2.6 volumes at 110°, whereas the true values on a clean surface were 6.85 volumes and 6.0 volumes, respectively. This is a decrease of approximately 57%. In an analogous way the adsorption of carbon monoxide itself at 110° declined from 19.2 volumes on a clean surface to 7.3 volumes, a decrease of 63%, when the surface had been exposed previously to carbon monoxide, and then only evacuated. This would indicate that it is possible to render only about 40% of the platinum surface free from carbon monoxide even by heating the metal to 110° in a vacuum. In this case, as in the usual practice, the evacuation was continued until the quantity of gas which could be obtained during an interval was less than 3 mm³. This was calculated to be equivalent to a pressure of less than 0.002 mm of mercury. Consequently even when pressures of carbon monoxide not exceeding a few centimeters exist, it is reasonable to suppose that the platinum surface remains covered so thoroughly with carbon monoxide that hydrogen or other gases are unable to reach it. Bancroft[2] has already predicted that carbon monoxide would tend to prevent the adsorption of hydrogen by platinum. In confirming this view our experiments demonstrate the cause of the inhibition noted by Harbeck and Lunge[3] when carbon monoxide was present in the hydrogenation of ethylene.

"Platinum sponge showed no adsorption of either ethylene or carbon dioxide. On the other hand, platinum black ad-

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[1] Sabatier: "La Catalyse en Chimie organique," 197 (1920).
[2] Jour. Phys. Chem., 21, 734 (1917).
[3] Zeit. anorg. Chem., 16, 50 (1898).

sorbed more ethylene than hydrogen, and even adsorbed appreciable quantities of carbon dioxide."

"Investigations of catalytic adsorbents of the type dealt with in these experiments show results which are in marked contrast to the results of adsorption measurements in which porous, chemically inert materials such as charcoal and silica gel are used. In the case of metallic catalytic agents the adsorption is pronouncedly specific. In one of such cases hydrogen is more markedly adsorbed than other gases. For example, nickel adsorbs more hydrogen than carbon monoxide. On the other hand, the reverse is the case with iron and cobalt, these metals showing hydrogen adsorptions which are decidedly smaller than those of the other gases. The parallelism observed in the case of porous, inert adsorbents, such as charcoal, between adsorption, compressibility, and ease of liquefaction of the gas does not appear to hold in the case of adsorption by the metal catalysts which we have studied. The adsorption isotherms are also different, saturation capacity of the adsorbent being attained at rather low partial pressures of the gases.

"All of this evidence is in agreement with the view that adsorption in the case of metal catalysts is a surface phenomenon somewhat chemical in nature, possibly involving rearrangements of electrons in both the adsorbent and the gas. In the case of bodies like charcoal and silica gel, the phenomenon may be attributed frequently to the presence of pores which fill gradually with liquid, although covering of the surface by an adsorbed gas film can undoubtedly occur in this case also. At any rate, the experiments which have been performed demonstrate that the problem of adsorption by *solid* adsorbents is a far wider one than hitherto indicated, and that it promises to be more interesting by reason of the wide range of possibilities. A comprehensive scheme of study in this field has been planned and undertaken.

"The measurements with active nickel catalysts and with inactive nickel obtained by reduction of the oxide at elevated temperatures form, we believe, convincing experimental

demonstration that the destruction of catalytic activity is accompanied by an almost complete suppression of adsorptive power. In addition, these results indicate clearly one reason for variability in catalytic behavior with variation in mode of catalyst preparation, a phenomenon widely known, but hitherto little understood. The varying adsorptive capacity of the material would account for such variable catalytic behavior. The results suggest, moreover, the necessity of obtaining, in the kinetic studies of catalytic action, the actual behavior of the catalytic agent as an adsorbent.

"From an examination of our adsorption measurements, it is evident that maximum catalytic activity does not occur at temperatures at which maximum adsorption is shown. Indeed, in the case of copper, the hydrogenation of ethylene begins only at a temperature where the adsorption of ethylene is ceasing to be a measurable quantity.[1] It is true that nickel begins to hydrogenate ethylene at ordinary temperatures, where adsorptions are very large, but it will be observed that at the optimum temperature for this reaction, 130° to 150°, the adsorption of ethylene is considerably less than that at the temperature at which reaction commences. Similar observations may be made with respect to a cobalt catalyst with carbon monoxide and hydrogen, and with nickel in the case of carbon dioxide and hydrogen.

"We regard this evidence concerning diminishing adsorption and increasing catalytic activity with temperature as demonstrating the necessity, in many catalytic reactions, of a free evaporation of both reactants and resultants from the catalyst surface. A strong or irreversible adsorption of any of the participants in a reaction undoubtedly tends to render the catalyst surface inactive. At the same time it is possible that such an irreversible adsorption may, in certain cases, lead to a reaction between gases which only occurs with difficulty in the gas phase. Our experiments with palladium and

[1] [Since then copper has been prepared of high catalytic activity at 0°, at which temperature adsorption is high. H. S. T.]

platinum with carbon dioxide and hydrogen may be cited in illustration. The experimental data show that carbon monoxide is adsorbed tenaciously by both metals, and that at moderate partial pressures the gas probably covers the metal surface. In such case, hydrogen in presence of carbon monoxide can be adsorbed only on a surface of carbon monoxide and not on the metal. The union of carbon monoxide with palladium to form a Pd-CO surface complex is apparently such that at ordinary temperatures the reactivity of the carbon is enhanced, and with hydrogen, methanation results. With platinum, on the other hand, no reaction occurs at any temperature and the Pt-CO surface complex remains undecomposed. The evidence cited by von Hemptinne[1] as to the behavior of Pd-CO surface complexes at low temperatures (—20° and lower) is quite parallel to that occurring with Pt-CO complexes at all temperatures within the range investigated. There is evidence that the production of sulfur trioxide in presence of platinum is caused by the interaction of a Pt-O surface complex with sulfur dioxide molecules. In this case the slight tendency of sulfur trioxide molecules to evaporate constitutes a complicating factor.

"When such strong or irreversible adsorptions are not present, when evaporation of the reacting gases is relatively rapid, the conclusion seems inevitable that the condensation process disturbs the electron field of one or the other, or both of the reacting gases, thus bringing them into a reactive condition. Subsequently, on evaporation, by re-adjustment of the electron field, the active molecules may either regain their normal state, or, on the other hand, may collide with other molecules bringing about reaction. That the adsorption effect is not singly the cause of reaction has been suggested in the preceding paragraphs. We are disposed, therefore, to consider reaction as the resultant of at least two factors, the adsorption factor and the temperature factor. There is evidence as to how these two factors operate. For example,

[1] Von Hemptinne: Zeit phys. Chem., 27, 429 (1898).

it is known that ethylene and hydrogen can be caused to react by purely thermal means. The temperatures required are high, being in the region of 500°. With a nickel catalyst present, reaction occurs from room temperatures upward, and strong adsorption of both gases is shown by nickel. With copper a temperature of 150° is required for incipient action, and adsorption by this metal is much less pronounced than in the case of nickel. Similar observations hold in respect to the conversion of carbon monoxide and hydrogen by means of nickel and cobalt, the temperature required in the case of cobalt, the less efficient adsorption agent, being some 90° higher than with nickel for similar rates of reaction.

"It would, therefore, appear that the adsorptive capacity is an index of the temperature at which reaction can be induced. Where adsorption is strong we have, presumably, a more marked or more frequent displacement of the stable configuration of the molecule than with a weak adsorption. Consequently, a lower temperature will effect interaction. In such manner it is possible to correlate, qualitatively at least, the present data on adsorption with the known catalytic activity of the metals in the reactions chosen for study. The importance of this conclusion is sufficient to warrant a detailed study of the same with a view to obtaining a quantitative relationship between the temperature factor and the adsorption factor. Such a study undoubtedly involves an analysis of catalytic action in its relation to radiation theories. An experimental investigation upon such lines is in progress." A forthcoming paper by R. N. Pease discusses the interaction of ethylene and hydrogen on copper of varying degrees of adsorptive power.

Taylor and Neville[1] have made a study of catalysis in the interaction of carbon with steam and with carbon dioxide. The first stage in the reaction may be written

$$C + H_2O = CO + H_2 \text{ (steam-carbon reaction).}$$

In the absence of catalytic agents as, for example, with the

[1] Jour. Am. Chem. Soc., 43, 2055 (1921).

ash-free carbon obtained by the thermal decomposition of hydrocarbons, this reaction takes place practically exclusively. Ordinarily, however, we have a second reaction taking place,

$$CO + H_2O = CO_2 + H_2 \text{ (water-gas reaction)},$$

the ash content of the coke acting as a catalytic agent.[1] Iron oxide is an important constituent of catalytic agents preferred technically in this process. Since the equation for the water-gas reaction represents an equilibrium which is exothermic in the direction of hydrogen production, it follows that low temperatures and excess of steam favor the elimination of carbon monoxide from the products of the reaction. Temperatures in the neighborhood of 500° are therefore employed in the production of hydrogen by the water-gas catalytic process.

"Various attempts have been made to conduct these two reactions in a one-stage technical operation whereby steam is to be passed over carbon of suitable form at a low temperature, so that the reaction products are, in the main, carbon dioxide and hydrogen. To do this efficiently, it is necessary to increase the activity of carbon toward steam by the addition of suitable catalytic agents to the reaction mass."

While many patents have been taken out, there is no published information "which would indicate the relative merits of the proposed catalysts, the optimum concentration of these, or the effect of temperature change upon the reaction. Neither is there any suggestion of the nature of the mechanism of the catalysis. It was therefore decided in this research to gain some knowledge upon these points by a systematic study of various catalytic agents in their influence upon the reactions. This study has led to a wholly unexpected development of the program of work, since the mechanism of the acceleration by catalytic agents is quite other than was anticipated at the outset.

"Many agents were found to catalyze the steam-carbon reaction of which the best were the carbonates of potassium

[1] Gwosdz: Zeit. anorg. Chem., **31**, 137 (1918).

and sodium. With the idea that their influence was to be ascribed to an acceleration of the water-gas reaction, $CO + H_2O = CO_2 + H_2$, this being known to be slower than the steam-carbon reaction in the absence of catalysts, known good catalysts for the water-gas reactions, for example, iron oxide, were tried as catalysts for the steam-carbon reaction. Iron oxide was found to be quite inactive in this respect, and it was evident, therefore, that another explanation of the mechanism must be sought.

"As a possible explanation of the observed catalytic effect in the steam-carbon reaction, it occured to us that the interaction of carbon dioxide and carbon might be facilitated by the catalytic agents in question and that this was the key to the mechanism of the former reaction. For, if such were the case, the carbon dioxide produced in the second stage of the steaming process, $CO + H_2O = CO_2 + H_2$, would then interact with carbon to form monoxide, $CO_2 + C = 2CO$, which gas, in the presence of the excess of steam, would react as above to form additional quantities of carbon dioxide and hydrogen, thus increasing the net yield of gas from the steam reaction. Experimental tests of this idea showed a complete parallelism between the catalytic effects in the two reactions. In this case reduced nickel was the only catalyst found by us to be superior to the alkali carbonates as accelerating agent, and investigation showed that the low activity of nickel in the steam-carbon reaction was due to a condition brought about by a side reaction, as will be described later. Poor catalysts in the steam-carbon reaction were found to be poor catalysts in the carbon dioxide-carbon reaction, and no material would catalyze this reaction which was not also active in the former case.

"As an explanation of the catalytic effect in the carbon dioxide-carbon reaction, it is shown that a mechanism involving alternate reduction and reformation of the alkali carbonates was not correct. These experiments, however, led us to make a determination of the adsorption capacity of carbon for carbon dioxide at the reaction temperatures con-

cerned, both when alone and when impregnated with various catalytic agents. The results of these experiments showed in a striking manner that good catalysts for both of the reactions under investigation also caused a marked increase in the adsorptive capacity of carbon for carbon dioxide as measured at 445°. Our experiments have indicated that this increased adsorption of carbon dioxide by carbon may be attributed to the action of the catalytic agents in facilitating the decomposition of "fixed oxygen" complexes on the carbon surface, thus cleaning the surface to an extent which would ordinarily be only attained by subjecting the carbon to considerably higher temperatures.[1] Definite evidence has also been obtained that such inactive oxygen complexes may be broken partially down into carbon monoxide and carbon dioxide by prolonged heating at the temperature of the experiments, even in absence of catalytic agents, and that they may be reformed by carbon dioxide under these conditions."

"Of the materials studied, potassium and sodium carbonates are the only efficient catalysts for the reaction, and potassium carbonate is about three times as active in this respect as the sodium salt. Other salts of the alkalies and alkaline earths have a slight catalytic effect. Iron oxide exerts no influence whatever. Since it is almost certain that the reaction progresses in two stages:

$$(a)\ C + H_2O = CO + H_2$$
$$(b)\ CO + H_2O = CO_2 + H_2$$

and since iron oxide is a very good catalyst for Reaction (*b*), it may be concluded: firstly, that the water-gas reaction attains its equilibrium under the conditions of these experiments; and secondly, that observed catalysis of the reaction between carbon and steam cannot be due to a catalysis of the water-gas reaction; but must be due to an acceleration of the first stage or of some other reaction concerned. The catalysis of the reaction,

$$C + CO_2 = 2\ CO,$$

[1] Lowry and Hulett: Jour. Am. Chem. Soc., 42, 1408 (1920).

satisfies these conditions and is considered sufficient to account for the increased production of gas when catalytic agents are used in the steam-carbon process."

"In presence of 20% $K_2CO_3$ one gram of carbon adsorbs 4.4 cc $CO_2$, which drops to 2.0 cc with 20% $Na_2CO_3$, to 0.4 cc with 20% NaCl, and to 0.3 cc with no catalyst, all at 445°. Special experiments showed that the adsorption by potassium carbonate alone at the same temperature was practically zero. Taylor and Neville point out that the adsorption "is more marked at temperatures higher than those at which adsorption ordinarily plays a part, and this is consistent with the fact that the specific catalytic effect of the same substances increases with temperature. We are inclined to regard such factors as strong presumptive evidence of a C-$CO_2$ complex formation."

These experiments of Taylor and Neville apparently explain why the English at one time heated their charcoals with salts to activate them. The question arises whether the American method of heating charcoal with steam at just over 900° is really the best way of activating charcoal. We changed from oxidation by air to oxidation by steam because the latter was more selective. It seems probable that the selective oxidation will be more marked the lower the temperature. If so, passing steam through a charcoal impregnated with potassium carbonate should give an even better carbon. If Taylor and Neville are right, one would get the best results with carbon dioxide and could then use the carbon monoxide to make phosgene.

Vignon[1] claims that, in presence of lime, steam reacts with carbon at a lower temperature than when no lime is present. The lime increases the reduction of CO or $CO_2$ to methane. Theoretically we may have the reaction.

$$2\,C + CaO + 2\,H_2O = CaCO_3 + CH_4.$$

By a subsequent heating at a higher temperature we can regenerate the lime,

$$CaCO_3 = CaO + CO_2.$$

[1] Ann. Chim., 15, 42 (1921).

By working in two stages, we get, theoretically, the reaction

$$2\,C + 2\,H_2O = CH_4 + CO_2.$$

Actually Vignon never got a mixture which contained more than 33% $CH_4$ to 67% $H_2$ and his gas mixture also contained carbon monoxide and dioxide.

### Effect of Oxygen on Reduction

In the previous report it was pointed out that the presence of oxygen[1] in the platinum catalysts was apparently beneficial to reduction by hydrogen.[2] Further results along this line have been obtained in the laboratory of Hofmann.[3] "A palladium, platinum, or iridium contact mass catalyzes a mixture of hydrogen and oxygen very differently depending on the previous gas treatment. A preliminary treatment with oxygen increases the catalytic action of palladium thirty to fifty fold, of platinum about three fold, and of iridium three to ten fold as compared with a preliminary treatment with hydrogen. This increase in catalytic activity caused by the treatment with oxygen is not due merely to the conversion into water of the adsorbed or occluded oxygen because the amount of this is much too small. The presence of adsorbed oxygen makes possible a 'fresh' combination between metal and hydrogen which, in the case of platinum and palladium, acts much more rapidly on oxyhydrogen gas than does a surface which has been charged with hydrogen for a good while and which has 'aged.' The more quickly and the more completely this 'fresh' state develops, the more powerfully the metal acts as a catalytic agent. Iridium develops the further characteristic of behaving like an active oxygen electrode when in presence of oxyhydrogen gas containing more than the theoretical amount of oxygen.

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[1] Willstätter and Waldschmidt: Ber. deutsch. chem. Ges., **54**, 113(1921).

[2] Oxygen is not beneficial in hydrogenation with nickel. See Normann: Ber. deutsch. chem. Ges., **55B**, 2192 (1922).

[3] Ber. deutsch. chem. Ges. **49**, 2369 (1916); **53**, 298 (1920); **55B**, 273 (1922).

"The parallelism between catalytic action and electromotive force is probably due to a single cause, which is probably the presence of free or of metallically dissolved hydrogen atoms which determine both the hydrogen potential and also react with oxygen to form water. Under the conditions prevailing, platinum and palladium functioned only as a hydrogen electrode, while pulverulent iridium was able to function also as an active oxygen electrode in gas mixtures of high oxygen concentration. . . . .

"In general we may conclude that the highest catalytic action occurs only when the maximum hydrogen or oxygen potential is developed 'freshly' thereby reacting with the gas at the highest velocity. It is not sufficient for hydrogen and oxygen to be adsorbed in the proportions in which they react, at an electrically neutral surface."

In the 1922 paper[1] "no indication could be discovered of the peroxide-hydride to which Willstätter and Waldschmidt ascribe the favorable effect of oxygen on the catalytic activity of hydrogen. The volume of oxygen occluded by platinized earthenware is shown to be so small that any peroxide produced cannot bear any relation to the actual effect of oxygen on catalysis which is rather due to its influence on the catalyst surface. At the same time, the small amounts of gas adsorbed by porous surfaces render them much more suitable than platinum for determinations of variations of contact potential during catalysis. Measurements of the potential difference between such an electrode and one of platinum in contact with hydrogen at atmospheric pressure show that, whether the electrolyte be 17% sulphuric acid or 4% sodium hydrogen carbonate solution, porous materials impregnated with palladium, platinum, or iridium in contact with a mixture of hydrogen and oxygen are modified electrically in the opposite sense to that of their previous treatment (with one or the other of the gases), and the more rapidly this occurs the more rapidly is water-formation catalyzed. The activity diminishes

[1] Cf. Jour. Chem. Soc., 122 II, 276 (1922).

on prolonged treatment with hydrogen or, especially in the case of palladium, with oxygen. It is improved by repeated variation of this treatment, by repeated use with the stoichiometrical mixture of the gases, and by varying galvanic polarization. Light and moderate temperature changes are much less effective. Hydrogen exerts a greater effect on the catalysis potentials with increased hydrogen ion concentration of the electrolyte, whilst the reverse is true of oxygen. These results indicate that neither pure hydrogen nor hydrogen-oxygen mixtures produce any special oxidizing or reducing compound on the catalyst surface of the kind suggested by Willstätter which determines the potential. Direct instantaneous determinations of the effect on the same electrode potentials of the addition of hydrogen peroxide show that this always acts as a strong oxidizing agent, and renders it highly improbable that any peroxide-hydride could exert a strong reducing influence, apart from the extreme rapidity with which the known peroxides are decomposed by platinum metals. Although it is not improbable that hydrogen peroxide is an intermediate product in the formation of water, its existence is so transient as to elude all attempts to detect it."

The distinction that Hofmann makes between a freshly prepared and an old surface seems very suspicious in view of what we know about the poisoning of platinum. Berliner[1] has pointed out the extraordinary way in which palladium loses its power of adsorbing hydrogen when allowed to stand round. Bodenstein[2] has shown that the most intense catalytic action of platinum on the formation of water from oxyhydrogen gas occurs only when the platinum surface is very clean, a state of things which is very difficult to obtain and almost impossible to maintain. He points out that "in the experiments with an excess of oxygen the platinum once remained constant for several days. This looks as though the chief disturbing factor were the grease from the stopcock, which was

[1] Wied. Ann., 35, 803 (1888).
[2] Zeit. phys. Chem., 46, 730 (1903).

oxidized in this case." Long before Berliner or Bodenstein, Faraday[1] was very clear as to the connection between cleanliness and catalytic action. While it is by no means certain that the results of Willstätter and of Hofmann are due to a cleansing of the surface of the metal, it is unfortunate that they have not eliminated this possibility.

The work at the Princeton laboratory suggests another possible explanation of the phenomenon. Pease and Taylor[2] have studied the reduction of copper oxide by hydrogen. Wright, Luff and Rennie[3] report that even when working with an excess of hydrogen "the reduction commenced visibly by the formation of a red speck amongst the little mass of copper oxide at the lowest part of the bulb; this spread quickly, becoming rapidly larger and larger until practically the whole mass became a reddish metallic powder, the progress of the reaction reminding one of the slow deflagration of a quantity of touch paper, the reducing action being apparently propagated from particle to particle through the mass."

Pease and Taylor conclude that "it is evident from these results that the reaction is autocatalytic, copper being the autocatalyst in all probability. The reaction starts only after some time . . . with the formation of one or more visible nuclei of copper. From these as centers the zone of reaction, that is, the copper-copper oxide interface, spreads out and as its area increases, the rate of water formation increases. If the induction period is due to the initial absence of metallic copper, it should be possible to shorten it or to cause it to disappear altogether by adding already reduced copper to the oxide about to be reduced."

Preliminary experiments without copper showed that "reduction practically never started at the top where the preheated hydrogen first met the charge, but usually at some point near the middle of the charge along the side of the tube.

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[1] Experimental Researches in Electricity, 1, 165 (1839).
[2] Jour. Am. Chem. Soc., 43, 2179 (1921).
[3] Jour. Chem. Soc., 35, 522 (1879).

From these points as nuclei, the reaction zone appeared to spread over the whole mass." When a layer of previously reduced granules of copper was placed on top of the copper oxide, this hastened the setting-in of the reaction and nearly eliminated the incubation period. "An examination of the sample after reduction had proceeded for several hours showed that the reaction had begun at the top of the charge in contact with the copper and had proceeded downward in wave-front roughly normal to the direction of hydrogen flow. Since ordinarily reduction begins within the charge rather than at its surface, the top being reduced toward the end instead of at the beginning of the run, it would appear that the layer of copper had rendered the oxide in contact with it the more reactive, substantiating the assumption that the reaction is autocatalytic and takes place mainly and most easily at a copper-copper oxide interface."

Hydrogen was mixed with known amounts of electrolytic oxyhydrogen gas and passed over heated palladized asbestos to convert the oxyhydrogen gas into water vapor. When hydrogen and water vapor were passed through copper oxide at 150° "not only was reduction prevented during the exposure (reduction would normally have started in 1–1.5 hours) but electrolytic gas was shut off and pure dry hydrogen alone passed over the oxide. From these results it is clear that water vapor inhibits strongly the initial reaction between hydrogen and copper oxide—that is, it inhibits effectively at this temperature the formation of copper nuclei. Since it is a product of the reaction it clearly has no such powerful action on the subsequent reaction at the interface."

"Results obtained during the experiments on the catalytic combination of hydrogen and oxygen in the presence of copper indicated that the oxygen present inhibited the reduction of the oxide formed simultaneously with the water, for when the oxygen was shut off the rate of water formation always rose temporarily to a value considerably greater than that when oxygen had been present. . . . For the purpose of confirming these indications, the rates of reduction of copper

oxide by hydrogen containing oxygen were determined. Oxygen was added to the hydrogen by connecting with the hydrogen line the electrolytic gas generator used in the experiments with water vapor.. The oxygen concentrations are expressed in terms of the corresponding weight of water in milligrams which could theoretically be formed from the oxygen during a five-minute passage of the mixture. . . .

"As had been anticipated, it was found that the presence of oxygen interfered very seriously with the reduction reaction. In one experiment hydrogen containing oxygen equivalent to ten milligrams of water per five-minute interval was passed over copper oxide for five hours, during which period no formation of water could be detected. It appears, therefore, that under these conditions the oxide is not reduced appreciably nor does it possess appreciable catalytic activity toward the combination of hydrogen and oxygen. Normally, with pure hydrogen, reduction would have become measurable in 1–1.5 hours. Directly the oxygen was cut off, reduction set in, the maximum rate being much greater than in any other runs. The incubation period was therefore eliminated by this treatment. It will be recalled that similar treatment with water resulted only in postponing the incubation period. After reduction had been allowed to proceed for a short time, oxygen was again turned on. As a result, the rate of reduction was repressed very markedly, dropping from 31 to 5 mg of water per five-minute interval, and did not recover until the oxygen was shut off. Subsequent addition of oxygen resulted in a repetition of this effect. At 200° the effect of oxygen was to retard the reduction very strongly, though the latter was not prevented completely. The quantities of water formed under these conditions are undoubtedly due in part to catalytic combination; nevertheless, it is clear from the curve that at the end of three hours the charge had not been reduced appreciably, whereas reduction would normally have been nearly complete at the end of this time..

"The effects produced by oxygen are seen to be quite distinct from those produced by water vapor. (It was pos-

sible that they might have been due to the formation of the latter.) At 150°, preliminary treatment with hydrogen containing water vapor not only results in no water formation but postpones the incubation period till the water vapor is cut off. After reduction has commenced, however, further addition of water vapor has no marked effect. With oxygen in the hydrogen, on the other hand, the incubation period is eliminated (that is to say, reaction starts directly the oxygen is cut off) although no reduction takes place during the exposure; but addition of oxygen after reduction has started very markedly repressed the reaction. Clearly water vapor is only effective in the initial reaction between hydrogen and copper oxide. This may be attributed to the strong adsorption of water vapor by copper oxide. Comparisons of the quantities of water added to the hydrogen and quantities recovered from the effluent hydrogen during the first few minutes of the exposure to water vapor indicated that quite large quantities of water vapor must have been taken up. Oxygen, on the other hand, probably is effective only in the reaction taking place at the interface. At first sight it would appear that it also inhibits the initial reaction. However, the fact that reduction commenced directly the oxygen was cut off seems to indicate that the formation of copper nuclei had been going on during this period; that is to say, the elimination of the incubation period is taken to indicate that the primary reaction had taken place even in the presence of oxygen. The abnormally rapid rise to an abnormally high maximum after the oxygen had been turned off and reduction once started further indicates the existence at that time of numerous centers of activity. This is consistent with the observations of Dr. A. F. Benton in this laboratory that oxygen is not markedly adsorbed by copper oxide, at these temperatures.

"It has been suggested that the retarding effect of oxygen on the reaction at the interface is due to its adsorption by the interface. It is a little difficult to conceive of oxygen remaining long in the adsorbed state at the interface, the seat of ac-

tivity in the reduction reaction. Granting that oxygen may be so adsorbed, it would seem very probable that it would either immediately be converted to oxide or else react directly with hydrogen to form water (and such a view of the catalytic reaction has its advantages). The reaction to form oxide, if carried far enough, would eventually decrease the area of the interface materially and hence the rate of water formation. Thus, qualitatively, the effect of oxygen would be accounted for. However, the effect of the oxygen is immediate and it is doubtful whether sufficient oxygen is initially present to reduce the interface area by the required amount. This would certainly require all the oxygen present in the gas for a considerable time and yet it is known that even starting with a pure copper surface, the major part of the oxygen goes to form water, although the remainder does combine to form oxide. It is perhaps more satisfactory to assume for the present that oxygen is in fact strongly adsorbed by the interface and protects it from the hydrogen, and although constantly being consumed in the formation of water and oxide, is nevertheless renewed at a sufficiently rapid rate to maintain the protective film."

In a later paper Pease and Taylor[1] report on the catalytic formation of water in presence of copper and copper oxide. "Our results appear to indicate clearly that the factors which control the catalytic combination of hydrogen and oxygen in presence of metallic copper are identical with those which are active in the oxidation of the catalyst and the reduction of the resulting oxide. There is no question but that under the conditions of the majority of the experiments copper oxide is formed and that hydrogen is capable of reducing the oxide at the same temperature. It is equally true that in the temperature interval within which the catalytic activity drops sharply, namely, between 130° and 100°, the reducibility of the oxide formed during a run also abruptly falls off, and the rate of oxidation of the copper undergoes a considerable de-

[1] Jour. Am. Chem. Soc., **44**, 1637 (1922).

crease. Thus, with 10 mg of water equivalent of oxygen, a minimum of 2.5 mg of water is formed at 130°, and only about 0.1–0.2 mg at 100°; the initial rate of reduction of oxide is 5.8 (mg of water) at 130° and 0.6 at 100°; and the amount of oxide formed in an hour at 130° is about 50 mg (water equivalent) while it amounts to about 20 mg at 100°, although during this period about 50% of the oxygen is passing through as water vapor at 130° and only 1% at 100°.

"In view of these results, it appears that whatever the conditions may be that control the oxidation and reduction reactions, they also control the catalytic activity. This is in sharp contrast to the action of metallic nickel reduced from the oxide at 150°–200°, as preliminary experiments of ours have shown. Nickel so prepared will catalyze the combination of small quantities of oxygen in hydrogen with the hydrogen at room temperature. The catalyst will slowly oxidize in the air at this temperature but the oxide so formed is not reducible below 100°–150° and the oxidized material is inactive as a catalyst. Clearly, with nickel it is a case of purely contact action. The chemical properties of the catalytic material are in no way related to its activity as a catalyst. With metallic copper, on the other hand, it is quite clear that a close connection between the two does exist.

"Were it not for the inhibitory action of oxygen on the reduction reaction the mechanism could be at once set down as an alternate oxidation and reduction process; and only to the extent that this inhibition is complete is this mechanism ruled out. Now it has been found that at 200° the original oxide granules are progressively though slowly reduced by hydrogen containing 10 mg of oxygen and that the oxide formed during a catalytic experiment is very much more reactive than the original granules. It is, therefore, quite certain that there is some oxidation and reduction at 200° and probably also at the lower temperatures.

"While all of our results are consistent with the alternate oxidation and reduction mechanism, there is another closely related mechanism which cannot be ruled out and merits

consideration. This may be called the incipient oxidation mechanism. The reaction between an oxygen molecule and the copper atoms of the catalyst involves a disruption of the molecule and the subsequent formation of two oxide ions. It would appear that at the moment of this transformation, the oxygen would be in a particularly reactive state, since the stable electron structure of the molecule has been destroyed and that of the ion has not yet had opportunity to be built up. If, at this moment, the oxygen is struck by a hydrogen molecule, water would be formed, for this process represents the greatest decrease in free energy. The catalyst may, therefore, be able to activate the oxygen because of its ability to combine with it and in the process of combination to open it to attack by hydrogen. This power of the catalyst would evidently parallel closely its oxide-forming power and would decrease with the latter as the catalytic activity actually does. If this action can only take place at a copper-copper oxide interface it cannot be distinguished from that resulting from alternate oxidation and reduction, in which the oxygen actually reaches the ion stage. There is a little evidence, however, that if this can take place at any copper surface—and from the results of Wright and Mencke,[1] it does appear that oxidation is an interface phenomenon—this action does not predominate. For, as has been already demonstrated, a purely contact action appears to be excluded and the reasons adduced against such contact action are equally cogent in the present instance."

"It appears to us that our results are most simply explained by assuming that the combination of hydrogen and oxygen in presence of copper takes place mainly in two steps: the first, oxidation of the copper catalyst; and the second, reduction of the oxide so formed, the latter reaction being complicated by the inhibitory action of free oxygen. The extent to which free oxygen interferes will depend upon the amount present. This in turn will depend upon the extent to which it is fixed by the copper, and this, finally, will depend

[1] Wright and Mencke: Jour. Chem. Soc., 37, 785 (1880).

not only upon the temperature but also upon the efficiency of the hydrogen in keeping the copper surface clear of oxide, for the more oxide there is already present on the surface, the less efficient the copper will be in fixing further oxygen. The efficiency of the catalyst depends upon a favorable balance being maintained among these separate actions. If the oxygen is all fixed in the top layers of catalyst and the oxide reduced as fast as formed, the reaction will proceed smoothly to complete conversion. This is evidently the situation at 200°. At 150° the inhibitory influence of oxygen is noticeable but the rates of oxidation and reduction are so nearly balanced from the start that this never becomes serious. At 130°, however, the rate of reduction at the start lags markedly behind the rate of oxidation and as this tends to interfere with the ability of the catalyst to fix oxygen, the influence of free oxygen soon begins to make itself felt. Eventually a further increase in free oxygen evidently can inhibit the rate of reduction no further and a steady state results. The behavior at 100° is the same except that free oxygen is probably present from the start.

"It will be seen that our observations are, therefore, consistent with the simple alternate oxidation and reduction theory and appear to exclude the possibility of any purely contact action predominating, at any rate. Of the contact actions, that made possible by the oxide-forming ability of the copper should perhaps have greatest weight. In fact, it would appear probable that at 200° and higher temperatures this action may become more and more important. The incipient oxide mechanism differs in general from the alternate oxidation-reduction mechanism only in the length of time the oxygen is fixed to the copper surface. If this is infinitesimal, the action is of the incipient oxide type; if the time is measurable, it is of the alternate oxidation and reduction type.

"These results throw no further light on the cause of the inhibiting influence of oxygen. An attempt was made to obtain evidence of adsorption of oxygen on partially reduced oxide but the results were negative. We are still of the opin-

ion that adsorption of oxygen at the copper oxide interface is the explanation. The difficulty appears to arise in obtaining sufficient quantities of surface interface to make the adsorption measurable."

Years ago Campbell[1] recommended the use of palladinized copper oxide in combustions. Any advantage must have been due to action at the interface. Lewis[2] found that finely divided platinum, silver, and manganese dioxide catalyze the dissociation of silver oxide into silver and oxygen. This is probably also a reaction at the interface and the same is probably true for the effect of finely divided platinum and certain metallic oxides[3] upon the dissociation of mercuric oxide. Voorhees[4] has shown that for hydrogenation purposes an extremely active oxide of platinum, possibly platinum trioxide, can be prepared by fusing chloroplatinic acid with an excess of sodium nitrate. When the cooled melt is washed with water, a brown oxide is obtained, which is probably identical with an oxide obtained electrolytically by Hittorf,[5] using a platinum anode in a fused sodium nitrate bath. The brown catalyst turns black during the actual hydrogenation, presumably changing to a lower oxide. "The time necessary for this change of the catalyst depends to a considerable extent upon the way in which the catalyst has been formed and the nature of the solvent used. For the catalyst, the preparation of which is described in this paper, the time necessary varies from a few seconds to fifteen or twenty minutes. As soon as it becomes black it either becomes spongy in appearance or takes on a finely divided form which readily remains suspended in the reaction mixture. The platinum which is now present is essentially the same as a very active platinum black

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[1] Am. Chem. Jour., 17, 681 (1895).

[2] Zeit. phys. Chem., 52, 310 (1905); 55, 449 (1906); Jour. Am. Chem. Soc., 28, 139 (1906).

[3] Taylor and Hulett: Jour. Phys. Chem., 17, 565 (1913); Jour. Am. Chem. Soc., 44, 1443 (1922); Kendall and Fuchs: 43, 2017 (1921); 44, 1447 (1922).

[4] Jour. Am. Chem. Soc., 44, 1397 (1922).

[5] Pharm. Zentralblatt, 1848, 23.

made in the usual way and is similar in all its properties. In many cases the reduction will take place so rapidly that the reaction mixture will actually become hot; but the speed of reduction depends upon the nature of the compound which is being studied. When the reduction is complete, the suspended platinum can be made to settle merely by shaking the reaction mixture with air for a short time, after which it may readily be filtered off or the solution may be decanted. After an amount of catalyst has reduced so much of the unsaturated compound that it has lost the greater part of its activity, it may be revivified by shaking a short time with air just as is customary when using platinum black.

"It is obvious that the oxide of platinum prepared as described is not a catalyst in itself, but is converted by the hydrogen into the lower oxide of platinum which presumably is the active catalyst. In the study of the various oxides of platinum there is, therefore, a third condition which must be observed in the preparation, namely, that a product is formed which is readily reduced by hydrogen to the active catalyst. It was observed that when the sodium nitrate and chloroplatinic acid are fused at a temperature of 700° or higher, an oxide is formed which catalyzes the reduction of organic substances only slowly; moreover, in certain instances, from one to two hours is required before the brown oxide turns black and becomes active as a catalyst."

The experiments of Voorhees confirm the conclusions of Hofmann and of Willstätter that the initial presence of oxygen on the platinum accelerates the reducing action. These experiments do not show whether the brown oxide is reduced completely to the black form or whether the black form is an oxide or the metal itself and they do not therefore prove that the reaction is taking place at an interface; but they are distinctly suggestive for all that.

The explanation by Hofmann[1] of the catalytic action of platinum black on oxyhydrogen gas involves reaction at an

[1] Ber. deutsch. chem. Ges., 49, 2369 (1916).

interface. He considers that the reaction is electrolytic in nature, being due to the juxtaposition of hydrogen and oxygen electrodes. When the space between the electrodes becomes a surface, the reaction takes place at the resulting interface.

### Reaction at an Interface

Langmuir[1] claims that wherever we have to deal, according to the phase rule, with separate phases of constant composition, the reaction occurs only at the boundaries of phases. Thus in the dissociation of calcium carbonate by heat, the carbon dioxide is produced only at the boundary between the calcium carbonate and the calcium oxide phases. When discussing the work of Taylor on the reduction of copper oxide by hydrogen Langmuir[2] says that "all the phenomena. . . . . are in accord with the view that this is another case in which the reaction occurs only at the junction between phases. In conventional nomenclature we may say that we have here an example of autocatalysis, the metallic copper accelerating the reaction. It seems much more profitable, however, to analyse the phenomena in terms of the probable mechanism.

"The oxygen atoms in copper oxide are thoroughly saturated chemically, which means in this case that they have taken up two electrons from the copper atoms and have thus completed their octets, and leave the copper in the form of ions. There is thus no reason for expecting a strong tendency to react with hydrogen at moderate temperatures. In view of Taylor's experiments, we conclude that the oxygen ions in cupric oxide are in fact very inert towards molecular hydrogen. Let us assume that, owing to some local imperfection in the space lattice of the atoms of the copper oxide, an ion of copper has taken up electrons and has formed a neutral atom. It is to be expected that such an atom should behave towards hydrogen molecules like metallic copper or other metallic substances. We have already seen that hydrogen molecules are

[1] Jour. Am. Chem. Soc., 38, 2263 (1916).
[2] Trans. Faraday Soc., 17, 607 (1922).

adsorbed by platinum and by tungsten (and therefore probably by other metals) in the form of atoms. This action is presumably caused by the attraction of the 'free' electrons of the metal upon the hydrogen nuclei. The hydrogen adsorbed by the copper in atomic condition can then react with the oxygen ions merely by the shifting of the hydrogen nuclei from the copper atoms to the oxygen ions, the electrons being transferred to another copper atom. Each hydrogen molecule thus supplies two electrons and is capable of converting an adjacent copper ion into a neutral atom. By such a mechanism it is clear that the reaction could proceed only at the junction between the phases."

There is no question but that this way of looking at things shows how a reaction may take place at an interface; but one would like some proof that it does take place this way. According to Langmuir's point of view all metals should behave alike; but Pease and Taylor found that copper and nickel act quite differently in the catalysis of oxyhydrogen gas. Also, if each metal adsorbs molecular hydrogen in the form of atoms, why is there so much difference in the hydrogen over-voltage at different cathodes?

In a second paper Langmuir[1] discusses the catalytic oxidation of carbon monoxide and of hydrogen in presence of platinum. "When mixtures of carbon monoxide and oxygen at pressures up to a few hundred bars (0.1 mm) are brought into contact with a smooth platinum surface at 500° to 700° K, they react at a rate proportional to the partial pressure of oxygen and inversely proportional to the pressure of monoxide. The reaction velocity increases rapidly with the temperature, about 1.6 fold for 10° at 600°.

"With the platinum at 750° to 1050° K the velocity is practically independent of the temperature, being limited largely by the rate at which the gases can come into contact with the surface. With an excess of oxygen, the velocity is proportional to the pressure of monoxide, while with an excess

[1] Trans. Faraday Society, 17, 621 (1922).

of monoxide the rate is proportional to the pressure of the oxygen.

"A theoretical quantitative analysis of the experimental results leads to the following conception of the mechanism of the reaction. Every oxygen molecule which strikes a *clean* platinum surface condenses on the surface in the form of single atoms combined with separate platinum atoms. This chemical union is so firm that there is no appreciable evaporation of the oxygen atoms from the surface even with the platinum at 1500° K. These adsorbed oxygen atoms are in a very active condition in regard to their ability to react with monoxide, for *every* molecule of carbon monoxide which strikes an adsorbed oxygen atom reacts with it to form dioxide. When monoxide molecules strike a clean platinum surface, every one condenses on the surface, being held by chemical union between the carbon atom and two platinum atoms. An adsorbed film of monoxide thus consists of a monomolecular layer of oriented molecules. These adsorbed molecules are not as firmly held to the surface as oxygen atoms for they evaporate at an appreciable rate at temperatures as low as 500° K. Because of their orientation the monoxide molecules are very inert chemically towards oxygen. At 500° K only about one oxygen molecule out of $10^{12}$ which strike a surface covered with adsorbed monoxide reacts with the monoxide. The heat of evaporation of adsorbed monoxide is 31,800 calories per gram molecule; and at 700° K with a pressure of one bar of monoxide, at least half of the platinum surface is covered with adsorbed monoxide.

"In the low temperature range the surface is nearly completely covered by a monoxide film, and the reaction occurs only when monoxide molecules strike oxygen atoms which have become adsorbed in the spaces left vacant by the evaporation of monoxide molecules.

"In the high temperature range the surface is nearly covered with oxygen when there is an excess of oxygen, and the reaction velocity is then limited by the rate at which the monoxide strikes the surface. With an excess of monoxide

the surface is largely bare. The reaction velocity is limited by the rate at which the oxygen strikes the surface, for every oxygen molecule remains on the surface (in atomic condition) until struck by a monoxide molecule.

"At low temperatures (300° to 600° K) rather erratic results are obtained for the reaction velocity with mixtures of hydrogen and oxygen, for the velocity depends upon the previous treatment of the platinum. When the platinum is in a relatively inactive condition the results are similar to those obtained with carbon monoxide and oxygen, the velocity being roughly proportional to the pressure of oxygen and inversely to that of the hydrogen.

"At high temperatures (700° to 1900° K) the results correspond closely with those obtained with monoxide, the hydrogen having the same function as the monoxide. At these temperatures, the reaction is not sensitive to the previous treatment of the platinum.

"These results indicate that the adsorbed oxygen atoms are very reactive towards hydrogen, every collision between a hydrogen molecule and an adsorbed oxygen atom resulting in combination. Under certain conditions adsorbed hydrogen atoms are relatively inactive towards oxygen molecules, but the platinum can be brought into a condition which enables the adsorbed hydrogen to react with oxygen molecules or with the oxygen adsorbed in the adjacent spaces on the surface."

In the discussion Rideal[1] said: "There is an interesting problem which Dr. Langmuir mentioned of one gaseous molecule on platinum and how long does it vibrate before it comes off again. There is one reaction in which it appears possible to get the length of lives of molecules on the surface, viz., the combination of ethylene and hydrogen on the surface of nickel. If you take two volumes of ethylene and hydrogen and expose them to nickel, there is a long period of inductance and then reaction takes place. That is repeated and this same period of inductance is always found in mixtures of ethylene and

[1] Trans. Faraday Society, 17, 657 (1922).

hydrogen. If, however, one takes a vacuum and lets in hydrogen first and then the ethylene, the period of induction is very small; indeed it can hardly be measured. If you put in ethylene first there is a long period of induction, so what apparently happens is that the ethylene immediately coats the surface of the nickel and one has to wait until part of the ethylene evaporates and the hydrogen gets in, and I am hoping to get the average time which the ethylene actually sits on the surface of the nickel. It cannot be calculated out by the ordinary equation, because this assumes equilibrium where the ethylene is evaporating at a known temperature and condensing again, and we cannot find the rate of evaporation. If it evaporates from another surface, i. e., not an ethylene surface, then it will either evaporate more quickly or more slowly than it will on the ethylene surface itself. If the heat of adsorption is less, it will evaporate more quickly; if it is greater it will evaporate more slowly. However, this rate of evaporation from the film can also be regarded as a monomolecular chemical reaction, and we can develop the expression for the rate of such reactions just as in phosphine decomposition, and the rate of evaporation of the gas can be found provided you know the heat of adsorption. The difficulties here are very great for measuring the heat adsorption for one layer for an easily liquefiable gas. I think that we must regard it not only from the point of view of the mechanism of contact, which Dr. Langmuir has put forward, but we must also take into consideration the fact that the surface of a catalyst is by no means totally active and that the catalytic power can be enormously increased by the aid of promoters. Promoters can function sometimes by giving an extended surface although the apparent surface is the same. There is some evidence of this, as, for instance, the addition of a small quantity of potash to an iron mixture for combination of nitrogen and hydrogen. There are two or three purely chemical investigations of that type which are necessary to get a deeper insight into the reasons why these things do combine on surfaces. We have found cases in which adsorption definitely does take place but combi-

nation is not accelerated. Therefore, there must be orientation for which we have a certain amount of evidence in surface tension phenomena."

A striking case of action at an interface and one which has been known for a long time is the zinc-copper couple of Gladstone and Tribe.[1] With copper precipitated on, and in intimate contact with, zinc it is possible to decompose many of the alkyl halides at moderate temperatures. When the couple is made from zinc dust,[2] the preparation of zinc methyl can easily be shown as a lecture experiment. The couple decomposes bromoform, giving methane and acetylene.[3] Thorpe[4] used the couple as a means of reducing nitrates, iodates, and chlorates quantitatively, and, under his direction, Eccles[5] used it to determine chlorates in presence of perchlorates, the former being reduced to chlorides and the latter not. Devarda's alloy[6] seems to be another form of the same thing. It is not customary to consider the action of the zinc-copper couple as catalytic because the zinc reacts; but it is catalytic as regards the copper. In the aqueous solutions there is no question but that the action of the couple is electrolytic and very possibly the couple always acts in this way. With the organic substances the infinitesimal distance between the two metals counterbalances the high resistance of the organic liquid. The action of an aluminum-mercury couple is a less well known case of active contact catalysis. Cohen and Dakin[7] report that 0.5 g of such a couple will catalyze rapidly the chlorination and bromination of fifty grams of benzene, toluene,

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[1] Proc. Roy. Soc., **20**, 218 (1872); Jour. Chem. Soc., **25**, 461 (1872); **26**, 445, 453, 678, 961 (1873); **27**, 208, 406, 410, 615 (1874); **28**, 508 (1875); **30**, 37 (1876); **31**, 561 (1877); **33**, 139, 306 (1878); **35**, 107, 172, 567 (1879). Cf. H. Wislicenus: Jour. prakt. Chem., [2] **54**, 18 (1896).

[2] Lachmann: Am. Chem. Jour., **19**, 410 (1897).

[3] Cf. Sargent: Jour. Phys. Chem., **16**, 407 (1912).

[4] Jour. Chem. Soc., **26**, 541 (1873).

[5] Ibid., **29**, 856 (1876).

[6] Zeit. anal. Chem., **33**, 113 (1894); Allen: Jour. Ind. Eng. Chem., **7**, 522 (1915).

[7] Jour. Chem. Soc., **75**, 893(1899); **79**, 1111(1901).

etc. They state that the fragments of the couple remain unchanged during the reaction.

### Catalytic Oxidation

Quite a little work has been published on the catalytic oxidation of carbon monoxide by Hopcalite and similar substances. Rogers, Piggot, Bahlke and Jennings,[1] at the Johns Hopkins University, state that, in the preliminary work, it was observed that intimate mixtures of oxides were often more active than any one of the constituents. "For example, while neither chromium trioxide, $CrO_3$, nor yellow mercuric oxide oxidized carbon monoxide appreciably when a low concentration of this gas in air was passed through a tube containing these materials, a mixture of the oxides, containing chromium trioxide in excess of equivalent proportions was found to possess considerable oxidizing power and about fifty percent of the carbon monoxide was oxidized for a short period.

"Again, silver oxide which oxidizes carbon monoxide only slowly at room temperatures, when mixed in various proportions with calcium hydroxide showed markedly greater activity, evidencing the increased activity of mixtures over that of single constituents. Other important factors, more or less self-evident, in the use of mixtures of two or more substances are the fineness of subdivision and intimate admixture of these substances, the resulting product being essentially a solid solution in certain cases. When a mixture of silver and calcium hydroxides was prepared by the simultaneous precipitation of the hydroxides from a water solution of the nitrates of these metals, and the precipitate washed and dried at 120°–130° in a current of oxygen a material was obtained having marked activity. When dried in a current of air or oxygen the color of this mixture at times changed during the process of drying from a light brown to a slate color, a color change which indicates the decomposition of the silver oxide. On examination it was found that globules of metallic silver could be seen

[1] Jour. Am. Chem. Soc., 43, 1973 (1921).

in the material. This decomposition was observed at 100° in the air and at 130° in oxygen, whereas the decomposition pressure of silver oxide is but 0.2 atmosphere at 130°. This notable increase in the decomposition pressure of silver oxide is being investigated further to determine whether the phenomenon is due to fineness of subdivision or to some other cause connected with the presence of calcium hydroxide, one effect of which may be to prevent the increase in size of the silver oxide particles.

"The activity of these mixtures of silver oxide and calcium hydroxide was slightly increased by the addition of a small quantity of sodium hydroxide. The oxidation of the resulting material (about 80% for 20 minutes) was entirely due to the combined oxygen, as the amount of oxidation was never more than could be accounted for by the silver oxide present.

"Manganese dioxide was ultimately found to be an essential constituent of the best catalysts, and here also the same general statements made above apply. Mixtures of manganese dioxide and silver or copper oxide were found to be much more active towards carbon monoxide than either of the oxides used separately. The addition of a third component, sodium hydroxide, was advantageous in the preliminary experiments on manganese dioxide. The action of these mixtures containing sodium hydroxide was not catalytic. They functioned for only about forty minutes under the testing conditions given below and the amount of oxidation was not greater than could be accounted for by the active oxygen contained in the material.

"It was not until finely divided manganese dioxide was prepared, and special precautions, listed later, were used to secure the admixture therewith of other oxides, that the catalytic oxidation of carbon monoxide at room temperature was satisfactorily solved. The most satisfactory catalysts were obtained by using a mixture containing either silver oxide or copper oxide and manganese dioxide. Of these mixtures those containing silver oxide seemed to be more active than those containing copper oxide. Other oxides such as iron oxide may be tolerated in certain amounts in the final

products, but such oxides seem to act more as inert diluents and decrease rather than increase the activity of the material. However, when catalysts are prepared by properly mixing manganese dioxide with both silver and copper oxides such catalysts may be quite as active as those containing either copper or silver oxide alone.

"The conclusions reached from the preliminary work on manganese dioxide were, first, that the degree of subdivision was an extremely important factor in the activity of this material; and, second, that the activity is also greatly increased by properly incorporating with finely divided manganese dioxide, other metallic oxides such as copper and silver oxides."

"The present investigation relates entirely to experiments which were made for the purpose of affording protection against the poisonous action of carbon monoxide. It was done under the stress of war conditions when no opportunity was afforded to investigate the mechanism of the reactions involved. The physical structure of the oxides in the catalysts described is an essential factor in their activity; this matter is now being investigated by a careful study of their adsorption isotherms. However, certain facts were noted in the course of this work which appear to have relation to a possible chemical explanation of the reaction. The fundamental assumption of such an explanation is that the oxygen used for the oxidation of the carbon monoxide comes immediately from the oxide catalyst, and that in turn the catalyst is reoxidized by the oxygen of the air sufficiently rapidly to maintain its oxygen content and high activity. As the catalysts are mixtures of more than one oxide it is a question which of these plays the principal rôle. Since both silver oxide and manganese dioxide as prepared above will oxidize carbon monoxide at room temperature, either may be considered as the initial cause of the reaction. But both of these oxides when used alone suffer loss of oxygen, soon lose their activity and are not catalytic in their action. Copper oxide does not oxidize carbon monoxide at an appreciable rate at room temperature. As the catalysts described above all contain manganese dioxide

as an essential constituent, and as the physical condition of the manganese dioxide is of paramount importance it is assumed on the basis of the above facts that the manganese dioxide is the initial cause of the oxidation, probably functioning by reason of the variable valence of the manganese. Manganese dioxide prepared by any method yielding relatively coarse particles has very slight activity, whereas if its particles are practically of colloidal dimensions it uniformly produces a satisfactory catalyst. Fine subdivision of the particles of the other constituents and their intimate contact with the manganese dioxide particles tend of course toward the production of the most reactive material. On the basis of this explanation of the reaction, the single oxides are not reoxidized by oxygen fast enough to maintain catalytic action; the function of the other oxide or oxides is to increase the velocity of reoxidation of the manganese dioxide, and for this purpose silver oxide appears to be more efficient than copper oxide. In support of this view is the fact that a material prepared by simultaneous precipitation of manganous and silver hydroxides can be made very reactive by air oxidation at 125°. Of course the alternative is to assume that silver or copper oxide is the immediate cause of the action and that manganese dioxide catalyses the reoxidation of the reduced oxides. In favor of this assumption is the fact that manganese dioxide is a good catalyst for the decomposition of such metallic oxides as those of silver and mercury. The present work furnishes no proof of either view, and until further observations on the behavior of these oxide mixtures are available both views are tentative.[1]

"Another fact related to the intermediate oxide theory is that a mixture which is partially catalytic, as is the case when the catalyst is not sufficiently active or when the catalyst is poisoned by water vapor, always loses "available" oxygen. The first explanation of the poisonous effect of water vapor

[1] [Almquist, working at the University of California in 1921–22, was unable to detect loss of 'available' oxygen with an oxide catalyst working at low efficiency, either with or without the presence of water vapor. W. C. Bray.]

would be that the loss of activity results from a diminution of the large internal surface, so essential in the secatalysts, which is in part covered by liquid water. This, however, seems hardly to account for all the facts, since under these conditions the catalyst suffers reduction, therefore the carbon monoxide in the mixture has access to the catalyst. The loss of activity seems to result, therefore, primarily from the inability of the catalyst surface to recombine with oxygen. It is possible that this is due to a condensation of water within the pores of the catalyst which thereby separates the oxide particles and thus prevents the intimate contact of the oxides which is essential for the catalytic activity of the material. Some of these points are under investigation, and it is realized that a further discussion is premature until these results, especially those bearing on the adsorption of these catalysts, are available."

Merrill and Scalione,[1] formerly of the University of California, state that "it is well known that, in spite of the large decrease of free energy in the oxidation of carbon monoxide by atmospheric oxygen, the rate of this reaction at room temperature is entirely negligible in the absence of catalysts. The activity of platinum and palladium blacks in catalyzing this reaction has long been recognized, but no examples of active catalysts containing only the more common metals were found in the literature at the time the present investigation was begun. The work of Wright and Luff[2] on the minimum temperature of reaction of carbon monoxide with various metallic oxides had indicated the possibility of preparing oxides of sufficient activity[3] for use as oxidizing agents in carbon monoxide masks, although these investigators did not conduct their experiments in such a way as to show whether or not the oxidation would be catalytic in the presence of excess of oxygen.

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[1] Jour. Am. Chem. Soc., 43, 1981 (1921).

[2] C. R. A. Wright and A. P. Luff: Jour. Chem. Soc., 33, 1, 504 (1878); Cf. Fay, Southerland and Lane: Polytech. Eng., 10, 72 (1910).

[3] Lamb, Bray and Frazer: Jour. Ind. Eng. Chem., 12, 213 (1920).

"The present investigation was undertaken in an endeavor, by suitable variation of the chemical composition and physical properties of mixtures of metallic oxides, to prepare a solid substance which would oxidize dilute carbon monoxide-air mixtures with reasonable completeness at ordinary temperatures and fairly high rates of flow. These properties are of course more essential in a practical absorbent than is catalytic activity. Because of the desirability of the latter, however, the choice of materials for experimentation was based both on the suggestions obtained from the work of Wright and Luff and on the chemical theory of catalysis. According to this theory the catalyst actually takes part in the reaction, oxidizing the carbon monoxide and being itself reoxidized by the oxygen of the air. In order that this may take place it is necessary that the oxide be readily reduced and also that in its lower state of oxidation it be readily oxidized. Suitable couples of higher and lower oxide or oxide and metal are more likely to be found where more than one oxide of the metal is known than where the metal is readily oxidized to a single oxide. By the application of these ideas, it was found possible to prepare oxide mixtures (called for convenience Hopcalite or HC)[1] which catalyze the oxidation of dilute carbon monoxide-air mixtures at ordinary temperatures[2] for an indefinite length of time when protected from moisture, as by a layer of calcium chloride in the canister.

"An absorbent, to be suitable for use in gas masks, must have a very high activity in proportion to its volume.[3] Since, in heterogeneous catalysis, the amount of reaction that a catalyst is able to bring about is a function of the surface exposed, it was important to prepare the catalysts in a form ex-

[1] J. C. W. Frazer and C. C. Scalione: U. S. Pat. 1, 345, 323, June 29, 1920. C. A., 14, 2533 (1920).

[2] Rideal and Taylor (Analyst, 44, 89-94 (1919); C. A., 13, 1169 (1919)) have applied metallic oxides to the preferential oxidation of carbon monoxide in hydrogen but their catalysts apparently are not sufficiently active to oxidize carbon monoxide at room temperature. Cf. Harger and Terrey: Brit. Pat. 127,609, Apr. 28 (1917); Jour. Soc. Chem. Ind., 38, 577A (1919).

[3] Lamb. Bray and Frazer: Jour. Ind. Eng. Chem., 12, 213 (1920).

posing the maximum surface, and this was accomplished by preparing the oxide mixtures in the form of porous granules. The use of ignited oxides was not satisfactory because of their low activity at ordinary temperatures. Precipitated oxides were found to be more active, but granules prepared by simple drying and crushing of the filter cake were often lacking in mechanical strength; and no binders were found that did not materially reduce the activity of the resulting product. It was found, however, that fairly hard granules could be obtained by careful control of the conditions of precipitation, and that the hardness could be further increased by submitting the filtered precipitate to high pressure in a hydraulic press before drying.

"Among the various oxides and mixtures investigated there were two mixtures which were particularly active, and it was these which are studied in most detail. The first will be referred to as the four-component mixture (or Hopcalite I) and consisted of approximately 50% $MnO_2$, 30% CuO, 15% $Co_2O_3$ and 5% $Ag_2O$. About 7,300 kg of this mixture was produced on the large scale and used to fill about 40,000 canisters.[1] The second mixture referred as the two-component mixture, consisted ordinarily of sixty percent $MnO_2$ and forty percent CuO, and, although somewhat cheaper, was developed too late for use on the large scale."

The oxides prepared by high temperature reactions, as by oxidation of metals or ignition of nitrates, were found to have a much lower activity at ordinary temperatures than those prepared by precipitation. "Under the conditions of operation used in the standard tube-tests with dry carbon monoxide-air mixtures at room temperature, that is, using a 5 cm layer of 8- to 14-mesh granules and a rate of flow of 500 cc of 1% gas per $cm^2$ per minute, gold samples of either the two- or the four-component mixture operate at efficiencies closely approaching 100% for an indefinite length of time. Such samples also operate at high efficiency on more dilute mixtures

[1] Lamb, Bray and Frazer: Jour. Ind. Eng. Chem., 12, 220 (1920).

as shown by tests with concentrations of one-tenth percent or less. The theoretical temperature rise under adiabatic conditions due to the heat of the reaction is about 100° for a one percent mixture. Because of this heat effect, little difficulty is experienced in obtaining a complete oxidation at higher concentrations even with rather poor samples, although with concentrations much above five percent the temperature rise may be sufficient to impair the activity of the catalyst after cooling. With very high concentrations the catalyst may even sinter together and be entirely inactive when cold.

"The activity of the catalysts at low temperatures is of course very important when they are to be used in gas masks in exposed locations. The effect of the temperature of the carbon monoxide-air mixture on the activity is masked somewhat by the heat of the reaction, but it can be determined readily by using dilute gas mixtures so that the heat effect is small. In general for each particular sample of catalyst and gas concentration there is a minimum temperature at which the catalyst operates catalytically at 100% efficiency. Below this temperature the efficiency gradually falls off to a more or less constant value for each temperature but returns again to 100% when the temperature is raised. Most of the tests were made with one-half percent carbon monoxide and the catalyst was placed in a glass tube surrounded by a freezing mixture so that there was little opportunity for it to heat up by the heat of reaction. It was found that the two-component mixture operated better at low temperatures than the four-component mixture although individual samples varied somewhat especially when there were variations in the methods of pressing and drying. The samples prepared with high pressures were much better than those filtered at comparatively low pressures and adequate drying was found to be quite essential. A typical sample of the two-component mixture, when tested with one percent carbon monoxide at —15°, operated initially at high efficiency, but after a few minutes the efficiency began to fall and gradually decreased to about 35% where it remained in apparent equilibrium. When the temperature of

the gas and catalyst tube was allowed to rise to 0°, the efficiency gradually rose to 100%.[1] Similar experiments on manganese dioxide and copper oxide alone at higher temperatures indicated that under proper conditions this phenomenon is accompanied by reversible reduction of the catalyst, that is, the catalyst is partially reduced at the lower temperature and re-oxidized at the higher. This reduction is different from that obtained by treating the catalyst at a high temperature with carbon monoxide or other reducing agents in the absence of an excess of oxygen for in this case the reduction is more complete and is usually accompanied by a change in structure. The activity cannot then be restored by re-oxidation with air.

"The general effect of water vapor in the gas mixture is to diminish the activity of the catalysts so that higher temperatures are necessary for definite efficiencies than when operating with dry gas. Somewhat the same effect is brought about by a diminution of the oxygen content of the gas. While in gas-mask use, the oxygen requirements of the man are so high that such effects do not enter under any conditions under which a man could live, they are of importance in connection with the application of the catalysts to the removal of carbon monoxide from hydrogen by preferential combustion and in other industrial applications. It was found that for an equilibrium efficiency of 100% with 28 mm of water vapor, reducing the oxygen content of the gas to as low as 100% excess of that theoretically required for the combustion only necessitated an increase of temperature of about 10° over the temperature required with a carbon monoxide-air mixture containing the full oxygen content. It was also found that when operating with the two-component mixture on a mixture containing 0.5% carbon monoxide, 0.5% oxygen and 55 mm of water vapor at a space velocity of 6000 cc of gas per cc of catalyst per hour, 190 hours of coutinuous operation at 102° and an average efficiency of 93% did not result in any appreciable deterioration of the catalyst.

[1] Compare results by Almquist, p. 836.

"The humidity of the carbon monoxide-air mixture has a very marked effect on the activities of the various oxides and mixtures. The effect is best described as reversible poisoning, to distinguish it from the type of poisoning brought about by sulfur compounds and some of the war gases. While the two-component and four-component mixtures act catalytically for an indefinite length of time on dry gas mixtures at ordinary temperatures, with 1% gas mixtures half saturated with water vapor at room temperature the activity falls to 85% in about an hour and rapidly decreases from then on. If the mixture is changed from wet to dry at any time before the catalyst has stopped acting, the efficiency gradually returns to the original value of about 100% in the case of active samples. The rate at which the efficiency of the catalyst decreases is a function of the temperature at which the test is made and hence indirectly of the concentration of the gas, since the heat of the reaction raises the temperature of the catalyst. At temperatures somewhat above room temperature, the catalytic oxidation proceeds indefinitely even with gas mixtures of high humidity. At intermediate temperatures and humidities, the activity does not fall to zero but only to a fairly definite value for any particular sample of catalyst. These efficiencies are approximately the same when approached from either side if sufficient time is allowed for conditions to become constant."

"While in many cases the activity of a mixture of catalysts is merely a composite of the activities of the several components, it has often been found that mixtures of catalysts are more active than any of their components. The complete explanation of this co-activation of catalysts is still lacking; but the results of the present investigation indicate that the chemical nature of the components and the physical properties of the mixture are very important factors. The use of mixed catalysts was found to be quite essential in obtaining the requisite activity towards carbon monoxide at low temperatures. Of the common oxides tried, none acted alone as an active catalyst with the exception of cobaltic oxide. The lat-

ter, however, is itself a mixture of oxides, since, as prepared, the ratio of oxygen to cobalt is about 1.6 : 1."

The point in regard to cobalt oxide is either sophistical or it proves too much. If the catalytic action is due, as is assumed by Merrill and Scalione, to a reversible change from a higher to a lower oxide, any oxide may equally well be considered as a mixture. If the cobalt oxide owes its activity to being a mixture, it seems scarcely justifiable to consider the catalytic action as due to successive or simultaneous reduction and oxidation of the catalyst. The work at the Princeton laboratory suggests the possibility that the catalysis takes place chiefly, perhaps wholly, at an interface, in which case a mixture of oxides would be similar in theory to a mixture of copper oxide and copper.

Merrill and Scalione tried substituting nickelic oxide for cobaltic oxide in the four-component mixture. "These resulting mixtures did not operate catalytically towards dry gas for an indefinite length of time at room temperature. The oxidation of the carbon monoxide was accompanied by gradual reduction of the catalyst and loss of activity unless the temperature was slightly elevated. Ferric oxide was found to be even less active than nickelic oxide in these mixtures."

Piggot[1] has studied the action of manganese dioxide catalysts on the oxidation of ammonia to nitric oxide. He finds that the catalytic action of manganese dioxide can be increased very much by adopting a suitable method of preparation. "The physical structure of the material is of great importance, extremely fine subdivision, giving a large adsorbing surface with very small pores, being conducive to greater activity." The incorporation of silver oxide or copper oxide with the manganese dioxide increases the catalytic action of the latter very much, the added oxide functioning as a promoter. "Manganese dioxide is apparently reduced in the course of the reaction to some lower oxide of manganese, and the promoter serves to aid the oxygen to reoxidize it back to the dioxide.

[1] Jour. Am. Chem. Soc., 43, 2034 (1921).

This is indicated by the fact that when used alone, after several hours, the greater part of the manganese dioxide is reduced to the lower reddish colored oxide. That part of the material which remains black ($MnO_2$) is always a thin layer on the top of the catalyst bed, being that portion which first comes into contact with the air and is consequently more readily re-oxidized. When a promoter is mixed with the manganese dioxide very little of the material shows reduction after several hours' use; in this case the reduced area (if any) is always at the bottom of the catalyst bed and is never very great.

"Manganese dioxide produced by the action of methyl alcohol on potassium permanganate and, consequently, consisting of comparatively coarse particles, was always less completely re-oxidized by the promoter than that prepared by the Fremy method, thus indicating qualitatively the relation of subdivision to reactivity.

"When silver and copper were used together as promoters with manganese dioxide prepared by the Fremy method there was no indication whatever of permanent reduction of the latter. This would indicate that these two materials tend to act as very efficient carriers of oxygen to the manganese. On the other hand, however, the temperature and oxygen pressure at which the material was used was far above the dissociation temperature of silver oxide, which would lead to the conclusion that finely divided silver alone is as effective a promoter as silver oxide. This agrees with the conclusion of Lanning[1] drawn from his work on the carbon monoxide catalyst in this laboratory.

"The low yields of nitric acid obtained from the three-component mixtures, coupled with the fact that no ammonia was detectable in the effluent gases, indicate that this material (the catalyst used for carbon monoxide oxidation) is very active and that a very small time of contact is sufficient for it also to favor the decomposition of the nitric oxide once formed. This is analogous to the behavior of platinum black when used

[1] Lanning: Dissertation, Johns Hopkins Univ., June, 1920.

alone for this reaction. Some mixture should be possible which would be just active enough to favor the formation of nitric oxide while preventing the liberation of elementary nitrogen.

"It was shown that alloys of manganese exist which possess considerable catalytic activity for this reaction and the data point toward an alloy of rather restricted composition which gives promise of high efficiency. Such an alloy should exist within the following limits of composition: Mn, 55–65%; Cu, 25–35%; Ag, 5–15%; Fe, 1–5%; Si, 0–3%.

"Small changes of composition apparently have great influence on the catalytic activity and efficiency and it is believed that further investigations in this more restricted field will develop a catalyst which will yield an efficiency of 90–95%, or even greater."

Lamb, Scalione and Edgar[1] have studied the preferential combustion of carbon monoxide in hydrogen. "An important factor in the commercial success of the Haber process for the synthesis of ammonia is the cost of the pure hydrogen which it requires. At present this hydrogen is usually obtained by "converting" mixed water- and producer-gas, using a considerable excess of steam and a suitable catalyst, into a mixture relatively rich in hydrogen and carbon dioxide, and poor in carbon monoxide. The carbon dioxide is then largely removed by a thorough water-scrubbing under moderate pressures. The compositions of these gaseous mixtures are as follows, according to R. S. Tour.[2]

| | After conversion | After water-scrubbing |
|---|---|---|
| | % | % |
| $H_2$ | 52–52 | 73–72 |
| $N_2$ | 17–17 | 24–23 |
| $CO_2$ | 29–27 | 0.1–1.0 |
| CO | 2–4 | 3–5 |
| X | 0.4–0.8 | 0.5–1.0 |

where X = argon, methane, etc.

[1] Jour. Am. Chem. Soc., **44**, 738 (1922).

[2] Jour. Ind. Eng. Chem., **12**, 844 (1920).

To remove the three to five percent of carbon monoxide remaining in the gaseous mixture after the water-scrubbing, the practice has been to scrub thoroughly under high pressure with ammoniacal solution of cuprous salts. By this means the carbon monoxide content can be reduced to between 0.1 and 0.01%. This degree of purity may be adequate, but the process is difficult and costly. It is desirable therefore, if possible, to devise one which is simpler and more economical.

"With this requirement in mind, we have investigated the behavior of an absorbent for carbon monoxide called Hopcalite, developed during the war by the U. S. Bureau of mines, and Chemical Warfare Service of the U. S. Army.[1] This material, consisting of a mixture of metallic oxides, is not strictly speaking an absorbent, for it operates by burning the carbon monoxide catalytically at the expense of the oxygen of the air; and if the air is adequately dried, it is not itself altered in the process. If this material should prove to be unaffected by hydrogen under any feasible conditions at which it would catalytically oxidize carbon monoxide, there appears to be the possibility of a cheap simple method for the removal of carbon monoxide from the above mentioned mixture."

They found "that Hopcalite, which oxidizes carbon monoxide in air rapidly and catalytically at room temperatures, does not affect hydrogen in air under similar conditions, and that by its means carbon monoxide can be removed completely and continuously from a dry mixture containing, for instance, 0.5% of carbon monoxide, 89.5% of hydrogen, and 10% of air, without any noticeable action on the hydrogen. A similar mixture containing one percent of carbon monoxide, on the other hand, liberates so much heat that under these conditions oxidation of the hydrogen sets in, and the catalyst is soon heated to incandescence and is destroyed.

"Moist mixtures of carbon monoxide and air, and of hydrogen and air require much higher temperatures for oxidation. In the presence of water vapor at a pressure of 50 mm

[1] Lamb, Bray and Frazer: Jour. Ind. Eng. Chem., 12, 213 (1920).

of mercury, carbon monoxide in a 0.5% mixture with air is oxidized completely at a temperature of 90° or lower. Hydrogen, on the other hand, mixed with air does not begin to be oxidized under these conditions until a temperature of 120°–125° is reached. It is possible, therefore, to remove carbon monoxide completely and continuously from a mixture having, for instance, the composition 0.5% of carbon monoxide, 0.5% of oxygen, 24.75% of nitrogen, and 74.25% of hydrogen, and containing water vapor at a pressure of 50 mm of mercury without any considerable oxidation of the hydrogen. On the other hand, in a similar mixture containing one percent of carbon monoxide the hydrogen soon catches fire, and the catalyst becomes incandescent."

The Harger-Terry process U.S.P. of removal of carbon monoxide from industrial hydrogen has already been operated with success in this country using a steam-iron process hydrogen containing 0.5 percent carbon monoxide. Use may be made of an iron oxide catalyst containing as promoters such oxides as those of chromium, cerium, and thorium. These catalysts operate at 200°–250° C in presence of both steam and carbon dioxide. They are very robust and insensitive to considerable temperature elevation.

Berger and Delmas[1] have studied the effect of some of the oxides on the combustion of charcoal and of lamp-black. They mixed with the charcoal or lamp-black four percent by weight of the oxides, moistened the mass with one percent of a twenty percent dextrine solution, and compressed the mass into cylinders 18 mm in diameter and 15–20 mm high. In the case of the lamp-black one or two drops of alcohol were added to facilitate the wetting by the dextrine solution. The densities of the compressed masses were approximately 0.75 for the charcoal samples and 0.80 for the lamp-black. The cylinders were lighted at one end and placed with the other end down. Some stopped burning very soon and others burned more or less vigorously. The time of burning was

[1] Bull. Soc. chim. France, [4] 29, 68 (1921).

usually about an hour. The oxides added were those of calcium, magnesium, cobalt, nickel, copper, lead, silver, tin, antimony, iron, molybdenum, vanadium, uranium ($U_3O_8$) and manganese ($MnO_2$ and $Mn_3O_4$). Experiments were also made with lead chromate. With charcoal all the cylinders burned, including the one with no added oxide; but the most fierce burning was with the samples containing CoO, CuO, PbO, $Sb_2O_5$, and $PbCrO_4$. Treatment to remove the ash slowed down the rate of burning of the charcoal very distinctly.

With lamp-black there was good burning only with the samples containing CuO, PbO, $Sb_2O_5$, $MoO_3$, and $PbCrO_4$, the one with copper oxide burning the most brilliantly. The samples containing $Fe_2O_3$, $Cr_2O_3$, and $V_2O_5$ burned for a few minutes and then went out. The others stopped burning as soon as the igniting flame was removed. The cylinder containing four percent of manganese dioxide did not burn, but did when two percent of sodium carbonate was added. Zinc oxide was not tried either with charcoal or lamp-black.

Berger and Delmas also analyzed the products of combustion and grouped the oxides in three classes depending on whether they increased, decreased, or had practically no effect on the ratio of carbon monoxide to carbon dioxide. They consider that CaO, MgO, $Cr_2O_3$, and $Mn_3O_4$ have practically no effect on the ratio of carbon monoxide to dioxide; that $PbC_2O_4$ and $V_2O_5$ increase this ratio, and that $U_3O_8$, $SnO_2$, $Sb_2O_5$, $Fe_2O_3$, $MoO_3$, CuO, PbO, NiO, CuO, $MnO_2$, and $Ag_2O$ decrease the ratio, the effect being slight with uranium to iron, quite distinct with molybdenum to cobalt, and very strong with manganese and silver. In the last two cases the proportion of carbon monoxide dropped to three percent. These figures do not mean very much unless one knows the temperatures.

Brandt[1] has studied the familiar experiment of putting a little ash on a lump of sugar and lighting the sugar with a

[1] Chem. Abstracts, 15, 976 (1921).

match. He finds "that it is the alkali carbonates and not the ferric oxide in cigar ash which induces the combustion of the sugar. Experiments with a large number of solids, liquids, and solutions showed that catalytic oxidation is not essential, but that in general those substances which are wet by melted sugar catalyze its combustion. As soon as a small portion of the sugar is carbonized, it acts like a wick, and the combustion proceeds. Effective substances act in solution as well as when applied in solid form. A comprehensive theory of the phenomenon cannot be formulated as yet; but it is certain that its causes are purely physical."

Hedvall[1] obtained quite different results though this may be because the experiments were done differently. "If cane sugar is heated in the flame of the Bunsen burner it will turn brown and fuse. A foreign substance, previously added to the sugar, may cause a very different phenomenon, depending upon the nature of the substance which is added. The sugar may behave as before (Type I); may burst into flame, emitting smoke rings, and leave a normal ash (Type II); or finally may burn with a flame and smoke rings, and, in addition thereto, form a black porous residue (Type III). The intensity of the flame and smoke rings, and the amount and shape of the residue vary with the substances added to the sugar. The following substances belong to Type I since they cause no change when added to the sugar: BeO, $Al_2O_3$, $Al(OH)_3$, $TiO_2$, $SiO_2$, $SnO_2$, $As_2O_3$, $Cr_2O_3$, $MoO_3$, $U_3O_8$, MnO, $Fe_2O_3$ (under certain conditions), NiO, Al and Ni filings (see reduced Ni below), reduced Fe, $HNO_3$, $CH_3CO_2H$, $CaF_2$, $BaSO_4$, and $(NH_4)_2CO_3$. The oxides of the alkalies, earths, and heavy metals, except those listed above, fall into Type II. The flame produced is more vigorous with the alkalies than with the earths and least so with the heavy metals. To the flame producers also belong the metals: Ag, Cu, Pt, Zn, reduced Ni, and Co. Of these last the zinc gave the most flame and the nickel the least. The following substances belong to Type III, giving

[1] Chem. Abstracts, 14, 200 (1921).

both a flame and carbonaceous residue when added to cane sugar to be tested by the flame: halogens and halogen salts (except $CaF_2$), $P_2O_5$, $H_2SO_4$, $SO_2$, alkali and alkaline earth salts except $(NH_4)_2SO_3$, $CuSO_4$, and $FeSO_4$."

Somewhat less extensive measurements have been made by von Euler and Josephson.[1] "If one end of a five-millimeter strip of pure filter paper, supported horizontally in a space free of drafts, is ignited and the flame then extinguished the smoldering dies out almost immediately. In case the line of smoldering travels along the strip, its rate of travel depends on the balance between (1) the heat required to decompose the cellulose, and (2) the heat furnished by combustion of the decomposition products, especially the solid ones. The presence of small quantities of inorganic salts influence markedly this rate, or the duration of the smoldering; usually there is an optimum concentration at which uniform propagation takes place, but above and below which the smoldering dies out. Paper containing $Na_2SO_4$, $CaCl_2$, $BaCl_2$, $Na_2HPO_4$ and $BaCO_3$ in quantities ranging from $0.3 \times 10^{-5}$ to $2.68 \times 10^{-5}$ equivalents per square centimeter gave definite times of smoldering, ranging from 2 to 5.7 seconds, while paper containing KCl, $KNO_3$, $K_2CO_3$, $K_2SO_4$, NaCl, LiCl, $Li_2CO_3$, NaBr and $Na_2CO_3$ in approximately the same quantities smoldered at constant rates, varying from $5.8 \times 10^{-1}$ to $19.6 \times 10^{-2}$ cm./sec. Comparison indicated that potassium and lithium were the most effective ions while the chlorine ion exerted a retarding effect. The influence of traces of ash in lowering the burning temperature of cane sugar suggested investigation of the catalytic effect of various salts in its thermal decomposition. Mixtures of the substance in question with powdered sugar were heated slowly in recesses in a brass block containing a thermometer, the temperature of decomposition being indicated by gas evolution and discoloration (burning will proceed at any temperature which produces this decomposition). The substances tried were $CaCl_2$, $Na_2CO_3$, BaO, NaCl, $BaCl_2$,

[1] Chem. Abstracts, 15, 334 (1921).

$CaO$, $Na_2SO_4$, $CaCO_3$, $BaSO_4$, and $CaSO_4$, which were effective in the order named. Calcium chloride lowered the decomposition temperature extraordinarily; 0.4% of the dry salt (especially purified to eliminate traces of possible catalytic impurities ) lowering this temperature from 212° to 182°. The gases given off contained 8–12% unsaturated hydrocarbons, 33–35% CO, 28–46% $H_2$, less than 1% $O_2$ and $CO_2$, and apparently traces of $CH_3CO_2H$, $H_2C_2O_4$, $CH_3COCH_3$, HCHO and furfural."

While it is natural to assume that with copper oxide we may have a case of reduction and oxidation, this explanation cannot apply to zinc oxide. The effect of this substance should be tried in all these cases. If it proves a catalytic agent for each case, we shall then have to find some explanation for its action. This winter people have been putting spelter in the furnaces to clean the soot out of the chimneys. We are not quite sure whether it works and nobody knows why it works. It would be very interesting if zinc oxide should really cause soot to burn loose from the flues.

It has been found by Jewett[1] at Cornell that the decomposition of hydrogen peroxide in alkaline solution is catalyzed both by nickelous oxide and by nickelic oxide; but that neither was changed appreciably. This was shown both analytically and electrometrically. The catalysis in this case seems not to be connected necessarily with any oxidation or reduction, which makes one wonder whether there is any necessary connection in the other cases. While it is quite certain that we do have a gradual reduction of such mixtures as Hopcalite by carbon monoxide, there are no data as yet to show that this reaction takes place rapidly enough to account for the catalysis.

Hedvall[2] considers that the acceleration of the decomposition of barium peroxide may be due to at least two different causes. Pure barium peroxide begins to lose oxygen at a

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[1] Unpublished data.

[2] Zeit. anorg. Chem., **104**, 163 (1918); **108**, 119 (1920).

measurable rate only when heated above 800°. In presence of silica oxygen begins to come off at about 200° and more or less barium silicate is formed, the amount depending upon the form in which the silica is present. He believes that the peroxide is decomposed catalytically by silica at about 200° and that the nascent barium oxide reacts to some extent with the silica, the amount of the reaction increasing with rising temperature until the formation of silicate comes to an end owing to the barium silicate forming a protecting film between the barium oxide and the silica. While the tendency to form silicate would lower the chemical potential or vapor pressure of barium oxide and would therefore increase the tendency of the peroxide to decompose, Hedvall implies distinctly that the amount of barium silicate formed is not an accurate measure of the barium peroxide decomposed. If this is true, we must have a decomposition taking place at the interface and it is practically impossible to account for this on the assumption of oxidation or reduction of silica.

Copper oxide also accelerates the decomposition of barium peroxide starting at about 200° and there is no evidence that barium oxide reacts with copper oxide. It is possible to postulate that half the oxygen comes from the copper oxide, which would be changed to cuprous oxide and would then be re-oxidized; but this seems improbable because cuprous oxide causes a very violent reaction, quite different from that which one gets with cupric oxide. It is also possible to postulate the intermediate formation of copper peroxide; but we have no experimental proof of this as yet.

In the second paper Hedvall studied the behavior of a number of other oxides besides those of silicon and copper.

"Compounds between barium oxide and specified oxides of the following elements were found on heating these or the lower oxides: $Zn^{II}$, $Al^{III}$, $Ti^{IV}$, $Pb^{IV}$, $V^{V}$, $As^{V}$, Sb , $Ta^{V}$, $Cr^{VI}$, $Mo^{VI}$, $V^{VI}$, $U^{VI}$, $Mn^{VI}$, $Fe^{VI}$, $Ni^{IV}$(?), and $Co^{IV}$(?). An oxidation without formation of a compound with barium oxide occurred with $Cu_2O$ and $Bi_3O_3$, while oxidation and formation of a compound occurred with $As_2O_3$, $Sb_2O_3$, $Sb_2O_4$, $Cr_2O_3$,

$U_3O_8$, MnO, $Mn_3O_4$, $Mn_2O_3$, $MnO_2$, $Fe_2O_3$ and the oxides of nickel and cobalt(?). While a catalytic decomposition of barium peroxide takes place also with several of these oxides, a purely catalytic evolution of oxygen without a chemical reaction of any sort[1] was proved with CuO, MgO, CaO,[2] CdO, $La_2O_3$(?), and $CeO_2$. Of all the oxides examined the only ones to have no effect were SnO, $SnO_2$, and $ZrO_2$. In some cases enormous reaction velocities were observed in the temperature region of about 200–300°, particularly with $Cu_2O$, $V_2O_5$, $Sb_2O_3$, $Cr_2O_3$, $MoO_3$, and MnO. The reaction spread almost explosively through the mass and the rate of temperature rise increased often forty-fold."

## Specific Activation

The effect of a catalyst does not depend exclusively upon the increased concentration due to adsorption. All the people agree that the effect of the catalyst is specific. Armstrong and Hilditch[3] confirm the experiments of Sabatier that copper and nickel do not behave alike towards alcohol at the same temperature. Though both tend to convert alcohol into acetaldehyde and hydrogen, nickel is much more likely to decompose the aldehyde into carbon monoxide and methane. "In the case of copper, not only is the ratio of aldehyde to hydrogen close to that calculated but the unchanged alcohol may be recovered almost quantitatively, the yield of aldehyde being about 90–85 percent of that to be expected from the amount of alcohol used. There is a striking absence of the secondary products observed when aldehyde together with an excess of hydrogen is passed over the metal at the same temperature."

Of course, this is not what Armstrong and Hilditch are trying to say. The unchanged alcohol can also be recovered quantitatively from the experiments with nickel and also the question whether the yield of aldehyde is high or low has

[1] It is possible that solid solutions may be formed.
[2] Cf. Wöhler and Liebig: Pogg. Ann., 24, 172 (1832).
[3] Proc. Roy. Soc., 97A, 259 (1920).

nothing to do with the recovery of the unchanged alcohol. What the experiments actually showed was that the ratio of aldehyde to hydrogen was about 36% of the theoretical with nickel at 250° and about 97% with copper at 300°; and that with nickel the gas contained 60% $H_2$, 20% CO, and 15–17% methane. The specific effect occurs also during hydrogenation, though the difference is not so marked. "Aldehyde may be converted into alcohol by passing the vapor, together with hydrogen, over either copper or nickel (Sabatier); but in presence of the latter metal, probably owing to the special affinity of nickel for the carbonyl group, the aldehyde is prone to undergo decomposition into carbon monoxide and methane." With copper at 200° less than four percent of carbon monoxide is formed; but the amount increases markedly at 300°, the decomposition of the aldehyde being greater with copper at 300° than with nickel at 120°–150°. On the other hand, with hydrogenation of alcohol by copper at 300°, "there is a striking absence of the secondary products observed when aldehyde together with an excess of hydrogen is passed over the metal at the same temperature."

Armstrong and Hilditch consider that both alcohol and water are adsorbed selectively by copper, thus decreasing the adsorption of the aldehyde and protecting it from decomposition. The presence of water in the hydrogenation of aldehyde is not an advantage. Although it decreases the decomposition of the aldehyde by copper at 300°, it cuts down the rate of hydrogenation very much.

Armstrong and Hilditch do not agree absolutely with Sabatier as to the cause of dehydrogenation. "Sabatier has attributed the dehydrogenation of alcohol as well as of hydrocarbons by finely divided metals to the supposed aptitude of such metals to form hydrides, the attraction of the metal for hydrogen being regarded as the impelling force. But it is obvious that the relative affinities of all the agents concerned in such interactions must come into play. In the case of aldehyde, we are inclined to regard the affinity of the carbon compound rather than that of the hydrogen to the metal as of

prime importance, indeed, as the determining factor; the marked influence of the metal in causing secondary decomposition is in itself a clear indication that the attraction exercised upon the aldehyde at the metallic surface is considerable."

Weiss and Downs[1] showed that as yet it is only with molybdenum oxide or vanadium oxide that one can stop the oxidation of benzene at all conveniently at the maleic anhydride stage. This is in part a question of temperature regulation, but probably not entirely. "The total amount of oxygen needed to burn one molecule of benzene completely is fifteen atoms. It is conceivable that the intermediate products previously mentioned are formed and burned immediately to the more highly oxidized form even in the ordinary combustion of benzene but that they cannot be isolated as such because of the extreme velocity of the combustion reaction. The function of a catalyst, which by its use allows the separation of the intermediate products of combustion is, of course, problematical; but it would appear that by its presence the range of temperature between the formation of one intermediate product and its combustion to a higher degree of oxidation is broadened, and that, by a close temperature regulation within this range, throughout which this intermediate is stable, it may be isolated. Another contact substance which either shows no reaction or produces complete combustion at a higher temperature does not provide this sufficiently broad temperature range and the only products of reaction are those of complete combustion. An example of the former contact substance is vanadium oxide, and examples of the latter are cerium oxide, platinum, and numerous others. Even with these it is possible that sufficiently close regulation will result in the isolation of intermediate products and it is further possible and even probable that in other cases suitable control would make possible the isolation of other products, such as phenol. . . . The heat developed in the formation of maleic acid from benzene is nearly sixty percent of that developed by a benzene flame."

[1] Jour. Ind. Eng. Chem., 12, 228 (1920).

Burdick[1] finds that the catalytic oxidation of nitric oxide to nitrogen peroxide is extremely specific. "The only materials possessing catalytic properties of any pronounced value were the special charcoals and the activated coke. The two samples which were the most reactive were the cocoanut and peach-kernel charcoals. A sample of coke subjected to steaming at 600° to 800° was found to possess a pronounced but much lower catalytic activity. It is to be expected that the highly absorptive silica gels would act in the same manner as the charcoals; but this material was not available for testing at the time these experiments were performed. The order of catalytic activity that these materials possess is quite remarkable; thus, the specific reaction velocity of cocoanut charcoal was found to be about 11000, or more than five hundred times that observed for ordinary porous materials. The time required therefore to produce a given degree of oxidation in a given gas mixture is less in the same proportion. For example, to secure the conversion to nitrogen peroxide of ninety percent of the nitric oxide in a gas containing three percent of nitric oxide and three percent of oxygen requires five hundred seconds with inert material and only one second in the presence of the catalyzer.

"Water vapor has a very considerable effect on the catalytic properties of the charcoals. To retain activity the catalyzer must be maintained at a temperature above the condensation point of the aqueous nitric acid which would be in equilibrium with the gas phase in contact with it. Condensation on the catalyzer or soaking in nitric acid had no permanent harmful effect, as the material resumes its activity when dried. . . . With dry gases the catalytic activity is only slightly decreased by an increase of temperature. When, however, moisture is introduced into the gases, the reaction rate drops greatly, in the case of the cocoanut charcoal at 25°, one percent of water vapor in the gas causing a decrease in the rate of reaction constant from 11000 to 1100. With moist gases the effect of

[1] Jour. Am. Chem. Soc., 44, 244 (1922).

temperature is the opposite of that found with dry gases, the rate of reaction increasing as the temperature difference above the condensation point of the aqueous nitric acid becomes greater.

"A slight amount of water vapor present in the gases inhibits the activity of the catalysis to a considerable degree; but, except in the immediate neighborhood of the condensation point where the catalysts are very sensitive to differences in water vapor concentrations, concentrations of water vapor in excess of one percent seem to exert no further depressing effect. Even with a water vapor content as high as fifteen percent, as would be encountered, for instance, in the gases from ammonia oxidation, the catalytic activity of the charcoals is well maintained, provided the temperature of the reaction space is sufficiently elevated. The decrease in the rate of reaction with elevation of temperature, observed in the case of the dry gases, is probably occasioned by the decreased absorptive ability of the charcoal at the higher temperatures. The increase in the rate of reaction with temperature rise in the presence of water vapor is likewise probably to be explained by the lowering of the surface concentration of absorbed water in the charcoal caused by the temperature increase, thus enabling a relatively greater proportion of the active mass of the catalyzer to take up its duty.

"With respect to the life of the charcoal catalysts, their properties do not seem to be impaired at all with time, tests over many weeks' duration showing no decrease in activity. The charcoals were also tested for possible slow combustion; but in no case was there any evidence of carbon dioxide formation."

The best catalytic agent for forming phosgene, $COCl_2$, is charcoal; but Atkinson, Heycock and Pope[1] report that certain charcoals are much better than others. "On the introduction of carbonyl chloride as a weapon of chemical warfare, it becomes necessary to ascertain which method of preparation was most adaptable as a works process for manufacture, and

[1] Jour. Chem. Soc., 117, 1410 (1920).

one described by Paternò[1] presented itself as probably the best for this purpose. Paternò states that, on passing a rapid current of mixed carbonic oxide and chlorine at the ordinary temperature over animal charcoal, carbonyl chloride is produced very rapidly, with considerable evolution of heat.

"Difficulties were encountered in carrying out the Paternò method of preparation; a number of samples of commercial animal and vegetable charcoals proved almost without effect as catalysts. Ultimately a charcoal was prepared which gave quite remarkable results in inducing the combination of carbonic oxide and chlorine; this was made in the following manner. Fresh ox bones were crushed, embedded in sand in a clay crucible, and burnt in a muffle furnace; the residual charcoal was then well extracted with hot hydrochloric acid, washed with water, and heated, as before, in sand. Finally the bone charcoal was kept at a red heat for some time in a current of dry chlorine.

"The charcoal prepared in this way was crushed into small fragments, and, after sifting off the dust, 10 grams were filled into a U-tube immersed in a water bath; a rapid current of mixed carbonic oxide and chlorine, in which the former was in rather the greater volume, was then passed over the charcoal. Carbonyl chloride was produced freely when the water-jacket was kept at the ordinary temperature, but, on raising the bath temperature to between 40° and 50°, combination proceeded at a greater rate than that at which it was possible to supply the mixed gases. Using the bone charcoal catalyst in the manner described, and liquefying the carbonyl chloride by means of a freezing mixture, about 10 kilograms of the compound were produced without any sign that the activity of the 10 grams of charcoal had suffered diminution.

"It is thus shown that Paternò's method for preparing phosgene is correctly stated, but that certain precautions are necessary in the preparation of the animal charcoal used. Further investigations showed that certain kinds of vegetable

[1] Gazz. chim. ital., 8, 233 (1878).

charcoal act even more vigorously in inducing the condensation of carbonic oxide and chlorine, and the highly activated wood charcoal used in the Army box respirator proved more efficient as a catalyst than the bone charcoal described above. A U-tube containing 10 grams of the box-respirator charcoal, which had been heated in a current of chlorine gas, proved extremely efficient when the water-jacket was maintained at 14°, and one such tube kept at this temperature yielded more than 20 kilograms of carbonyl chloride, with no sign that the catalytic activity had diminished. In the work subsequently described in this paper, this active vegetable charcoal was used.

"The carbonic oxide required for laboratory work on the preparation of carbonyl chloride is conveniently prepared by passing carbon dioxide over red-hot coke contained in iron tubes heated in an ordinary combustion furnace; the resultant gas, after passing over slaked lime and drying over sulphuric acid, is practically pure carbonic oxide. In industrial operations, it is to be expected, however, that the available carbonic oxide will contain hydrogen. It thus becomes of importance to compare the reactivity of carbonic oxide and hydrogen with chlorine under the catalytic influence of charcoal.

"A series of experiments was therefore arranged in which varying proportions of hydrogen were mixed with the carbonic oxide and chlorine passed over the catalyst. It was found that the vegetable charcoal was so active at 14° in inducing the combination of carbonic oxide and chlorine that no advantage accrued from heating it to 90°, and that, working at temperatures below 70°, no hydrogen chloride was produced; at 80°, a small proportion of hydrogen chloride was formed, and this was greatly increased at 90°. It is thus shown that an active form of charcoal will effect the complete conversion of a mixture of carbonic oxide and chlorine into carbonyl chloride at a temperature 50° below that at which it begins to exhibit catalytic activity towards a mixture of hydrogen and chlorine. This conclusion seems of importance in connection with the manufacture of carbonyl chloride from carbonic oxide containing hydrogen."

In this country the gas-mask charcoal was not found satisfactory for making phosgene, presumably because it adsorbed the product too strongly. A special, commercial, vegetable charcoal was used instead.

Gillet[1] shows that the butylene obtained from normal butyl alcohol varies with the nature of the dehydrating catalyst used. This is not especially surprising because Sabatier and his co-worker, Senderens, had shown that different catalysts decompose the esters in different ways; but Adkins[2] has succeeded in duplicating many of these results with the same catalyst prepared in different ways.

"Alumina, titania and thoria at temperatures in the vicinity of 400° cause the formation from ethyl acetate of varying proportions of ethylene, carbon dioxide, acetic acid, acetone, alcohol and water. Sabatier[3] summarizes the action of these catalysts in three equations.

$$2CH_3CO_2C_2H_5\ (Al_2O_3) \longrightarrow (CH_3)_2CO + 2C_2H_4 + CO_2 + H_2O \quad (1)$$

$$CH_3CO_2C_2H_5\ (TiO_2) \longrightarrow CH_3CO_2H + C_2H_4 \quad (2)$$

$$2CH_3CO_2C_2H_5\ (ThO_2) \longrightarrow (CH_3)_2CO + C_2H_4 + C_2H_5OH \quad (3)$$

It has been shown in a previous article[4] of this series that these equations do not completely express the facts and that the type of reaction which a given oxide induces is dependent not only upon the metallic element present in the catalyst but is primarily dependent upon its method of preparation. It seemed probable that the character of the surface of the catalyst rather than the stability of hypothetical intermediate compounds was the determining factor in establishing the relative efficiency of the catalyst for decarboxylation or for dehydration. An idea obtained from an article by Briggs[5] made it possible to test this matter experimentally.

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[1] Jour. Chem. Soc., 120 I, 490, 553 (1921).
[2] Jour. Am. Chem. Soc., 44, 385, 2175 (1922).
[3] Sabatier: "La Catalyse en Chimie organique," 341 (1920).
[4] Adkins and Krause: Jour. Am. Chem. Soc., 44, 385 (1922).
[5] Briggs: Proc. Roy. Soc., 100A, 88 (1921).

"Briggs considers that the activation of charcoal for adsorption of gases is dependent upon interstices of molecular dimensions formed by the elimination of carbon atoms from the carbon molecule or space lattice. It must be understood that this has reference to the cavities of molecular size not to those much larger, microscopically visible pores or capillaries which apparently have little to do with adsorption. If Briggs is correct and it is assumed that catalytic activity in heterogeneous systems is conditioned by adsorption, or is due to the same causes as adsorption, then it should be possible to activate a catalyst selectively towards one or two reactions by modifying the size of the pores which are of molecular dimensions, for it is unlikely that two dissimilar reactions would meet their optimum conditions for reaction in the same-sized molecular pores.

"An alumina catalyst is prepared, or activated, by heating aluminum hydroxide, thus expelling water molecules. The molecular porosity, that is, the pores of molecular dimensions of the catalyst may then be supposed to be dependent upon the size of the water molecules, which are eliminated.

"If one could make an alumina catalyst from aluminum ethoxide according to the following reaction, $2Al(OC_2H_5)_3 + \text{heat} \longrightarrow Al_2O_3 + 3C_2H_5OC_2H_5$, the size of the pores would be increased, for the molecule eliminated (ether) would be about 4 times as large as in the former case. This is not feasible, however, because the aluminum alkoxides derived from the primary and secondary alcohols are quite stable towards heat and do not decompose quantitatively in the sense of the equation given. It is also true that these alkoxides melt at relatively low temperatures, and hence one would be comparing the decomposition products of the liquid alkoxides with that of the solid aluminum hydroxide. This difficulty can be avoided in working with the non-fusible magnesium alkoxides, and it is intended to study the selective activation of magnesia by the use of these compounds.

"Alumina catalysts have been selectively activated by preparing them from the aluminum alkoxides by an indirect

method. In the solid aluminum ethoxide, for example, it may be assumed that there is a definite space-lattice formation and that the distance between the aluminum atoms is a certain definite value. If aluminum ethoxide, in the solid state is allowed to react with water vapor (or absorbed water) the reaction, $Al(OC_2H_5)_3 + 3H_2O \longrightarrow Al(OH)_3 + 3C_2H_5OH$, takes place.

"Aluminum hydroxide is formed but the distance between the aluminum atoms and the size of the cavity now occupied by the hydroxyl group is determined not by the volume of that group but by the volume of the ethyl (or ethoxyl) group whose place was taken By the hydrogen (or hydroxyl). In other words, the size and shape of the alkyl group would be a determining factor in the size of the interstice left in the catalyst when the hydroxyl group is later eliminated as water during the heating of the aluminum hydroxide.

"Assuming the above as a working hypothesis, eleven different alumina catalysts were prepared and their effects upon the reactions of ethyl acetate in the gas phase determined.

"The order of efficiency for ethylene production by alumina catalysts is as follows. (1) By far the most efficient are those catalysts derived by the formation of hydrated alumina from water and aluminum amalgam, or from aqueous solutions of inorganic salts with ammonium hydroxide or by the action of water upon a xylene solution of aluminum ethoxide. The numerical value for the ethylene efficiency of these catalysts is about 150%. In these catalysts the size of the molecular pores is least because it is determined by the size of the water molecules which are driven from the alumina nuclei during heating. (2) The ethylene efficiency of the alumina derived from the true aluminum hydroxide is much lower, having a value of about 107%. While the suggestion that this is due to an increase in molecular porosity of the catalyst is not so strongly made by the method of preparation, as in the case of the alumina from the alkoxides, yet its behavior is entirely in accord with the hypothesis advanced in the introduction of this paper. It seems that larger pores nearer to the central

aluminum atoms would be formed by the elimination of the elements of water from aluminum hydroxide than by the expulsion of water of hydration from the colloidal form. (3) Of much less efficiency are those catalysts derived by the formation of aluminum hydroxide from the solid aluminum alkoxides, without destroying the space relationships of the aluminum or attached groups. Of these the alumina derived from the normal butoxide is most efficient as an ethylene producer, that from the ethyl and propyl alkoxides less so, and that from the branched-chain isobutyl and isopropyl alkoxides least efficient of all. Of these last two catalysts the less efficient is the one derived from the isopropoxide in which the branching takes place from the carbon atom which is attached to the oxygen that holds the aluminum atom. In this case the branching is nearest the central aluminum atom, and hence gives the maximum size of pore within atomic distances of the central atom. If this hypothesis is correct, that increase in the size of the molecular pores decreases ethylene efficiency, the alumina derived from the alkoxides of the tertiary alcohols should be least efficient. As yet it has not been found possible to prepare these alkoxides, although repeated attempts have been made using both tertiary-butyl and amyl alcohols. The long, straight butyl chain may be considered to give the smallest or narrowest pore and hence the catalyst is more efficient as an ethylene producer than the catalysts derived from the other shorter or branched chain alkoxides.

"Alumina catalysts have been prepared which split ethylene from about 32% to 97% of the molecules of ethyl acetate actually decomposed. These same catalysts varied in the reverse order with respect to their ability to decarboxylate the acid residue. The variation may be expressed numerically by saying that carbon dioxide and acetone were formed from 95% to 60% of the molecules of ethyl acetate actually decomposed by the catalyst. According to the hypothesis advanced, increase in the size of the molecular pores or of the distances between aluminum atoms increases the activity of the catalyst for decarboxylation.

"Certain anticipated results have been obtained. The author realizes quite well that the hypothesis on the basis of which they were anticipated is not, therefore, necessarily correct. Evidence for or against the hypothesis is being sought in this laboratory by the use of the different types of alumina in the catalysis of various organic reactions. If the hypothesis be true, it is hoped to relate the size of the molecular pores of the catalyst to the type of the reaction induced. Two problems suggested by this work which are outside the scope of a laboratory of organic chemistry involve a study by means of X-rays of the space lattices of the different types of alumina and also a study of their absorption of various gases."

This work of Adkins seems fundamental though we are by no means clear how it should be interpreted. One point of view would be to consider that Sabatier's three equations do not represent three different reactions but merely three stages in the same reaction.[1] The first stage would then be in all cases the formation of acid,

$$CH_3CO_2C_2H_5 = CH_3CO_2H + C_2H_4.$$

The next stage would be

$$CH_3CO_2H + CH_3CO_2C_2H_5 + C_2H_4 = CH_3COCH_3 + CO_2 + C_2H_5OH + C_2H_4,$$

and the final stage would be

$$CH_3COCH_3 + CO_2 + C_2H_5OH + O_2H_4 = CH_3COCH_3 + CO_2 + 2C_2H_4 + H_2O.$$

From this point of view the different aluminas would represent more or less effective catalysts and would not introduce anything which was new theoretically. While this may perhaps be the right point of view for the particular case of the esters, it is an explanation which cannot apply in all cases. The two decompositions of alcohol, into aldehyde and into ethylene, are fundamentally distinct reactions and yet a given catalyst may accelerate both. With such a catalyst, it is extremely

[1] Bancroft: Jour. Phys. Chem., 27, 92 (1923).

probable that the ratio of the two decompositions may vary with the way in which the catalyst is prepared. Mlle. Peytral[1] has shown that, in the pyrogenic decomposition of alcohol in a platinum tube at a bright red heat, the relative rates of formation of acetaldehyde and of ethylene are independent of the speed with which the vapor is passed through the tube. This is true, however, only for the catalyst prepared in a given way—as a smooth metal tube. With a platinized tube the ratio would undoubtedly change.

While Adkins has not yet carried out a series of experiments with alcohol and alumina prepared in different ways, he has done so for the two decompositions of formic acid[2]—into carbon monoxide and water and into carbon dioxide and hydrogen. The spacing of the aluminum atoms has a very marked effect on the relative proportions of the two primary reactions.

"The catalyst prepared from colloidal alumina is much less active toward the decarboxylation reaction and much more active towards the dehydration reaction than the alumina prepared from the isopropoxide. The alumina from the isopropoxide was less active for dehydration and more active for decarboxylation than the alumina or pumice from the normal butoxide. It is not permissible to compare alumina on pumice with alumina in pills, for the pumice is slightly active towards the formic acid. However, since alumina from the butoxide on pumice gives a higher monoxide ratio than that from the isopropoxide on pumice, we are justified in saying that the effectiveness for the decarboxylation is greatest for the alumina from isopropoxide, less for the butoxide, and least for the colloidal alumina. This order, as well as the relative differences, is similar to that observed for the reaction of ethyl acetate. Selective activation of the alumina was thus very evident for the reactions of formic acid as had been previously demonstrated for the reaction of ethyl acetate."

Since it is not sufficient to assume that the different

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[1] Bull. Soc. chim. France, [4] 27, 34 (1920).

[2] Adkins and Nissen: Jour. Am. Chem. Soc., 45, 809 (1923).

aluminas vary only in effectiveness, Adkins considers that it is a case of selective re-arrangement of adsorbed molecules. "The dependence of the ratio of the two reactions of formic acid upon the spacing of the atoms upon the surface of the catalyst and upon the concentration of the acid in the gas phase over the catalyst is understandable upon the basis of an extension of the Langmuir theory[1] of the mechanism of reactions. As interpreted by us, this theory is briefly as follows: A compound is adsorbed on the surface of a catalyst through the agency of certain of the electrons of the outer shell of one of the atoms of the molecule. This union of the adsorbed material with the catalyst produces a shifting of the electrons within the molecule of the adsorbed material with possibly a resultant increase or decrease of the ease of reaction of this compound with either a molecule later impinging upon it or with a molecule adsorbed on an adjacent unit of the space lattice of the catalyst. For example, Langmuir showed that oxygen in the form of single atoms combines with separate platinum atoms under certain conditions. The oxygen atoms are in such an active condition that every atom of carbon monoxide which strikes them forms carbon dioxide. When carbon monoxide strikes a platinum surface it is held by a union between the carbon and two platinum atoms. Only one oxygen molecule out of ten molecules which strike the carbon monoxide reacts to form carbon dioxide.

"The theory may be developed further for use in those cases where intramolecular rearrangement takes place at a surface resulting in either one of two sets of products, as in the case of formic acid and alumina. A catalyst might be conceived of causing two reactions from one kind of a molecule through either one of two mechanisms. In the one case the molecule might be oriented in one position at certain points on the surface, and in another position at other points. Selective activation of a catalyst would then consist in increasing the number of points on the surface oriented in one position

[1] Trans. Faraday Soc., 17, 607 (1922).

and decreasing those which are oriented in another position. Selective activation of a catalyst would then be associated with selective adsorption of compounds. However, in the case of the simple acids and esters which have only one point in the molecule which is strongly active, it seems very probable that all the molecules are oriented in one position. This fact, taken in connection with the importance of the spacing of the aluminum atoms in the catalyst, points towards the second mechanism as developed below. Suppose that a molecule of formic acid was attached to an aluminum atom or other active point. It is possible for it to re-arrange in two ways to give either carbon dioxide and hydrogen or carbon monoxide and water. If the space between the active points in the catalyst is of a certain dimension, then re-arrangement may take place to produce one set of products. If it is of a certain other dimension, re-arrangement may take place to produce the other set of products. It is essential then not only that the formic acid be attached to the catalyst but that there be free spaces on adjacent active points of the catalyst."

This explanation is of course only tentative and is necessarily rather vague. It is a question whether the phrases "atomic spacing" and "molecular pores" may not be misleading. It is not a matter of differences in space lattices as this term is ordinarily used. It is a question of a much coarser arrangement, such as the difference between a plane and a pitted surface. As an extreme case let us consider two plane, parallel surfaces a little more than a molecular diameter apart. A molecule of formic acid will tend to attach itself to one wall at a given point in the molecule and will also tend to attach itself to the opposite wall at the same point in the molecule. It cannot do both these things at once and it is evident that the molecule of formic acid will be under quite a different strain from that which it would experience were there only one plane surface present. Another molecule coming into the space between the two planes will tend to strike the adsorbed molecule amidships, whereas it would tend to strike the free end of the molecule if there were one plane surface. Since the

two plane, parallel surfaces are the limiting case of a pit, we see that the reactions may be different at a pitted surface from those at a plane surface and that we may get anything between the two limiting results, depending on the physical structure of the surface. Since the catalytic activity increases markedly with the porosity of the surface, it seems proper to conclude that the conditions at a plane surface, including an adsorption layer only one molecule thick, are not the ideal ones for catalysis. It is desirable to distinguish sharply between the important experimental results which Mr. Adkins has obtained and the hypotheses which he or anybody else may make to account for those results.

Professor Taylor writes that "these studies of formic acid decomposition, though apparently simple reactions, reveal themselves as complex. This probably arises from several causes. The alumina surface is not a single elementary surface but a mixture of two elements, aluminum and oxygen. Varying methods of preparation give varying surfaces at least as far as groups of alumina molecules are concerned, possibly also as regards orientation. Furthermore, formic acid, and to a greater extent, esters may orient themselves in varying modes on the several surfaces. Thus, there are many variables. It is possible that we may approach the solution of this problem by a preliminary study of similar examples of greater simplicity. One such possibility is at present under study at Princeton and gives promise of fruitful results. A study of ammonia decomposition at metal catalyst surfaces is being undertaken. Here we have only atoms of one kind in the surface—and, in the case of several metals, attachment of adsorbed ammonia at the nitrogen atom. The diversity of behavior of ammonia-metal systems is noteworthy and shows the extent to which the metal determines subsequent behavior. Reduced copper and iron both adsorb ammonia freely in the temperature range 0–100°. For several reasons, it is fairly certain that the attachment is $(Me)_x$–N$\begin{smallmatrix}H\\-H\\H\end{smallmatrix}$. With copper,

the adsorption is completely reversible. All the adsorbed ammonia can be recovered by evacuation or gentle heat. With reduced iron the adsorption is practically irreversible. Little ammonia is recovered from the surface. On applying heat hydrogen is first obtained in preponderating amount ($H:N>3:1$) showing the extreme stability of the iron-nitrogen linkage, for which the existence of iron nitride $Fe_4N_2$ suggests a bonding Fe—N. The iron-nitrogen linkage is obviously stronger than Fe

the N-H linkage with ammonia adsorbed on iron. At higher temperatures, the iron-nitrogen linkage breaks and nitrogen becomes the predominant gas in the evacuation system. Contrast the behavior of these two elements with the known behavior of sodium and potassium towards ammonia. In these cases an adsorption complex $Me\text{-}NH_3$ is evidently first formed,—but, owing to the readiness with which the valence electron of the metal may be given up, it or one of the electrons is evidently transferred to a hydrogen nucleus giving a hydrogen atom —which in its turn forms hydrogen molecules. The residue is the stable configuration $Me.NH_2$. In all three cases, it is undoubtedly the influence of the metal electrons on the electronic configuration of the ammonia molecule which gives rise to the varying behavior. Furthermore, temperature is also a determining factor in the behavior of metal-ammonia systems; for, whereas at 0°–218°, ammonia is reversibly adsorbed by copper, at higher temperatures some other arrangement has the upper hand. At high temperatures ammonia is decomposed into its elements in presence of copper—though less so than in presence of iron at the same temperature. A variety of metals and a variety of behaviors towards ammonia are now being studied. Recent theories of atomic structure should help in the elucidation of the behavior noted in each case."

Palmer[1] found that electrolytic copper does not dehydrogenate ethyl or isopropyl alcohol at any temperature between

[1] Proc. Roy. Soc., 98A, 15 (1920); 99A, 412 (1921).

200° and 300° regardless whether the copper is precipitated from an acid or an alkaline bath. Palmer puts forward a rather surprising hypothesis to account for this. "If it is granted that pure metallic copper as obtained by the electrolysis of a copper salt is not catalytically active, two possible theories of the source of the activity in reduced copper seem to offer themselves:

1. The activity is due to an oxide dissolved as a solid solution in the bulk of the metallic copper.

2. The activity is due to one or more labile forms of copper, which pass only slowly into stable inactive forms.

It should be possible to gain insight into the applicability of (1) or (2) in the following way. The deterioration of the catalyst according to (1) would be due to a gradual reduction of the oxide to metal. The velocity at which this takes place should be markedly influenced by temperature, since the reaction would be strongly exothermic.

"According to (2), deterioration of the catalyst is due to a slow change, labile form ⟶ inactive stable form. This change recalls allotropic changes, and might be expected to proceed without any marked heat effect; the rate of deterioration would hence be only slightly influenced by temperature.

"Experiments based on these suggestions are now in progress. Certain experiments already carried out showed that the activity decreases smoothly with the time of use, after a period of one to two hours, during which the initial activity remained constant.

"The reduction of copper oxide to metallic copper is very probably a complex reaction, resulting in the production of molecules of copper containing atoms of different valency. For example, the three reactions

$$CuO + H_2 = Cu'' + H_2O,$$
$$2CuO + H_2 = Cu_2O + H_2O,$$
$$Cu_2O + H_2 = 2Cu' + H_2O,$$

probably proceed simultaneously when cupric oxide is reduced. The resulting copper consists of two types of molecules, one

type composed of atoms of cupric copper, and the other type of cuprous copper atoms. These two sorts of molecules would be heterotopic and possess different chemical properties,[1] and certainly very different surface lattices, and so exhibit different adsorptive characteristics.[2]

"The proportion of one type of molecule to another type would naturally depend on the reducing agent used and on the temperature at which reduction took place. The inactivity of electrolytic copper demonstrates the lack of catalytic power in molecules formed entirely of divalent copper. Experiments are now in progress to find the effect of reducing agents other than hydrogen upon the catalytic activity of the copper."

In the second paper Palmer says that the fact that the activity of the catalyst does not necessarily increase continuously as the temperature of preparation from the oxide is lowered "conflicts with the view that the real catalytic agent is an oxide of copper dissolved in reduced (metallic) copper; but it could be readily reconciled with the theory put forward in the previous paper, namely that metallic copper produced by reduction of cuprous oxide is the active agent. The proportion of active material formed by reduction would depend on the mutual relation of the velocity curves for the two reactions.

$$CuO + H_2 = Cu + H_2O;\ 2\,CuO + H_2 = Cu_2O + H_2O.$$

In support of this hypothesis, it may be mentioned that copper reduced from cuprous oxide is attacked more readily by ordinary reagents than metal produced from cupric oxide.[3] It will appear from the later discussion that the inactivity of 'cupric' copper is to be attributed to its lack of adsorbing

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[1] Soddy: Jour. Chem. Soc., **115**, 23 (1919).

[2] [Samples of copper prepared by Dr. A. F. Benton by reduction of different samples of copper oxide at different temperatures all showed the characteristic copper metal lattice when examined by the X-ray method at the Research Laboratory of the General Electric Company at Schenectady. H. S. T.]

[3] Private communication from Mr. E. K. Rideal.

power for alcohol, and not to any other cause." Professor Taylor reports that experiments at Princeton have shown that all varieties of comparative activities of copper can be obtained by suitable manipulation of the experimental procedure irrespective of the origin of the copper or from what oxide prepared.

One great difficulty about Palmer's theory is that copper precipitated electrolytically is not "cupric" copper. The author is relying on Luther's assumption that copper passes directly to cupric ions; but Briggs[1] has shown that it is more satisfactory to drop this assumption. "We shall assume that Luther's second reaction—the direct ionization of copper to cupric ions—does not actually take place. Furthermore we shall assume that cupric ions are always produced by oxidation, either chemical or electrolytic, of cuprous ions as intermediate product. In a similar manner we shall postulate that metallic copper is deposited at the cathode by the discharge of cuprous ions and never by the discharge of cupric ions. When copper is deposited from solutions of cupric salts, cupric ions must be reduced electrolytically or chemically before actual deposition can take place. The theory may be summarized by saying that the electrolytic behavior of copper is determined by two electrochemical reactions (or their reverse) as follows:

$$Cu + \oplus \longrightarrow Cu^{\cdot}$$
$$Cu^{\cdot} + \oplus \longrightarrow Cu^{\cdot\cdot}"$$

It is rather surprising that Palmer should not have tested his theory by precipitating copper electrically from a cyanide solution in which the copper is present practically completely as cuprous salt. We really do not need to go far afield for an explanation of the results. Copper, as usually precipitated electrolytically, is not porous in the sense that we mean when speaking of a catalytic agent and consequently it does not act as a catalytic agent. If it were precipitated electrolytically in a suitable form, it would undoubtedly act as a catalytic agent.

[1] Trans. Am. Electrochem. Soc., **40**, 231 (1921).

The electrical disintegration method of Bredig and Svedberg gives a good catalytic platinum and we ordinarily platinize electrodes electrolytically. There is no reason to suppose that a copper catalyst cannot be made electrolytically.

It is far simpler to account for Palmer's results on the ground that a smooth surface has a relatively low catalytic power. This is practically the conclusion reached by H. Briggs.[1] "When we turn from a consideration of the gas adsorbed to an analysis of the characteristics of the solid substance, which acts both as condenser and as reservoir for that gas, we meet with phenomena, such as that of activation, whose effects can be studied by experiment; but whose intrinsic nature, to a great degree, yet remains in doubt.

"It is unsatisfactory to speak of gas molecules being condensed upon the surface of the solid, since, if the gas is to be referred to the molar scale, so must the solid; such a statement, indeed, compels the question: The surface of what? In the present state of our knowledge of the constitution of solids, there appears to be no clear answer to that question; we are reasonably sure, however, that, in solid substances such as carbon and silica, we are not dealing with the ultimate molecule[2] but with elaborate polymers.

"Apparently, the only solid structures which are impervious to gas are the crystal and the glass. As is well known, the former can hold indefinitely gas 'included' under pressure while the latter, whether common glass, vitreous porcelain, or fused silica, can hold a high vacuum—and there is no better test of tightness—as long as the character of the glass remains unchanged. That these two forms possess so unusual a characteristic in common makes it probable that they have analogous structures; that, in fact, in place of being a molecular aggre-

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[1] Proc. Roy. Soc. **100A**, 97 (1921).

[2] I am indebted to Sir James Walker for suggesting the expression "ultimate molecule" to distinguish between $H_2O$ and $H_{2n}O_n$, for example, or between the ultimate molecule $SiO_2$ and the polymeride $n(SiO_2)$. The expression removes much of the ambiguity of meaning attaching to the word "molecule," which is not now always used in the original sense.

gate (which would be pervious to gas), a piece of glass, like crystal, is a single atomic linkage, and as such is entirely free from interstices on the molar scale. If this view be allowed, it is clear that an adsorbent must be non-vitreous—an aspect of the question which is further considered below.

"It has already been seen that the chemical character of the material affects its properties as a gas-adsorbent. With any given material, there are two factors which have a profound influence on adsorptive power, namely, (*a*) the degree of canalisation of the substance, i. e., its porosity on the microscopic or ultramicroscopic scale, and (*b*) the degree of porosity on the molar scale.

"The microscopic or ultramicroscopic canals, whose presence in an intricate network of connected passages is so striking a feature of a high-capacity adsorbent, important though their function is, do not alone determine adsorptive power. A high-capacity silica may be de-activated by prolonged heating, and though, in the de-activated state, one-fifth of the original internal gaseous volume remains, the amount of gas it can take in is virtually *nil* even at liquid air temperature. Evidently the capillaries are only of use when they traverse a medium in a suitable physical condition. Again, powdered graphite, which has no capillary passages, is able to adsorb 5.6 times its gross volume of nitrogen at —190° C.

"The largest canals of charcoal can be seen under the microscope and Saussure, who measured the size of the cells of charred wood, found them to be, on the average, $10^{-3}$ cm in diameter, or about 13,000 times the diameter of a nitrogen or oxygen molecule. On the other hand, Lamb, Wilson and Chaney, from a study of the vapor-pressure curves of adsorbed liquids, estimated the average diameter of the pores (assumed to be cylindrical) of activated charcoal—including the finest with the coarsest opening—to be about $5 \times 10^{-1}$ cm, which is less than seven times the diameter of the gas molecule. It may be inferred from these figures that the greater part of the internal gaseous space of an efficient adsorbent consists of passages which are not greatly larger than the gas molecule.

"To draw an analogy: the coarser canals traversing the adsorbent may be compared with the bronchi of the lungs and the finer openings with the alveoli. Either kind of passage is useless without the other and their functions differ: the coarser canals convey and distribute the gas with a minimum of impediment, but (excepting in conditions approaching total saturation) they do not hold it; the gas is chiefly held on the surfaces of the polymers in openings of molar dimensions.

"It will be evident that a higher degree of porosity on the molar scale and a greater exposure of surface will occur when the polymers are small rather than large; and that (other conditions remaining constant) if we can disrupt the elaborate polymers which build up a solid, the more active the material will become in adsorbing gas.

"Reference has already been made to the fact that a high-capacity silica may be converted into a non-adsorptive substance by heating. The change is not due to the destruction of the capillaries, for 20 percent of the original porosity remains after heating. Had adsorption been merely a matter of pore-space, one-fifth of the original capacity—or, at —190° C, about forty volumes of nitrogen per volume of silica—would have survived. Actually, the capacity fell almost to zero. The question arises: What happened to this silica to cause deactivation? The microscope showed the particles to be unchanged in outward form, but here and there in the mass there was evidence of incipient fusion, which was revealed by the occasional presence of a few of the finest particles enclosed by a skin. At first it was thought that the formation of surface skins might explain the loss of adsorptive power, but when a sample was finely ground there was no improvement: the change had affected the whole mass.

"The evidence favors the explanation that the heating, without destroying the coarser passages, had vitrified the silica and blotted out the finest openings upon which adsorption so largely depends. In other words, the heating had converted a granule which was originally an aggregate of small polymers riddled with openings into a completely polymerized unit

impermeable on the molar scale." Professor Taylor writes that "the surface-activity relationships may be similarly discussed with reference to actual adsorption measurements on catalytic metals Dr. R. M. Burns and the writer showed that ninety-seven percent of the adsorptive capacity of nickel for several gases was destroyed by heating nickel from 300° to 600°. Now I do not believe that the new surface was but three percent of the original surface. Sintering did occur, but not to that extent, I feel sure. Rather, it seems better to assume that the *effective surface* diminished to three percent. The effective surface, those portions of the total surface capable of adsorbing the gases, were destroyed. It has seemed useful at Princeton to regard the effective surface as comprising those atoms of catalyst surface less effectively a part of the normal space lattice of the crystalline structure,—in other words, those surface atoms whose electrons are not mainly employed in building up with other metal atoms the atomic lattice. They are the atoms in the surface manifesting the maximum external free energy. They have a higher vapor pressure than the atoms normally placed in the space lattice. It is these relatively free atoms in the surface which have the highest adsorptive capacity which adsorb gases even at very low partial pressures, probably by reason of their available electrons. It is these atoms which hold catalyst poisons most tenaciously. Thus the adsorption of a less readily adsorbed gas in a mixture is affected most markedly by heat treatment or by poisoning of a catalytic agent."

It has been known all along that a sintered catalyst is usually ineffective and this is confirmed by the recent work. Gilfillan[1] showed that, by calcining thoria strongly or by heating it for a long time at a lower temperature, the oxide may be made practically inert so far as the dehydration of alcohol is concerned. Kramer and Reid[2] made a very inert thoria in an unexpected way. "When thorium nitrate is heated suddenly

[1] Jour. Am. Chem. Soc., **44**, 1323 (1922).
[2] Ibid., **43**, 882 (1921).

to a high temperature by being dropped into a red-hot crucible, a very light, porous thoria is obtained, seven grams of it occupying 200 cc of space. On account of its enormous surface, we expected this to be a wonderfully active form but found it inactive." Unless the thoria was not clean, about the only thing left is to postulate that it had a vitrified surface. This material should certainly be examined under a microscope and compared with an active material.

### Special Hydrogenations

Kahlenberg and Ritter[1] have studied the catalytic hydrogenation of cottonseed oil, trying a number of different metals as catalysts. They find, in agreement with their predecessors, that nickel is the most efficient of the common metals for hardening cottonseed oil. As against Sabatier's view that chlorides should not be used as the source of the catalyst, they find that nickel chloride reduced with hydrogen at 180°–250° is a good catalyst and hardens cottonseed oil fairly well at 170°. A half-and-half nickel-cobalt catalyst was more active than either metal when used alone. This reminds us of the behavior of the oxidation catalysts and is possibly a connecting link between these and the promoters used in the ammonia oxidation. The most active nickel catalyst was obtained by depositing nickel upon arsenic-free granulated zinc from a saturated solution of nickel chloride. This catalyst hardens cottonseed oil, under atmospheric pressure, at lower temperatures than any other nickel catalyst studied. One would like to see a zinc-nickel couple tried out as a substitute for the Gladstone and Tribe zinc-copper couple. Zinc carbonate, freshly precipitated in the presence of suspended, powdered aluminum, and reduced at 350°–504° made a fairly good catalyst and so did bismuth precipitated upon charcoal and reduced with hydrogen at 350°. The paper is avowedly a preliminary experimental study and no attempt is made to draw any theoretical conclusions.

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[1] Jour. Phys. Chem., 25, 89 (1921).

A very impressive programme is being carried out under the direction of O. W. Brown of Indiana University on the catalytic reduction of nitrobenzene. A number of papers[1] have already appeared. The first experiments were on the reduction of nitrobenzene to aniline and were made in an iron tube, which itself exerted a distinct catalytic action. The nickel catalyst was made by heating nickel nitrate to 450° and reducing the resulting oxide with hydrogen at about 380° both temperatures being important. If the nickel nitrate is heated to 535°, it undoubtedly sinters appreciably because the catalyst made from it is less efficient. If the reduction of the oxide with hydrogen takes place below 380°, say at 320°, the catalyst is too active and carries some of the nitrobenzene beyond the aniline stage to methane and ammonia. If the oxide is reduced at too high a temperature, the resulting nickel sinters and becomes less effective. These directions are relative and not absolute, because the authors have not determined whether the nitrate might not be ignited at a somewhat higher temperature if the oxide is reduced at a correspondingly lower temperature. The most satisfactory temperature for the reduction of nitrobenzene was about 190°.

Working under favorable conditions a ninety-five percent yield of aniline was obtained. With a constant rate of flow of nitrobenzene the yields drop off both with too much and too little hydrogen. When the hydrogen is run through too fast, the authors consider that the time of contact of the nitrobenzene with the catalyst is too short. When the rate of flow of hydrogen is low, the authors believe that the low yield is due to the aniline being reduced further. This does not seem very probable. If the rate of flow of nitrobenzene is constant, the time in contact with the catalyst must be the same and one would hardly expect that increasing the ratio of nitrobenzene to hydrogen would increase the degree of reduction of the nitrobenzene. With a constant flow of hydrogen the yield of aniline

[1] Brown and Henke: Jour. Phys. Chem., **26**, 161, 272, 324, 631, 715 (1922); **27**, 52 (1923).

was nearly constant, increasing only from 94 to 95.8% as the flow of nitrobenzene decreases to about one-fourth its original rate.

The copper catalyst first studied was prepared by ignition of the nitrate at 415° and reduction at 314°. When the oxide is reduced at a lower temperature, the resulting catalyst is active, but deteriorates rapidly, presumably sintering more readily than a catalyst prepared at a higher temperature. The copper catalyst is more sensitive to temperature changes than is the nickel catalyst. If the copper catalyst, prepared at 314°, is heated in hydrogen to 475°, it begins to lose its activity, which disappears immediately at 535°, whereas a nickel catalyst only loses its activity at this temperature gradually, as a result of use. The best temperature for the reduction of nitrobenzene in presence of a copper catalyst is about 260°. There is no danger of carrying the nitrobenzene beyond the aniline stage; but the copper catalyst is more sensitive than the nickel one to changes in the rate of flow, the yield dropping off rapidly with increasing rate of flow. In consequence Brown and Henke consider that, from a commercial rate of view, a nickel catalyst is better than a copper one because the higher yield of aniline which can be obtained with copper is purchased too dearly by the increase in time made necessary by the much lower rate of flow.

In a later paper Brown and Henke[1] studied the behavior of a copper catalyst made by precipitating the oxide from the nitrate by means of sodium hydroxide, Sabatier having said that this is more satisfactory than decomposing the nitrate by heat. The results confirm the statement of Sabatier, the catalyst obtained by reducing a precipitated oxide being more effective with low rates of hydrogen flow and being very much less sensitive to changes in the rate of flow. It is therefore possible to reduce nitrobenzene at a much greater rate with a copper catalyst prepared from the precipitated oxide than with one prepared from an oxide obtained by igniting the nitrate.

[1] Jour. Phys. Chem., **26**, 715 (1922).

"The copper catalyst from the precipitated oxide gave constant yields immediately. After the first few experiments with this catalyst the aniline produced seemed to be perfectly colorless as not a trace of color could be detected. However, upon titration the yield was only 97–98%. After a few days' use of this catalyst the product became slightly colored; but upon titration the yield was found to still be practically the same. After about three weeks' use, during which time this catalyst was used at temperatures as high as 300°, it showed a slight decrease in activity, the yields of aniline being about three percent lower than at first. When this catalyst was taken out of the furnace, it had a bluish black color, while the catalyst from the ignited oxide was red and more compact. Upon examining this catalyst (from the precipitated oxide) it was found to contain bright pieces of hard massive copper. Upon examining these catalysts under the microscope with a magnification of 100 diameters, the red copper catalyst looked as though it had been submitted to incipient fusion, the mass being made up of myriads of little spheres of copper. The catalyst from the precipitated oxide did not show this sintering to as great an extent as the red copper catalyst. When some of the hard massive particles of copper (from the catalyst from the precipitated oxide) were broken up and examined under the microscope, they showed a needle-like crystalline structure. From this and also from the slightly lower yields obtained after three weeks' use, it appears that the catalyst loses its activity slowly, probably due to a slow agglomeration or sintering of the small particles."

In order to prevent sintering, copper catalysts were prepared with asbestos and with pumice as supports. For short periods copper on pumice was better than copper on asbestos and both were better than the straight copper catalyst. The copper-on-pumice catalyst lost its activity quickly, the yield of aniline dropping from 92.3% on the first day to 75.2% on the second day. For this reason the copper-asbestos catalyst seems the better. The comparisons were made with equal volumes of catalyst which means 1.5 g CuO for copper-pumice, 3.0 g

for copper-asbestos, 13 g for precipitated oxide, and 27 g for ignited oxide.

The copper-asbestos gives good yields at higher rates of flow than can be used satisfactorily with the straight nickel catalyst. "At these rapid rates of nitrobenzene the catalyst loses its activity quickly. This loss in activity is probably due to a heating effect. Thus in one experiment with seventeen grams of nitrobenzene per hour the temperature, as indicated by the thermocouple, rose 20° in about eight minutes. It would be reasonable to suppose both that the temperature became much higher at the surface of the catalyst where the reaction took place than that indicated by the thermocouple, and that this heating causes the diminution in activity." The presence of small amounts of iron in copper oxide made by igniting the nitrate is distinctly beneficial and also appears to check sintering to some extent.

In the second paper Brown and Henke[1] studied the behavior of several other metals as catalysts. Cobalt was prepared by ignition of the nitrate at 445° and reduction of the oxide at 400°. "With cobalt the highest yield of aniline (48%) is obtained at a lower temperature than with nickel and the lower the temperature the higher the yield of aniline until 125° is reached, below which it was practically impossible to work. From the work of Sabatier this is exactly what one would not expect, for he found nickel to be more active than cobalt in other hydrogenations. The low yields of aniline with cobalt were not due to incomplete reduction of the nitrobenzene but to the fact that the cobalt was carrying the reduction too far; which was shown by the fact that the odor of ammonia was strong and that at the higher temperatures there was only a small amount of condensate, indicating that the cobalt was reducing some of the nitrobenzene even to methane. This variance from Sabatier's results may, however, be due to the fact that he freed his nickel very carefully from cobalt and his cobalt from nickel, while the cobalt nitrate that we used contained 0.51% nickel and

[1] Jour. Phys. Chem., **26**, 276 (1922).

the nickel nitrate contained 0.39% cobalt. Also Sabatier used a glass tube while we have used these catalysts in an iron pipe.

"The iron catalyst was prepared from ferric nitrate, which had been boiled down repeatedly with nitric acid to free it from chlorine. Ferric oxide was precipitated from the ferric nitrate solution by ammonium hydroxide," dried at about 110°, and then reduced in hydrogen at 415°. At temperatures below 300° the iron is oxidized by the nitrobenzene and ceases to be a catalytic agent because hydrogen does not reduce the oxide. At 300° iron is not satisfactory because it carries the reduction beyond the aniline stage.

This is a very interesting case because we have all the criteria of the intermediate compound. Iron is oxidized directly by nitrobenzene and the iron oxide is reduced by hydrogen. In spite of this it is very improbable that the catalytic action of iron involves the alternating oxidation and reduction of iron.

Silver carbonate was prepared by the action of ammonium carbonate on a silver nitrate solution. On drying, a part of the carbonate was converted into oxide. The mass was reduced by hydrogen at 280°. The resulting silver was a better catalyst than copper obtained through ignition of the nitrate because it could be used at much higher rates of flow of nitrobenzene. Antimony, manganese, and chromium were found to have some catalytic activity and the same was true of the lower oxides of molybdenum, vanadium, uranium, tungsten, and cerium, the oxides of molybdenum and vanadium being the most efficient of this group. Alumina showed a little activity but commercial metallic tellurium and the oxides of calcium, barium, and silicon showed none.

In the third paper Brown and Henke[1] have studied the problem of stopping the reduction of nitrobenzene at the azobenzene stage. Lead and bismuth seem to be the best catalysts for this purpose. The lead was prepared from sublimed, red, and yellow litharge, from white lead, and from

[1] Jour. Phys. Chem., **26**, 324 (1922).

orange mineral, which is an extremely finely divided red lead made by roasting sublimed litharge. With a lead catalyst some azoxybenzene may be formed but the product is chiefly azobenzene and aniline. As one might have expected, raising the temperature increases the yield of aniline at the expense of azobenzene. There is only a narrow temperature range within which a good yield of azobenzene can be obtained. With a catalyst from orange mineral, for instance, the yield was low at 270° because there was not much reduction and was also low at 308° because too much aniline was formed. At 290° a yield of over thirty percent was obtained. With other preparations and under other conditions yields up to fifty-five percent of azobenzene were obtained.

In general, a higher yield of azobenzene could be obtained in a glass tube than in an iron tube, apparently because the lead catalyst is not so active. "However in a glass tube the yield of azobenzene decreased rapidly with use while the aniline yield decreased also. Thus, catalyst from heavy litharge in glass gave a high yield of azobenzene, 42.5% in the first experiment but practically nothing in the second one. At the same time the aniline yield decreased from 46.7% to 19.7%. In an iron tube this same heavy litharge catalyst gave practically as high a yield of aniline in the third experiment as it did in the first experiment when used in glass. The azobenzene yield cannot be compared in this case, for the first experiment in the iron tube was carried out at a lower temperature than the first experiment in the iron tube. The azobenzene yield in iron and glass can however be compared with the catalyst from orange mineral that was made from sublimed litharge. . . . The catalyst from orange mineral gave a 38.2% yield of azobenzene and a 24.1% yield of aniline in the third experiment when used in glass, while the highest azobenzene yield when used in iron was 33.8% with a 35% yield of aniline. The azobenzene yield is increased and the aniline yield decreased when the catalyst is used in a glass tube. However both decrease very rapidly with use and in the second experiment in glass at 302° the azobenzene yield is practically nothing,

while when used in iron the yield of azobenzene was maintained for several experiments and the yield of aniline increased to 88.0%."

Unless we are to assume that the glass tube poisons the lead catalyst fairly rapidly, which seems improbable, we must assume that something in or from the iron tube keeps the particles of lead from coalescing. This latter seems to be the case, for very surprising results are obtained when small amounts of ferric oxide or copper oxide are mixed with the lead. "It will be noted that these catalysts have been used above the melting point of lead, the one with two percent copper oxide being used thirty-three degrees above its melting point. Also the lead catalyst containing two percent copper oxide was quite active, giving a yield of 90.5% aniline, when used at 360°, thirty-three degrees above its melting point. One would have expected that the particles of lead would have coalesced and run together when heated in hydrogen above their melting point and that this would have resulted in the catalyst losing its activity. However, this did not happen and one could not tell by inspection that the catalyst had been used above its melting point as it was simply a loose mass of black powder. The fine particles of lead were thirty-three degrees above the melting point of massive lead, yet something kept the particles from coalescing and running together. An oxide film is known to keep metals from coalescing; but one would hardly expect to find an oxide film on lead at a temperature of 360° in an atmosphere of hydrogen." A film of adsorbed ferric oxide or copper oxide might perhaps not be reduced under these conditions.

"This was the behavior of the catalyst from the heavy litharge. The catalyst prepared from white lead acted differently. After this catalyst had been heated to its melting point, it contained many little spheres of bright metallic lead and, in a few places, two to five grams had run together and formed a solid mass of bright metallic lead. This indicated that the particles of lead started to coalesce when heated to their melting point. This catalyst was not used above the melting

point and had been heated to that temperature by accident. However, it does show that the physical condition of the material from which the catalyst was made determines to a large extent whether or not the catalyst can be used above its melting point."

In addition to apparently preventing sintering, the iron tube has a tremendous influence in increasing the activity of the lead. "The effect of the iron is not merely additive. At 302° in a glass tube the yield of aniline was only 4.1% with practically no azobenzene while in an iron tube at 290° the second experiment gave a 37.5% yield of azobenzene and a 57.1% yield of aniline, making a total material yield of 94.6%. The activity of the catalyst should have been greater at 302° than at 290° instead of being less. In our first paper it was shown that an empty iron tube at 300° gave about fifteen percent material yields of aniline, so that the tremendous increase in activity of the lead catalyst when used in an iron tube instead of glass is surely not merely the added activity of the iron." There is nothing to show whether this is really an action at an interface; but this point should be studied. The question of the variations in a lead catalyst is only discussed empirically and incompletely. Within the limits studied the lead catalyst was more active the finer the material from which it was made and the finer the resulting lead. This was shown definitely for red lead of different degrees of coarseness. The catalyst made from red lead by roasting white lead was much more active than the one made from white lead directly; but there are no data to show why this should be so. The catalyst from the red lead made from white lead was also more efficient than the one from orange mineral made by roasting sublimed litharge.

The bismuth catalysts[1] were prepared by precipitating the hydroxide from a solution of the nitrate by ammonium hydroxide, drying, and reducing with hydrogen at 230°–240°. When the hydroxide was allowed to filter slowly without suc-

[1] Brown and Henke: Jour. Phys. Chem., 26, 343 (1922).

tion and was dried at about 110°, it remained light and fluffy. When the hydroxide was filtered rapidly with suction, it became packed in the funnel. It was then put in a small evaporating dish and heated in an electrically heated muffle at 415° for about fifteen minutes. This product was much denser and apparently more granular than that made by the other method. The fluffy oxide in a glass tube gave practically no azobenzene and very little aniline at temperatures of 230°–270° while in an iron tube it gave a seventy percent yield of azobenzene and a twenty percent yield of aniline at 270°. The catalyst from the dense oxide gave a ninety-two percent yield of azobenzene and over four percent of aniline on the first run in a glass tube at 230°, but only fifty-one percent azobenzene in the second run and practically none after that. In iron at 240° the yield was only a little lower and fell from eighty-nine percent azobenzene to fifty-eight percent on the second run. At 280°, the activity did not fall off in the iron tube and a pretty constant yield was obtained of 65–68% azobenzene and twenty-eight percent aniline. At 300° these figures are about reversed. The decrease in activity in the iron tube at 240° can scarcely be due to sintering because that would presumably be greater at 280°. It is probable that the bismuth catalyst is oxidized at the lower temperature and that the oxide is not reduced. Brown and Henke say that when a bismuth catalyst is taken out of the furnace, the end with which the nitrobenzene first comes in contact is found to be oxidized and the activity may be restored to some extent merely by heating in hydrogen as was also the case under some conditions with the iron, antimony, and lead catalysts.

Working as the authors did with equal volumes of catalyst, there is no question that the catalyst from the dense oxide was better than the one from the fluffy oxide; but there was more than twice the weight of catalyst in the first case and there are no data to show which would be more effective on equal weights, though that would seem to be a more rational basis of comparison. It must be admitted that the theoretical treatment by the authors is not on a par with their experimental technique.

In a discussion of results Brown and Henke say that "the action of different catalysts on this reduction of nitrobenzene seems to be more or less specific. Thus nickel reduces it to aniline or further, even to methane and ammonia, but gives no azoxybenzene or azobenzene other than enough to color the product slightly under certain unfavorable conditions. Copper and silver reduce the nitrobenzene to aniline and give no azoxybenzene or azobenzene. Neither do they carry the reaction farther than the aniline stage. Lead gives azoxybenzene, azobenzene, and aniline. This specific action of the different catalysts suggests chemical action. Sabatier looked upon nickel as forming a hydride with hydrogen, this hydride, and not the hydrogen, reacting with the organic compound. With lead and bismuth catalysts the oxide was observed at one end of the catalyst column. The peculiar behavior of iron and antimony was mentioned in our second paper. For the production of azobenzene the reaction may be looked upon thus: as

$$2C_6H_5NO_2 + 4Pb = C_6H_5N.NC_6H_5 + 4PbO.$$

Then $PbO + H_2 = Pb + H_2O$. It will be noted that only the removal of oxygen is necessary to produce azobenzene from nitrobenzene. To produce aniline, however, the introduction of hydrogen is necessary. However, it would seem altogether possible to have both metallic lead and a hydride of lead acting as reducing agents at the same time which would give both azobenzene and aniline."

Brown and Henke assume tacitly that azobenzene is not an intermediate stage in the formation of aniline, which is very possibly true but which has not been proved. They assume explicitly that azobenzene is formed by direct action of the metal; but there is no proof that this is the essential reaction in the presence of hydrogen. In the electrolytic reduction of nitrobenzene we get azoxybenzene and azobenzene as a result of hydrogenation and the splitting off of water. It is quite possible that this same reaction takes place to a greater or lesser extent in the catalytic reduction and this should have been discussed.

In the fourth paper Brown and Henke[1] experimented with a catalyst of purified thallium. It proved to be an excellent catalyst for reducing nitrobenzene to azobenzene as very little aniline is formed. At 260° a ninety percent yield of azobenzene was obtained; but the activity decreases very rapidly, probably owing to the thallium melting and the particles coalescing. Gold at 355° gives an almost quantitative yield of aniline but the activity decreases with use although asbestos was used. The ratio of gold to asbestos was much too high for efficient protection. It would be interesting to know what the purple of Cassius would do.

At Harvard Conant and Cutter[2] have raised a very interesting point. "The addition of hydrogen to certain classes of substances, such as quinones, is a strictly reversible reaction. It may be brought about in acid solution by such reducing agents as titanous chloride. By measuring the oxidation-reduction potential of the reducing agent on the one hand and the organic compound on the other, it is possible to state accurately the equilibrium between them in terms of the general principles of electrochemistry.[3] In the same way the equilibrium between such an organic substance and gaseous hydrogen in the presence of a metallic catalyst in aqueous solution will depend on the oxidation-reduction potential of the substance and the potential of the hydrogen in this solution. This potential of the 'catalytic hydrogen' is, of course, easily determined by the usual methods of measuring the hydrogen-electrode potential. Thus, the catalytic hydrogenation of all substances (organic or inorganic) whose reduction is *reversible* can be clearly stated in electrochemical or thermodynamical terms.

"The question arises whether or not the *irreversible* cata-

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[1] Jour. Phys. Chem., **26**, 631 (1922).

[2] Jour. Am. Chem. Soc., **44**, 2651 (1922).

[3] Haber and Russ: Zeit. phys. Chem., **47**, 257 (1904); Granger and Nelson; Jour. Am. Chem. Soc., **43**, 1401 (1921): W. M. Clark: Jour. Wash. Acad. Sci., **10**, 255 (1920); Biilman and Lund: Ann. Chim., **16**, 321 (1921); Conant, Kahn, Fieser and Kurtz: Jour. Am. Chem. Soc., **44**, 1382 (1922).

lytic hydrogenation of many organic substances can be similarly formulated.[1] The very fact that a certain process of reduction or hydrogenation is irreversible prevents our applying the usual thermodynamical equations and we cannot at present measure or define its oxidation-reduction potential. Nevertheless, we know in a rather qualitative way that in many instances the possibility of bringing about a certain irreversible reduction depends on the oxidation-reduction potential of the reagent employed. Thus, if we compare the irreversible reduction of two related substances,—maleic acid, HOOCCH=CHCOOH, and dibenzyl-ethylene, $C_6H_5COCH=CHCOC_6H_5$—we find that the former is rapidly reduced to succinic acid by chromous chloride in aqueous solution but is not affected by sodium hydrosulfite or titanous chloride. Dibenzoyl-ethylene, however, is reduced to dibenzoyl-ethane by all these reagents.

"Even without a quantitative method of expressing these facts, we can confidently predict that another reducing agent of nearly the same oxidation-reduction potential as sodium hydrosulfite will reduce the diketone but not the acid, whereas a reducing agent with as low a potential as chromous chloride will reduce both substances.

"Can a similar line of reasoning be applied to catalytic hydrogenation? A great many ethylene derivatives, which are not reduced by sodium hydrosulfite, are hydrogenated catalytically, for example, cinnamic acid. Is this well-known fact to be accounted for by the statement that the reduction potential of the hydrogen is greater (more negative) under the conditions of the experiment than sodium hydrosulfite? The results of our experiments with dimethyl-acrylic acid seem to give a definite negative answer to these questions. We have found that dimethyl-acrylic acid dissolved in 0.1 *N* hydrochloric acid is hydrogenated by hydrogen and a catalyst *but*

[1] [Is it correct to speak of *irreversible* catalytic hydrogenation even in the case of maleic acid—succinic acid? I can quite imagine that some one is clever enough to come along with maleic acid prepared from succinic acid by catalytic dehydrogenation. This reversal has been achieved with hexahydrobenzene, reduced naphthalenes and other substances. H. S. T.]

*is not reduced by a solution of chromous chloride* even after standing for several months. The potential of the hydrogen in this experiment is, obviously, about —0.05 volt on the normal hydrogen electrode scale; the potential of a mixture of equivalent amounts of chromic and chromous ions is —0.40 volt.[1] Thus the reducing agent employed was about *0.3 volt more powerful* than the hydrogen-catalyst combination and yet did not accomplish the reduction. The conception of reduction potential as applied to *irreversible catalytic hydrogenation* does not seem to be of value in correlating the known facts.

"We have performed these simple experiments with dimethyl-acrylic acid because most recorded instances of catalytic hydrogenation have involved the use of neutral or alkaline solutions. Under these conditions the value of the potential of the hydrogen electrode is so negative that no clear-cut distinction could be made between it and a reducing agent such as hydrosulfite.

"From our experiments with maleic acid and dibenzoylethylene it seems as if certain cases of irreversible reduction of ethylene derivatives could be qualitatively expressed in terms of reduction potentials. In the light of the experiments with dimethyl-acrylic acid, it appears that irreversible cases of catalytic hydrogenation cannot be so expressed. This being the case it is, perhaps, reasonable to suppose that the two cases represent different types of processes. We should like to present the hypothesis that in the first instance the process involves the addition of electrons and hydrogen ions, and in the second case the addition of hydrogen atoms only. The process involving electron addition is, from this point of view, a special case of the phenomenon of *reduction* such as we deal with in inorganic chemistry; the addition of hydrogen atoms can best be expressed by the term often used—*hydrogenation*. Equations 1 and 2 represent

$$(1)\ B + 2E + 2H^+ \longrightarrow BH_2 \qquad (2)\ B + 2H \longrightarrow BH_2$$

[1] Forbes and Richter: Jour. Am. Chem. Soc., 39, 1140 (1917).

the two processes. It is evident that Equation 1 represents a case of electronic reduction of the inorganic type which is peculiar for two reasons: first, because it is irreversible; and second, because it involves addition of hydrogen ions as well as electrons. Irreversible reduction without the addition of hydrogen ions is met with in certain steps in the reduction of nitro compounds and the conception of reduction potentials has long been applied to such processes which take place at a cathode in aqueous solutions.[1]

"These irreversible reductions are usually accomplished by such chemical reagents as sodium hydrosulfite, titanous chloride, and stannous chloride, all of which bring about rapid inorganic reductions in aqueous solution but which are not capable of reducing most ethylene derivatives, ketones, aldehydes, and nitriles.

"If the point of view here presented is correct, it is of great importance to extend this distinction between reduction and hydrogenation and to determine the factors governing both processes. This we hope to do in a subsequent paper. It will also be a matter of importance to decide whether the changes brought about by such reagents as zinc and acid or sodium amalgam are to be classed as reductions or hydrogenations. We are at present engaged in a thorough study of the types of reduction brought about by a very powerful inorganic *reducing agent*,—chromous chloride. With the information thus gained we hope to be able to make certain generalizations in regard to *irreversible reductions* as distinct from *irreversible hydrogenations*. We are also studying these reactions from an electrochemical standpoint."

They find that dimethyl-acrylic acid can be hydrogenated at room temperature in tenth-normal hydrochloric acid by means of hydrogen and colloidal platinum; but that chromous chloride in aqueous solution does not reduce dimethyl-acrylic

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[1] Haber: Zeit. Elektrochemie, **4**, 506 (1898); Zeit. phys. Chem., **32**, 193 (1900). Reductions during electrolysis are complicated by the heterogeneous system which is present as Haber and other workers have pointed out.

acid although its reducing power, as measured by its oxidation-reduction potential is 0.3 volt greater than that of a hydrogen electrode in tenth-normal hydrochloric acid. Maleic acid is reduced by chromous chloride in aqueous solution but not by sodium hydrosulphite, while dibenzoyl-ethylene is reduced by both reagents. The authors conclude that "the process of catalytic hydrogenation cannot be formulated successfully in terms of oxidation-reduction potentials. The reductions with chromous chloride and sodium hydrosulphite can be formulated in a qualitative manner. It is suggested that in one case we are dealing with a process of hydrogenation and in the other with a case of reduction (electron transfer) of an irreversible type."

These experiments are interesting but by no means convincing in their present form. The potentials for chromous chloride and for sodium hydrosulphite, on which Conant relies, were obtained in contact with platinum whereas the reductions were apparently made in the absence of platinum. The experiments should be repeated adding chromous chloride or sodium hydrosulphite to a solution of colloidal platinum. Since hydrogen will be given off, this must reduce the dimethyl-acrylic acid unless either chromous chloride or its decomposition product acts as a poison. This could be tested by showing that hydrogen does or does not reduce a solution to which chromous chloride has been added.

## Stabilization

Nine years ago Gröh[1] showed that the stabilization of colloidal platinum by gelatine causes a decrease in the catalytic action on hydrogen peroxide.

| Percent gelatine | Time for half decomposition | Percent gelatine | Time for half decomposition |
|---|---|---|---|
| 0.000 | 100 | 0.05 | 620 |
| 0.001 | 437 | 0.10 | 983 |
| 0.01 | 460 | —— | —— |

[1] Zeit. phys. Chem., **88**, 414 (1914).

Friend[1] says that "it will be observed that even small quantities of gelatine exert a most important influence, retarding the decomposition of the peroxide very considerably as is usual with a protective colloid. The gelatine, however, increases the stability of the colloidal metal solution, and tends to prolong its period of activity by preventing its precipitation by electrolytes, thereby enabling many reactions to be studied other than the decomposition of pure hydrogen peroxide solution."

All the subsequent work has confirmed the generalization that we pay for stabilization by a protecting colloid through decrease in the catalytic action. This effect may be masked to some extent if the protective colloid increases the dispersion and therefore the surface of the catalytic agent or if the protecting colloid is itself a catalytic agent. Rideal[2] found that gum arabic first increased and then decreased the catalytic reduction of phenyl-propiolic acid in presence of palladium or platinum. "There is an optimum concentration of gum arabic for each catalyst, two milligrams per ten milligrams for palladium, and four milligrams is required for the like amount of platinum. Since the atomic weight of platinum is practically twice that of palladium, this latter metal is peptized four times as easily as the former. It seems probable, however, that the phenyl-propiolic acid assisted in the peptizing of the colloid, since, when only small concentrations of gum arabic were employed, the sol would usually flocculate toward the end of the run, an indication that the unsaturated acid took part in the peptization; but that the saturated acid was less active in this respect, an hypothesis in accord with the accepted views on the chemical nature of adsorption phenomena."

"A series of runs was made in which ten milligrams of the mixed metals [palladium and platinum] in various proportions were precipitated together in the sol form. As stabilizing

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[1] "Text-Book of Inorganic Chemistry," **91**, 271 (1920).

[2] Jour. Am. Chem. Soc., **42**, 749 (1920).

colloid three milligrams of gum arabic were employed, this concentration permitting each metal in the pure state to exert almost its maximum activity. . . . In all cases where the sol was prepared from platinum containing small quantities of palladium there was a very marked improvement in stability and resistance to age over those prepared from the pure salts. This suggests the hypothesis that promoters may function in part as peptizing agents for colloidal catalysts, or for catalysts which pass through a colloidal stage at some point in their preparation.

"For this reaction there is a steady increase in the catalytic activity of the platinum sol on the addition of small quantities of palladium. . . A mixed sol containing about 9.8 mg of platinum to 0.2 mg of palladium (atomic ratio 26 to 1) is practically as active as a pure palladium sol in the hydrogenation of phenyl-propiolic acid." While it is possible that increased dispersion may account for the behavior of mixed platinum and palladium sols, it is also possible that the reaction may take place rapidly at the interface between the two metals.

Iredale[1] has studied the effect of protective colloids on the catalytic decomposition of hydrogen peroxide by colloidal platinum and finds that the stronger a substance is as a protective colloid the greater will be its inhibition of catalytic activity. The order of inhibitive effect is: gelatine and glue > egg albumin > gum arabic > sucrose, the last appearing not to affect the reaction at all. "In the case of a strong protective colloid like gelatine, the inhibitive effect is noticeable at a very great dilution, for example, 0.000005%, or one part in twenty million parts of water. The inhibition is explained on the ground of selective adsorption resulting in a decreased concentration of hydrogen peroxide at the platinum surface, and a consequent fall in the value of the velocity constant."

In a later paper Iredale[2] has determined the smallest

[1] Jour. Chem. Soc., **119**, 109 (1921).
[2] Ibid., **121**, 1536 (1922).

amounts of different protective colloids which have a perceptible effect in retarding the catalytic decomposition of hydrogen peroxide by colloidal platinum. When these inhibition numbers, as they are called, are compared with the gold numbers on the basis of the value for gelatine being 100 in each case Iredale gets for gelatine, egg albumin, dextrine, and starch, the values, 100, 20, 0.66, and 0.40 for the gold numbers and 100, 20, 1, and 0.33 for the inhibition numbers. Iredale concludes that "an inhibition number has been obtained which is defined as that percentage of protective colloid which is just insufficient to inhibit catalytic action. The rates of these numbers for different protective colloids are of the same order of magnitude as the ratios of the gold numbers."

Rocosolano[1] found that stabilizing Bredig's platinum with a little gelatine decreases the rate of decomposition of hydrogen peroxide to about one-third. With sodium lysalbate the rate passes through a minimum with increasing concentration, increasing when the effect of the alkalinity begins to count. There is no minimum with gum arabic and its effect on the reaction velocity is much less than that of an equal weight of gelatine, which is in harmony with Iredale's results.

In all these cases the catalytic agent is coated more or less completely by the protecting colloid. If, however, we fasten the catalytic agent on a rigid support, we shall prevent sintering more or less completely and there will be little or no decrease in the catalytic action.

Taylor and Gauger[2] have found that the adsorptive power of nickel, reduced at 300°, is destroyed if the nickel is heated to 500°. If the nickel is precipitated on kieselguhr or on diatomite brick, it can be heated to, or reduced at, 500° without any change in properties. Since there is always agglomeration when nickel is reduced at 300°, one might reasonably expect that nickel on kieselguhr or diatomite would adsorb more than straight nickel; but it is distinctly a surprise to

[1] Comptes rendus, **173**, 41, 234 (1921).
[2] Jour. Am. Chem. Soc., **45**, 920 (1923).

be told that it will adsorb ten times as much. Pollard[1] found that it is impossible to determine accurately the amount of hydrogen adsorbed by platinum black because the last thirty or more volumes cannot be pumped out except by heating to about 300° and at that temperature the platinum sinters to such an extent that the adsorption changes very much. In other words, adsorption measurements cannot be duplicated satisfactorily with straight platinum black. Platinized asbestos, however, can be heated to 400° without undergoing any change. Mond, Ramsay and Shields[2] obtained adsorptions of one hundred and ten volumes of hydrogen per volume of platinum with their best platinum black; but it is very certain that there were at least thirty volumes of hydrogen which they did not get out and consequently did not measure. This is so near to Pollard's value of about one hundred and sixty volumes that it would not be safe to claim that platinized asbestos adsorbs more or less hydrogen per gram of platinum than platinum black in the same state of subdivision.

In order to obtain reproducible copper catalysts Palmer[3] used cylindrical rods of china clay, each 3 x 80 mm, as supports. "The composition of these rods was: $SiO_2$, 65.27; $Al_2O_3$, 30.06; $Fe_2O_3$, 0.65; MgO, 0.173; CaO, 0.43; $K_2O$, 1.61; $Na_2O$, 0.723. They were rendered inactive as catalysts by igniting to bright redness for four hours. The rods were then immersed in a cold saturated solution of copper formate, and the pressure over the liquid reduced, by means of a water pump. After some time, the pressure was released, causing adsorption of the liquid into the porous rods. This operation was repeated several times. The rods so impregnated were dried at 100° and then ignited at 300° in a current of air. They then showed a quite uniform coating of black cupric oxide, which could not be detached by rubbing; the oxide was, however, removed instantly by nitric acid. It is, therefore, probable that all the copper on the rods was active catalytically,

[1] Jour. Phys. Chem., 27, 356 (1923).
[2] Phil. Trans., 186A, 657 (1895).
[3] Proc. Roy. Soc., 98A, 20 (1920).

as alcohol vapour could be expected to diffuse into the outer layers of the rods at least as quickly as nitric acid. An estimation of copper on spare rods prepared simultaneously to those actually used as catalysts showed that the total amount of copper was about 1.2 gram. . . . Before any quantitative experiments were carried out, the copper oxide was reduced at 250° and reoxidised again by air at 300° seven times successively. Owing to the design of the apparatus only 100 cc of alcohol were required even for an extended series of experiments. During the preliminary reductions of the copper oxide, this volume of alcohol was passed repeatedly over the copper in order to remove possible catalyst 'poisons.'

"After this preliminary treatment of the catalyst and alcohol, three quantitative experiments were made to find the extent of catalysis, and whether the catalyst was reproducible in successive reductions. . . . Between each determination the catalyst was oxidised for about one hour at 300° with air." At 246° the three experiments gave 0.46, 0.455, and 0.450 grams of acetaldehyde per hour.

Armstrong and Hilditch[1] have determined the apparent volumes of various types of nickel oxide and of the corresponding reduced metals. "Kelber[2] showed that, whilst nickel oxide *per se* gave a moderately active catalyst when reduced at about 300°, reduction of the same material at 450° gave a product of but feeble activity; yet nickel oxide deposited upon kieselguhr, and reduced at 450°, gave a catalyst much more active than the unsupported metal prepared at 300°. In Table I are given data which compare the apparent volumes of various oxides of nickel and their reduction products with their densities, pyrophoric character, and catalytic activity. The apparent volumes were measured by shaking down the substances in narrow-stoppered, graduated tubes, and are given as the volume (number of cubic centimeters) occupied by one gram of the material.

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[1] Proc. Roy. Soc., 99A, 490 (1921).

[2] Ber. deutsch. chem. Ges., 49, 55, 1868 (1916).

The samples studied were:—

A. Powdered fused oxide, prepared by igniting finely-divided nickel in a current of oxygen, and grinding the cooled mass of fused oxide.

B. Nickel hydroxide, prepared from the sulphate or nitrate by precipitation, washing, and cautious drying.

C. Nickel hydroxide on kieselguhr, prepared as in the last case, but in the presence of kieselguhr.

TABLE I

| Mark | Oxide used | Density | Apparent volume | Temperature of reduction |
|---|---|---|---|---|
| A | Powdered, fused oxide | 6.96 | 0.35 | 500° |
| B | Precipitated hydroxide | 5.41 | 0.87 | 300°<br>500° |
| C | On kieselguhr | 1.63 | 3.22 | 500° |

Reduced nickel

| Mark | Density | Apparent volume | Pyrophoric character | Catalytic activity |
|---|---|---|---|---|
| A | 8.14 | 0.52 | None | None |
| B | 7.85 | 0.83 | Pronounced | Fair |
| | 8.18 | 0.56 | Medium | Very little |
| C | 1.85 | 2.67 | None | Very active |

"Attention is drawn to the apparent volumes of the reduced, precipitated hydroxide: at 300° this is almost the same as that of the unreduced substance; but considerable shrinkage has occurred during reduction at the higher temperature of 500°. The fused oxide, on the other hand, occupies less than half the bulk of the precipitated hydroxide, although its specific gravity is not much greater; and, during reduction, a certain amount of expansion (increase in porosity) is noticeable, but the product is quite inactive. On the other hand, in the supported nickel, the kieselguhr, which does not shrink on heating, determines almost wholly the bulk of the product, and the activity is correspondingly great. The column showing the pyrophoric character of the reduced metals is added only because it illustrates that the paralellism between this property and catalytic activity, at one time supposed to be

complete, is in reality by no means so: the most active catalyst of the series is not pyrophoric, or at least only in a very small degree." There is a curious misconception here. The backing of asbestos would tend to keep the temperature down and would therefore interfere with the metal being pyrophoric.

"It has frequently been observed, with unsupported nickel oxide, that partially reduced oxide is more active than the same when completely reduced. . . Since, as our bulk gravity figures show, there is a tendency to contraction when a light, precipitated oxide is reduced, it is obvious that a partially reduced oxide will consist of a film of nickel dispersed over the central core of each particle, and it is practically certain that the superior activity of this product over the fully reduced metal is due to its being a 'supported' catalyst (nickel distributed on nickel oxide) and therefore of the same type, although not of the same degree of activity, as nickel upon a support such as kieselguhr."

Nelson and Hitchcock[1] find that there is no evidence that the adsorption of invertase by charcoal or alumina necessarily affects its activity towards sugar. "A comparison has been made of the amount of sucrose hydrolyzed in a given time by invertase combined with an adsorbent and not combined but distributed uniformly throughout the solution. When all conditions are the same except the presence or absence of the adsorbent and the velocity of hydrolysis is relatively large, then the amount hydrolyzed in a given time is less in the presence of the adsorbent. The decrease in rate appears to be due largely to the uneven distribution of the invertase in the reaction mixture because the extent of the retardation is diminished by preventing the settling of the adsorbent combined with the enzyme. When the velocity of hydrolysis is relatively small, then it is practically the same irrespective of whether the enzyme is combined with aluminum hydroxide or not. As a tentative explanation it is suggested that under

[1] Jour. Am. Chem. Soc., 43, 1956 (1921).

these conditions the rate of diffusion of the sucrose to, and the invert sugar from, the enzyme combined with the adsorbent is probably greater than the rate of hydrolysis of the sucrose."

While the high temperature at the surface of the catalyst tends to sinter it and to make a support necessary, the actual occurrence of the reaction tends to disintegrate the mass. Bone[1] has shown that a metal surface becomes roughened when flameless combustion occurs at it and it is well known that a platinum gauze undergoes similar changes[2] when used to oxidize ammonia and thereby becomes a more efficient catalyst. In fact Landis[3] claims that the style of surface varies with the impurities in the ammonia and that a platinum gauze must be activated anew if one changes to ammonia from another source, as from Haber ammonia to coke oven ammonia or to cyanamide ammonia.

Tribe[4] has described some experiments on agglomeration which seem to have escaped attention. He had been told that "the black substance which deposits on zinc when that metal is immersed in a dilute solution of copper sulphate does not streak metallically when submitted to the burnisher." On testing this statement he found that a metallic streak was obtained more readily the more concentrated the copper sulphate solution and also the more dry the deposit. The deposit from a 0.35% copper sulphate solution did not give the least metallic streak when wet and only slightly and with great difficulty when dry. The results were practically the same whether an excess of zinc or of copper was used.

"It is well known that the cohesion of metallic particles is prevented when their surfaces are coated with oxide, and also that the state of division of certain metals exerts a considerable influence on their oxidizability. In the black deposit, copper exists in an extremely finely divided condition, and hence it appeared to me probable that the difficulty of burnishing

[1] Phil. Trans., 206A, 1 (1906); Jour. Franklin Inst., 173, 101 (1912).
[2] Parsons: Jour. Ind. Eng. Chem., 11, 541 (1919).
[3] Trans. Am. Electrochem. Soc., 35, 300 (1919).
[4] Jour. Chem. Soc., 27, 415 (1874).

might be caused by surface oxidation of the metallic particles. With the object of removing this supposed oxide, I treated some black deposit with acetic acid, when immediately the granular particles of which it consists, aggregated or agglomerated, with an apparent increase of bulk, to a sponge-like mass of a greyish-black colour. On submitting this spongy material to the burnisher, a metallic streak was not only produced with the greatest ease, but it readily welded upon slight pressure. Dilute hydrochloric and sulphuric acids produced a similar aggregation, the resulting spongy metal being, however, of a dark chocolate colour in both cases. . . .

"In the hope of throwing some light on the cause of the phenomenon, I treated some black deposit with a solution of potassium hydrate, when immediately its particles aggregated to a black, spongy mass with almost the same readiness as with dilute acids. As potassium hydrate has no solvent action on copper oxide, this experiment shows that the phenomenon could not have been produced by its removal. . . .

"In reflecting on the results obtained, it became evident that the agglomeration did not arise from the subtraction of any of the foreign bodies with which copper-black becomes mixed in its preparation, but from some action of the reagents employed upon the constituents of the deposit. The action of those reagents which produce the agglomeration, being such as would, in every case, result in the formation of hydrogen, led me irresistibly to the conclusion that the change was due to the action of that element on the finely divided metal. To test this conclusion further, I placed a piece of zinc in contact with some purified copper-black covered with dilute sulphuric acid (three percent). Hydrogen was evolved at once, and almost immediately the metallic particles near the zinc became agglomerated. The negative platinum electrode was then placed in contact with some copper-black in acidulated water, when on immersing the positive pole in the liquid, the metal in the vicinity of the escaping hydrogen again agglomerated. In both experiments the aggregated copper was somewhat of a chocolate colour, and in portions of that pro-

duced by the electrolytic hydrogen, it was decidedly coppery.

"It now appeared of interest to ascertain whether hydrogen would produce the agglomeration of the finely-divided particles of those metals which are already known to condense it, especially as I thought, if it were found to do so, additional evidence would be adduced of the truth of the conclusion arrived at with respect to the agglomeration of copper, and perhaps some light would thereby be thrown on the cause of the phenomenon. The readiness with which palladium can be obtained in a finely divided state, coupled with its great power of condensing hydrogen, induced me to select it for experiment. The metal I employed was separated from a dilute alkaline solution of the sulphate by heating it with potassium formate, and, after washing, it was dried at 100°. It was jet-black and in an extremely fine state of division. I placed some of this palladium in a watch-glass, and covered it with dilute sulphuric acid, which produced no change in its agglomeration. When, however, it was touched with zinc the agglomeration took place, and this without any change in colour of the metal. Some palladium on the negative platinum electrode of a battery was now placed horizontally at the bottom of a vessel containing acidulated water, the positive electrode being near the surface of the liquid. It could be seen that almost immediately the aggregation of the metal had taken place, and that without change of colour.

"Platinum was also prepared in a finely divided state by heating a dilute solution of it with potassium formate. It was greyish-black and agglomerated easily when acted on by hydrogen, like palladium, although not so readily. Lest it might be contended that the aggregation was due to the agitation of the liquid produced by the escaping gas, I mixed intimately some sodium bicarbonate with palladium-black, and then added very dilute sulphuric acid to the mixture. Gas escaped much in the same manner as it does from copper-black when mixed with zinc in quantity and treated with acid but without producing the least agglomeration. Some palladium was next placed on the positive platinum electrode of a

battery immersed horizontally in acidulated water. Oxygen was evolved abundantly, yet not a trace of agglomeration took place. The current was now reversed, and the finely divided metal began at once to agglomerate. On again reversing the current, I was gratified to find that the agglomerated palladium-black de-agglomerated.

"Graham, in his researches on the occlusion of hydrogen by metals, found that the gas could be readily extracted from palladium by reversing the latter in the decomposing cell of a battery, and also that neither palladium nor platinum absorbs oxygen. [We know no wthat platinumm black and palladium are oxidized very readily.] The reason, therefore, that oxygen does not produce the phenomenon, but actually reduces the agglomerated metals to their original condition, is doubtless because, in the first place, it is not condensed; and secondly, that it combines with the condensed hydrogen on which the agglomeration depends.

"That the agglomeration is due to a property perhaps specific to hydrogen, there can be no reasonable doubt, and the explanation which has presented itself to me is that the minute particles, in virtue of a species of adhesive attraction, become surrounded by films or layers of liquid hydrogen, the coalescence or partial coalescence of these films producing the spontaneous inward movement of the finely divided metal which is characteristic of agglomeration. . . . The comparative ease with which the agglomerated metals weld or burnish is probably due to the closer approximation of the metallic particles, and also perhaps to liquid hydrogen being less viscous than water. Of course cleanliness of surface would have some influence, and hydrogen might be supposed to produce this were there surface oxidation; but were this the sole cause of the particles of agglomerated metals being more cohesive, the assumption must be made that even finely divided platinum oxidises superficially under ordinary circumstances, and also by electrolytic oxygen during the act of de-agglomeration.

"My friend Mr. Oakley-Coles, while experimenting on the applicability of agglomerated platinum for dental purposes,

found that it combines very readily with mercury, forming an amalgam which becomes solid in a few hours."

The explanation rejected by Tribe is undoubtedly the right one. The hydrogen removes the oxide film and permits two clean surfaces of the metal to come in contact. The fact that agglomerated platinum combines readily with mercury shows that the surface is clean. Platinum is only wetted by mercury under special conditions.[1] "Mercury, which holds even a very little sodium in solution, has the power of wetting platinum in a very remarkable manner. . . . The sodium removes the oxide film and permits the mercury to come in contact with the platinum." Iron, copper, bismuth, and antimony are also wetted by mercury if their surfaces are first touched with sodium amalgam.

Marsh[2] has studied alternating-current electrolysis between platinum electrodes A and D in dilute sulphuric acid. "It was soon observed that the rate of gas evolution was by no means uniform, but fell off rapidly, and finally ceased altogether. Simultaneously the platinum changed from its usual appearance to a dull black or greyish black. It appeared that this was the normal procedure with all specimens of platinum used under the conditions of the experiment. Experiments were made with a view to the restoration of such used platinum to its original state as regards gas evolution. To this end a third electrode of platinum was introduced. . . . A and D were connected together, and a direct current was passed between A and D acting as anode and the middle electrode, which served as cathode. This direct current was allowed to pass for different times, and, after each such passage, alternating current was passed through until no further evolution of gas took place. The volume of a gas given off by the alternating current was to some extent an indication of the degree of recovery of the electrode due to the passing of direct current. During the passage of direct current, the elec-

[1] Guthrie: Proc. Roy. Soc., 13, 458 (1864).

[2] Proc. Roy. Soc., 97A, 124 (1920).

trodes A and D were surrounded by nascent oxygen, and it was observed that the degree of recovery of the electrodes depended in some measure upon the duration of the direct current. . . During the passage of the direct current, the surface of the electrodes changes from greyish-black to dull grey. The restoration is never perfect. The longer the time of passage of direct current, the greater is the volume of gas evolved subsequently by alternating current, but there appears to be no simple relation between the two quantities. If the electrodes after use with alternating current are heated strongly they recover, in part, this power of evolving gases."

"The experiments show that in all cases the activity or power of the electrode in promoting recombination increases with time for a definite frequency, and increases very rapidly with frequency." There is always an excess of hydrogen in the gases evolved. Taken in connection with Tribe's experiments the general phenomenon is clear enough though the data are insufficient to account for all the details. The electrodes are disintegrated during the electrolysis and the roughened surface is agglomerated by the excess of hydrogen, thereby becoming a better catalyst and preventing the setting free of oxyhydrogen gas. When the electrodes are made anodes, de-glomeration occurs to some extent and the platinum surface becomes oxidized, both changes making it a less effective catalytic agent. The same effect will take place when the roughened electrode is heated, the finely divided platinum sintering together. The excess of hydrogen is probably due in part to the formation of hydrogen peroxide which is the normal product when oxygen is reduced. One cannot tell whether the hydrogen peroxide piles up in the solution or whether some of it breaks down away from the electrodes, so that that portion is not collected.

## Poisons

While we are still very much at sea on the theory of contact catalysis, there is practically universal agreement that any-

thing which decreases the rate at which the reacting substances reach the surface of the catalytic agent will poison the catalyst. While a decrease in the amount of adsorption will act in the same way, other factors remaining the same, it does not follow that the maximum adsorption corresponds to the maximum catalysis. There are two factors which may work against this. The reaction products may be adsorbed too strongly and thereby poison the catalyst. There is also the possibility that at low temperatures adsorption may not be accompanied by activation. Both these points have been brought out by Taylor and Burns,[1] and their views have been given earlier in this report.[2] Reference has previously been made to the fact that Taylor and Burns[3] have shown that carbon monoxide does decrease the adsorption of hydrogen by platinum black. The same result has been obtained by Pollard[4] rather more strikingly. With platinized asbestos, kept very clean from grease, he obtained one hundred and sixty volumes of hydrogen adsorbed per volume of platinum. On introducing carbon monoxide the hydrogen adsorption dropped to about seven volumes, which is practically negligible under the conditions of the experiment.

Paternò and Mazzuchelli[5] find that phosgene is surprisingly stable in presence of concentrated hydrochloric acid or of other acids, in spite of the fact that the reverse reaction between hydrochloric acid and carbon dioxide does not take place to any appreciable extent. The most plausible explanation of this is that the reaction takes place only at the walls of the containing vessel[6] and ceases when these walls are poisoned by adsorbed acid. Unfortunately, there is as yet no direct experimental proof of this.

The most complete experimental study of poisons made so

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[1] Jour. Am. Chem. Soc., 43, 1285 (1921).
[2] Jour. Phys. Chem., 27, 808 (1923).
[3] Jour. Am. Chem. Soc., 43, 1283 (1921).
[4] Jour. Phys. Chem., 27, 370 (1923).
[5] Gazz. chim. ital., 50 I, 30 (1920).
[6] Bancroft: Trans. Am. Electrochem. Soc., 36, 140 (1919).

far is by Maxted.[1] In these important papers he showed that "the occlusive power of palladium for hydrogen in the presence of occluded hydrogen sulphide varies linearly with the content of inhibitant, and that the activity of platinum for catalytic hydrogenation is also a linear function, down to a certain point of inflexion, of the content of various catalytic poisons" such as lead, mercury, sulphur, arsenic, and zinc. One-tenth to six-tenths gram-atom per atom of platinum will decrease the rate of catalytic hydrogenation to about one per-cent of its original value. In the fifth paper it is shown that the presence of lead decreases both the hydrogen adsorption by, and the catalytic action of, palladium. "It will be noted that, although the catalytic activity, for the main portion of the curve, and the occlusive power for hydrogen, probably for the whole of the curve (compare the case of hydrogen sulphide), and certainly for the greater portion, are each a linear function of the content of an inhibitant, yet the slope of the linear graph connecting respectively the occlusive power and the catalytic activity with the content of inhibitant is not the same. It requires, for example, a ratio of 0.17 gram-atom of lead to one gram-atom of palladium to reduce the occlusive power to one-half of its original value, whilst, in order to reduce the catalytic activity to one-half, only about 0.02 gram-atom of lead to each gram-atom of palladium is necessary. It appears not improbable that the reason for this lies in the fact that, whilst occlusion of hydrogen is not confined to the surface only of the palladium, catalysis is mainly a surface phenomenon. This view is strengthened by the observation that slope of the poisoning line for catalytic activity varies with the fineness of division of the catalyst, so that the same stock catalyst has to be used throughout the series of measurements, whilst the poisoning coefficient for the inhibition of the occlusive power does not vary from preparation to preparation of the same metal, at any rate in the case of palladium."

[1] Jour. Chem. Soc., **115**, 1050 (1919); **117**, 1280, 1501 (1920); **119**, 225, 1280 (1921); **121**, 1760 (1922).

In some recent experiments by Rideal and Thomas[1] on the behavior of different samples of fuller's earth with methylene blue, it was found that the adsorption and the bleaching did not run parallel at all; but this was explained by the fact that the degree of adsorption depended on the extent of the surface while the bleaching or oxidation was primarily a function of the ferric oxide content of the samples.

In the most recent paper Maxted[2] describes experiments made with mercuric chloride, mercuric nitrate, and lead acetate on platinum prepared by Loew's method, the catalysis of hydrogen peroxide being taken as the test of the poisoning. With mercuric chloride little or no difference was noticed between the activity of a catalyst which had been subjected to the action of the poison for thirty minutes and for twelve hours respectively. The curve obtained by plotting the catalytic activity of the platinum against the poison content is approximately linear until at least seventy percent of the original activity has been suppressed. "In view of the probability that catalyst poisoning of the type studied is due to a preferential adsorption of the inhibitant on the surface lattice of the catalyst, an investigation of the degree of this adsorption is of considerable interest. From preliminary experiments, it would appear that dilute solutions of inhibitants such as catalytically poisonous metals are adsorbed strongly by platinum catalysts; but the adsorption is incomplete, except probably in the presence of relatively large concentrations of catalyst."

"A series was begun with arsenic in the form of sodium arsenate; but the toxic properties of this substance, in contrast to its effect in catalytic hydrogenation (in which arsine is probably the active inhibitant), were found to be relatively low, an effect which was also noticed by Bredig."

Dr. R. N. Pease has shown recently that the vapor from one cubic millimeter of liquid mercury introduced into one hun-

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[1] Jour. Chem. Soc., 121, 2119 (1922).
[2] Ibid., 121, 1760 (1922).

dred grams of a reduced copper catalyst completely inhibits reaction between hydrogen and ethylene at 0°. Furthermore, the reaction is still extremely slow even at 100°. The striking feature of these experiments is, however, that the effect of the mercury vapor so introduced is to suppress, practically completely, the adsorption of hydrogen by the copper. On the other hand, the adsorption of ethylene is impaired but slightly.

Palmer[1] finds that adding small quantities of oxides of magnesium, manganese, zinc, and iron to copper decreases the hydrogenating power of the latter. Adding 5.30 atomic percents increases the activity over pure copper in the case of magnesium and manganous oxides but not in the case of zinc and ferric oxides. Since magnesium and manganous oxides have less dehydrogenating power than copper alone the curves for these two substances with copper must pass through a maximum as well as through a minimum. There is nothing to be got out of Palmer's own conclusions because he discusses his results in terms of the radiation theory.

Decarrière[2] claims that sulphur is not as harmful in ammonia oxidation as had been assumed because it can be removed by hydrogen; but then one does not want to do that. He also says that acetylene from calcium carbide in cyanamide is very deleterious, the effect being cumulative. Hydrogen sulphide is said to decrease the poisoning action of acetylene.

Ueno[3] has studied the effect of various additions to the nickel catalyst in the hydrogenation of oils. There is nothing in the abstract to show whether any theoretical conclusions were drawn, so presumably that was not the case. "All of the six alkali metals act as negative catalyzers; magnesium, strontium, barium, calcium, and beryllium retard it; aluminum and cerium are negative catalyzers; a large amount of iron also retards it. Manganese and cobalt are apparently negative, chromium is hardly negative; zinc and cadmium show

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[1] Proc. Roy. Soc., **101A**, 175 (1922).
[2] Comptes rendus, **172**, 1663; **173**, 148 (1921).
[3] Chem. Abstracts, **15**, 1226 (1921).

negative reaction. Copper and lead are poisons; mercury retards; silver, thallium, bismuth and antimony are poisons, while vanadium, tin, thallium, uranium, and tungsten are not. Gold, platinum, iridium, and osmium do not retard the hydrogenation. Sulphur and selenium are poisons; but tellurium is not to such an extent. Among nickel salts the chloride and sulphate act as pronounced poisons. Cyanogen and cyanides are strong poisons as is phosphorus. Boric acid is not negative when added to the catalyzer; but is when present in oils. Presence of organic matter has no effect if treated at high temperatures."

Taylor[1] has a valuable paper on the theory of negative catalysis, more especially with reference to homogeneous systems; but a general discussion of this problem can be postponed until the next report, by which time there will be more data.

Schwarz and Friedrich[2] have found that "the catalytic decomposition of hydrogen peroxide in the presence of colloidal platinum is retarded by Röntgen rays, the effect being observed when the mixture of the substances is exposed to the radiation or when the platinum sol is treated in this manner separately and added shortly afterwards to the hydrogen peroxide; the latter alone does not undergo an appreciable change under the influence of Röntgen rays. The maximal value of the retardation is seventy-seven percent (calculated on the percentage of hydrogen peroxide) and the highest values are observed in the sixth and seventh hours of the experiments. The cause of the phenomenon does not appear to lie in coagulation, diminution in the degree of dispersion, or alteration in the charge of the particles, as is shown by special experiments, and is rendered improbable by the further observation that the illuminated sol recovers its activity completely within about sixteen hours. It appears probable, therefore, that the platinum sol suffers a reversible change at its surface which must be attributed to the presence of water.

[1] Jour. Phys. Chem., 27, 322 (1923).

[2] Ber. deutsch. chem. Ges., 55, 1040; Jour. Chem. Soc., 122 II, 436 (1922).

Since the action of the Röntgen rays is accompanied by an emission of $\beta$-rays from the platinum particles which are able to decompose water, it is possible that an oxide of platinum is formed or that hydrogen is adsorbed by the sol. If, however, it is assumed with Haber that the platinum catalysis of hydrogen peroxide is conditioned by the presence of dissolved or combined oxygen in the catalyst, the formation of an oxide would in all probability accelerate the change. It is therefore more likely that the first stage of the catalysis is delayed because the platinum charged with hydrogen is not immediately able to form the intermediate product $Pt_xO_y$. The first stage of the action therefore consists in the combustion of the dissolved hydrogen by oxygen derived from the peroxide, after which catalysis can take place in the sense of Haber's theory. The recovery of the platinum sol within sixteen hours is attributed to the gradual decomposition of the platinum-hydrogen alloy, and this hypothesis is supported by the known complete instability of the product at 100°. It is also possible that the removal of hydrogen is effected by dissolved atmospheric oxygen; but direct experiments in the absence of oxygen do not lend support to this view, although their interpretation is hampered by the extreme difficulty of excluding oxygen completely in such observations. Pure water is not altered by exposure to Röntgen rays in such a manner as to give rise to contact poisons.

"Catalase, also, is altered in such a manner by Röntgen rays that its power to catalyse the decomposition of hydrogen peroxide is lessened; as with the platinum sol, the enzyme recovers its activity completely after several hours. A satisfactory explanation of the phenomena cannot yet be given."

## Miscellaneous

Kramer and Reid[1] have studied the catalytic preparation of mercaptans. "By passing alcohol vapor and equivalent hydrogen sulphide at the rate of one mol per hour through a

[1] Jour. Am. Chem. Soc., 43, 880 (1921).

tube containing pumice coated with 12.5 g of thoria at 380°, the following percentage yields of mercaptans were obtained: methyl, 41%; ethyl, 35%; propyl, 45%; iso-butyl, 45%; iso-amyl, 47%." Sabatier claimed to have got a yield of seventy percent with iso-amyl alcohol; but Kramer and Reid have found that propyl, butyl, and iso-amyl mercaptans give constant-boiling mixtures with the corresponding alcohols and ternary mixtures with the alcohols and water. They consider that the alleged high yield obtained by Sabatier is "probably due to the method which he used to separate and estimate his product, namely, fractional distillation. Assuming that he used a very good column for his separations and that he obtained the constant-boiling mixture of 77.11% mercaptan, the actual yield would then have been but 54%. If he used only one of the customary columns, the fraction which he collected, boiling at 116°, would unquestionably have had a much lower mercaptan content than the constant-boiling mixture, as has been found from experience. With these points in mind, our yield of 47% does not compare so unfavorably with his results. A specimen of isoamyl mercaptan purchased before the war from Kahlbaum was found to contain 71% mercaptan."

Milligan and Reid[1] have shown that "by passing the vapors of aldehydes mixed with ethyl alcohol over ceria at 300°–380° the aldehyde is hydrogenated to the corresponding alcohol and the ethyl alcohol is dehydrogenated to acetaldehyde. Benzyl, phenyl, ethyl, and heptyl alcohols, and citronellol have been prepared. The yields are low and the life of the catalyst is short on account of fouling, probably due to condensations of the aldehydes." This means that the hydrogen dissociation pressure of ethyl alcohol is higher than that of the other alcohols.

Milligan and Reid[2] have done another interesting piece of work involving catalysis, though not contact. "According to McDaniel,[3] benzene dissolves three volumes of ethylene at

[1] Jour. Am. Chem. Soc., 44, 202 (1922).
[2] Ibid., 44, 206 (1922).
[3] Jour. Phys. Chem., 15, 805 (1911).

22°, two and a half volumes at 50°, and probably not over two volumes at 80°. The dissolved ethylene may react ever so rapidly, but the formation of the product will be slow unless the solution is re-saturated quickly. With high-speed stirring it has been found possible to cause benzene containing aluminum chloride to react with eight volumes of ethylene per minute, the ethylene being totally absorbed, so that ethyl benzene and its higher ethylated homologues become readily available." The stirrer was run at ten to twelve thousand revolutions per minute. These experiments prove that the reaction velocity depends in this case primarily on the rate of diffusion of the ethylene. In this way it was found a simple matter to convert benzene into ethyl benzene, di-ethyl benzene, or tri-ethyl benzene. "Naphthalene can be readily ethylated to various products by heating it with poly-ethyl benzenes and aluminum chloride under intensive agitation."

Reid and Brown[1] have studied the amination of primary alcohols with a variety of catalysts. Midgley, of the General Motors Research Laboratory, reports that blue tungstic oxide converts alcohols very satisfactorily into olefines, and mixtures of alcohols and ammonia into the ensuing amines. Sabatier and Kubota[2] found that this same oxide decomposes allyl alcohol very rapidly, a number of products being formed.

Gilfillan[3] finds that "alcohol vapors alone, or in the presence of carbon dioxide, may be passed over pumice at 500° without undergoing appreciable decomposition. By calcining thoria strongly, or by prolonged heating at a lower temperature, this oxide may be inactivated for dehydration of ethyl alcohol. Thoria is not exclusively dehydrating in its action upon ethyl alcohol. Under certain conditions a considerable amount of aldehyde is produced by dehydrogenation. The titanium oxide employed as a catalyst effected practically no dehydration of ethyl alcohol at temperatures upon 355°.

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[1] Unpublished data.

[2] Comptes rendus, 173, 17, 212 (1921).

[3] Jour. Am. Chem. Soc., 44, 1323 (1922).

The blue oxide of tungsten at lower temperatures is a much more active catalyst for the production of ethylene than is thoria, but at higher temperatures they are practically of equal efficiency. No ether was produced from alcohol in the presence of any of the catalysts. By operating over thoria in the presence of carbon dioxide, a considerable quantity of acetal was formed from ethyl alcohol. Pure, dry carbon bisulphide, when vaporized over pumice or over the blue oxide of tungsten, suffers no decomposition at temperatures up to 400°. A trace of moisture, however, causes decomposition and the evolution of hydrogen sulphide. In the presence of any of the three metallic oxides employed as catalysts, a mixture of absolute alcohol and carbon disulphide produced considerable quantities of ethyl mercaptan. Titanium dioxide, which had been almost without action upon alcohol alone, proved the most active catalyst for this esterification. This new method may be advantageous for the synthesis of certain mercaptans."

Mailhe and de Godon[1] have alkylated aniline with methyl or ethyl alcohol, using alumina as the catalyst. Reid and Brown find that specially prepared silica gel is the best catalyst for the alkylation of aniline with alcohols.

Mailhe[2] has used zirconia to cause esterfication with alcohols and acids. Milligan and Reid have found that silica gel is an admirable catalyst for the production of ethyl acetate from ethyl alcohol and acetic acid, the yield being higher than corresponds to the equilibrium concentration for these substances in the liquid phase at the same temperature. This does not necessarily involve a displacement of equilibrium by the catalytic agent because Edgar[3] of the University of Virginia has shown that the equilibrium in the vapor phase is considerably further to the ethyl acetate side than it is in the liquid phase.

The question of equilibrium comes up in another form in a

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[1] Comptes rendus, **166**, 467, 564 (1918); **172**, 1417 (1921).
[2] Chem. Abstracts, **15**, 622 (1921).
[3] Unpublished results.

paper by Armstrong and Hilditch.[1] They find that with a copper catalyst and otherwise constant conditions the percentage conversion of carbon monoxide to carbon dioxide by steam rises rapidly as the temperature increases from 200° to 300° and then falls off slowly as the temperature rises from 300° to 500° this curve running approximately parallel with, but much lower than, the theoretical curve for equilibrium. While not definitely so stated, it might be thought that we have a displacement of equilibrium here. "Whereas, however, iron oxide at a suitable temperature causes the action to proceed almost to the point of equilibrium, copper, even at its optimum temperature, does not effect more than fifty to seventy percent of the possible amount of chemical change; the exact proportion is to some extent a function of the composition of the mixture used."

Armstrong and Hilditch have succeeded in proving that "a mixture of carbon monoxide and steam under the conditions of our experiments [at about 350°] but in the absence of any catalyst may give rise to the momentary formation of small but not quite detectable quantities of formic acid." They consider that with the copper catalyst there is a direct decomposition of the formic acid rather than of the steam, and they point out that "the relative activities of (*a*) copper and (*b*) iron oxide to carbon monoxide and steam at the lower ranges of temperature are closely parallel to their respective powers of decomposing (*a*) formic acid and (*b*) steam." This of course has nothing to do with the question of equilibrium and, until further evidence is available, we are forced to conclude that the differences between copper and iron oxide as catalysts above 350° would disappear nearly completely if the reacting gases were passed more slowly over the catalysts. It is rather a pity that Armstrong and Hilditch did not settle this question one way or the other while they were studying this problem.

Rideal[2] has studied the change of the equilibrium constants

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[1] Proc. Roy. Soc., 97A, 265 (1920).

[2] Ibid., 99A, 153 (1921).

with the temperature for the dehydrogenation of ethyl and isopropyl alcohols. "In confirmation of Sabatier's experiments the application of the Nernst approximation formula indicates that the variations of the dissociation constants of the equilibria

$$CH_3CHO + H \rightleftharpoons CH_3CH_2OH \text{ and } CH_3COCH_3 + H_2 \rightleftharpoons CH_3CHOHCH_3,$$

with the temperature are extremely large. The velocity of decomposition at the surface of a solid catalyst is shown to be very much higher than the reverse reaction of hydrogenation. The variation of the values of the dissociation constants with the temperature was determined experimentally with a constant-volume thermometer containing carefully reduced copper as catalytic material. Concordant values could not be obtained at atmospheric pressures; but a closer approximation to reversibility was obtained when low pressures were employed. The value of $\Delta U_0$ for the decomposition of ethyl alcohol was found to be 11,500 calories, whilst the mean value determined from the heats of combustion is 10,700. In the case of isopropyl alcohol the respective values for $\Delta U_0$ are 21,300 and 11,800. In the latter case an error of less than one percent of the heat of combustion of the alcohol would account for the discrepancy."

Hinshelwood, Hartley and Topley[1] state that "it is generally agreed that the very rapid increase with temperature of the velocity of chemical change is only to be explained by the assumption that the reactive molecules are those of relatively large internal energy-content. Whether the activation of molecules is brought about by collisions with other molecules, or by the absorption of quanta of radiation, is at present a matter of controversy. But, given that activated molecules are produced in one of these ways, the further question arises as to whether every molecule with the necessary critical energy reacts at once, or whether, in addition to possessing this, it must

[1] Proc. Roy. Soc., 100A, 575 (1922).

be in a certain phase. In the first case the velocity of a chemical change would be governed simply by a 'time of relaxation' in the sense of the kinetic theory, while in the second case an additional specific factor would be concerned."

They find that in soda-glass bulbs the two decompositions of formic acid, into carbon monoxide and into carbon dioxide, take place practically completely at the surfaces of the bulb and not in the gas phase. The reaction producing carbon dioxide has a much larger temperature coefficient, the ratio for 10° rise averaging 1.83 as against 1.35 for the reaction producing carbon monoxide.

"It appears, therefore, that the heterogeneous reactions involved in these two modes of decomposition of formic acid really have very different temperature coefficients, and that one of them is of the same order as that characteristic of a homogeneous reaction. This obviously lends support to the theory of heterogeneous catalysis which assumes the reaction to take place slowly in a unimolecular layer at the surface of the catalyst, rather than to the old theory, which assumes the reaction to take place rapidly on the surface of the catalyst, its velocity being determined by the rate of diffusion through an absorbed layer of considerable thickness. In the case investigated, both reactions would be affected equally by the rate of diffusion of the formic acid.

"Calculating the critical increments for the two reactions from the formula $\frac{d \log k}{dT} = \frac{E}{RT^2}$ we find for the decomposition giving the monoxide $E_{CO} = 16{,}000$ calories per molecule (approx.) and, for the dioxide $E_{CO_2} = 28{,}000$ calories (approx.). (An assumption underlies this procedure, namely, that the extent of the glass surface covered does not vary with temperature. This can only be approximately true, but, since the reactant is the same in each reaction, the relative value of the two critical energies will not be seriously in error.)

"Since the numbers of molecules activated for the two reactions are proportional to $\epsilon^{-28000/RT}$ and $\epsilon^{-16000/RT}$ about $\epsilon^{10}$

molecules should yield carbon monoxide for one yielding the dioxide. Actually, the rates are of the same order. Hence the idea of a phase restriction.

"The following suggestion is only intended to illustrate how the phase condition may be interpreted physically. Suppose the formic acid molecule adsorbed on the surface by the residual affinity of the >CO group. In the case of a sufficiently activated molecule, a violent collision between the —H and —OH groups may occur, and a hydrogen molecule be split off. Although the requisite degree of activation may be obtained but rarely, nevertheless, a high percentage of these collisions in the activated molecules may result in this type of decomposition. On the other hand, for water to be eliminated and carbon monoxide left, a high degree of activation is not required, possibly as the removal of an —OH group, as a whole, from an organic compound is a much less profound change than the fission of the hydrogen and oxygen, but very few of the activated molecules may decompose because it is necessary to await the contingency that the forces holding the —OH and —H to the carbon should be in a weak enough condition simultaneously to allow "uncoupling" of the molecule.

"We are well aware that this is an *ad hoc* hypothesis, but it appeared better to attempt a physical interpretation than to leave the phase-factor as a purely mathematical conception."

Adkins and Nissen[1] have commented on the paper by Hinshelwood, Hartley and Topley saying that these latter advanced an hypothesis giving a typical interpretation of the reaction based on the observation that when formic acid decomposed in glass the carbon dioxide reaction had the higher temperature coefficient. "Their hypothesis apparently loses whatever value it may have had in view of the fact that it is now shown that the catalyst determines not only the relative amounts of the two reactions at a given temperature, but also which one has the higher temperature coefficient."

In a second paper Tingey and Hinshelwood have studied

[1] Jour. Am. Chem. Soc., 45, 814 (1923).

the influence of temperature on the same two reactions "on catalytic surfaces of silver and platinum, in order to ascertain whether the behaviour of the formic acid on these catalysts is analogous to its behaviour on glass. The problem is rendered more difficult by the extreme variability of the catalytic surfaces, and special devices have had to be adopted to obtain the desired information about temperature coefficients.

"The results are briefly as follows. On platinum, from 235° down to 80°, reaction (*a*) yielding carbon dioxide and hydrogen predominates almost exclusively. As the reaction on platinum at 80° is preceding much more slowly than it does on glass at temperatures where reaction (*b*) greatly predominates, the behaviour on platinum is not analogous to that on glass. The temperature coefficient of the reaction on platinum is, however, approximately the same as that of the corresponding reaction on glass, 1.7–1.8, the "heat of activation" being 22,000 cals. per gram-molecule, whilst that for glass is 28,000.

"On silver, the main reaction taking place is that yielding carbon dioxide and hydrogen. Although varying amounts of carbon monoxide are found in the reaction products, some of this may be attributed to the reaction taking place on the glass reaction-bulb; it is however, doubtful whether all the carbon monoxide formed can be thus accounted for. The temperature coefficient for the carbon dioxide reaction is again high, as on glass and platinum, being 1.9 from one series of experiments and 2.3 from another series, over a different range of temperature. These give a mean heat of activation of 31,000 cals."

"Platinum, which is the most efficient catalyst, is in this case associated with the lowest heat of activation, with respect to one and the same mode of reaction, namely, decomposition into carbon dioxide and hydrogen."

As a corollary to what has already been pointed out in the discussion of Adkins' results, and with regard to the Princeton work on ammonia adsorption and decomposition, it may here be emphasized that the production of hydrogen and carbon dioxide from formic acid preponderates when platinum and

silver are the contact agents. These contact agents are liberal sources of free electrons in contrast to the glass to alumina surfaces. Hence we would expect an electron gradient towards the hydrogen ends of the adsorbed formic acid molecule presumed adsorbed $Pt=O=C\langle^{H}_{OH}$. This is just what is required to enable the hydrogen nuclei, which are sharing electron pairs with carbon and oxygen respectively, to assume independent existence first as hydrogen atoms and then as molecules.

## General Theory

As far back as 1906 Raschig[1] gave an extraordinarily interesting lecture on catalysis which did not fit in with the prevailing views of the physical chemists[2] and which consequently has been ignored ever since. Raschig defines catalysis as "a change in the form of the molecules which causes a change in the reactivity and therefore in the reaction velocity. This change in form may be caused by imponderable forces (surface tension, adhesion, light, and heat) or by material substances (catalysts) such as platinum black, which remains unchanged and therefore acts only through the forces peculiar to its surface. This change in form may consist in the breaking down of molecules into atoms (ionization in the catalysis of oxyhydrogen gas by radium and probably the same in the activation of mixtures of hydrogen and chlorine by light). It may leave the molecular structure intact but consist in a displacement of the different parts of the molecule relative to one another (explosion of nitrocellulose). It is also conceivable that the vibrations of the atoms and atomic groups may become more violent, increasing in amplitude and perhaps in number; this occurs when we heat a substance and in this sense we may classify the change of reaction velocity with the temperature as a case of catalysis."

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[1] Zeit. angew. Chem., 19, 1748, 2083 (1906).

[2] Haber: Zeit. angew. Chem., 19, 1762; Bredig: 1985; Luther: 2049 (1906).

Earlier in the article we read that "in the platinum catalysis of oxyhydrogen gas we are dealing with a change in the form of the oxygen molecules caused by their adsorption on platinum. What this change in form is, we do not know at present; but, on the other hand, there is certainly a definite and perhaps different change in the form of the oxygen molecule which gives it the power to oxidize hydrogen at ordinary temperatures in the absence of platinum. Davis and Edwards[1] have shown that in presence of radium bromide hydrogen and oxygen react slowly. Now we know definitely that radium radiation ionizes oxygen, splitting the molecules into atoms. Atomic oxygen therefore oxidizes hydrogen at ordinary temperatures. The change of form which the molecules undergo when they dissociate into atoms makes the oxygen active.

"Adsorptions similar to those with platinum occur also with many other substances; they are very marked with charcoal. Charcoal has the power of condensing oxygen and thus increasing its activity, a property of which much use is made. Here there can be no intermediate reaction such as the formation of carbon monoxide. The adsorptive power of charcoal does not, it is true, suffice to give oxygen the form in which it attacks hydrogen; but another gas, chlorine, is made active by charcoal. In contact with charcoal chlorine acquires the power, which it did not previously have, of reacting in the dark quickly and completely with carbon monoxide to form carbonyl chloride. This is the way in which they make commercially the phosgene which is important in the dye industry.

"I say explicitly in the dark because through exposure to light in the absence of charcoal we can get the same activity which charcoal imparts to chlorine. In sunlight carbon monoxide and chlorine react readily. We probably also have the same cause of activity when hydrogen and chlorine react with an intensity which may easily become explosive. We see

[1] Zeit. Elektrochemie, 12, 342 (1906).

again that catalysis is not necessarily due to a given substance, a catalyst; but that we may get catalysis through the action of imponderable matter, such as light rays. I can find no other explanation than that, just as radium does with oxygen, the light causes changes in the form of the chlorine molecule, presumably in this case a splitting into chlorine atoms. It is then the most natural thing to assume that the material catalysts cause changes in the form of the reacting molecules, thereby increasing their reactivity."

At that time there were relatively few data on contact catalysis in organic chemistry and in the discussion of the paper Erdmann mentions that possibly the hydrogenation process of Sabatier and Senderens might some day find a technical application. Raschig was not able to suggest any general way of determining how a catalyst activates the molecule and the whole tendency of the time was in favor of making quantitative measurements of reaction velocities. Mathematical formulations were very much in favor and Raschig's really admirable contribution had no effect. In these days of oriented adsorption Raschig is likely to come into his own. Unless we succeed in making the solution definite, however, we shall fail as Raschig did.

Boeseken[1] has developed a dislocation theory which will be very valuable if it can be made more definite. "The catalytic action of aluminum chloride is due to a dislocation of the reacting molecules. This effect begins where the molecules are weakest [relatively to catalytic activity]. In the organic chlorides, it is probably the atom of chlorine which is activated." "In presence of aluminum chloride, chloral apparently dissociates $CCl_3CHO \longrightarrow CCl_2 + CO + HCl$." When iodine converts white phosphorus into red, the acceleration takes place when the $P_2I_4$ decomposes. The catalytic action of the iodine (or of aluminum chloride) lies in the splitting of $P_4$ into $P_2$. "A catalyst must be in a state of dissociation with the activated molecules . . . . and we approach the

[1] Recueil Trav. chim. Pays-Bas, 29, 85 (1910); 30, 381 (1911); 39, 622 (1920).

ideal catalysis only when the equilibrium between the catalytic agent and the activated molecules is as far as possible on the side of the free molecule."

"When studying the phenomena of catalysis, one is struck by the fact that the activated molecules are never exclusively monatomic substances; there is always involved a molecule with two or more atoms. We may consider the polyatomic molecules as closed systems and that is why they react so slowly or not at all. The essential duty of the catalysts is to open these systems, from which it follows that the catalyst itself must be an open system, which can transmit this peculiarity to the bonds which it activates. It is reasonable to expect, therefore, that the powerful catalysts will often be monatomic molecules (metals) or ions or molecules which are either unsaturated or have residual valences.

"We can see that such molecules might cause an intense disturbance in the internal equilibrium of the closed molecules. It is this disturbing action which I have called dislocation. During the very brief period of a collision between the catalyst and the molecule, the fields of the internal forces (or the orbits of the electrons) will be displaced so that these molecules will react at once. It is evident that a substance may have such an effect without being an ideal catalyst; but it is then paralyzed during the reaction (for instance, the reaction of Baumann and Schotten, most of the Friedel and Crafts reactions, etc.). It is also obvious that different catalysts may force a molecule into different states of dislocation, in which case the final product will vary with the nature of the catalyst. Sulphuric acid and zinc chloride, for instance, will act chiefly on the unsaturated oxygen of an aldehyde and will accelerate the formation of paraldehyde. Bases, on the other hand, will have a dislocating effect on one of the hydrogen atoms and will accelerate the formation of aldol."

The implied suggestion that hydrogen ion may catalyze the inversion of cane sugar because it activates the sugar as a result of specific bombardment has the advantage over the more orthodox explanations that it is not inconsistent with

hydrogen ion inverting a mixture of sugar and methyl acetate just as though each were present alone, whereas that is impossible if we postulate the formation of any appreciable amount of a compound between hydrogen ion and the catalyzed substances. Activation by bombardment is now a well-recognized phenomenon as shown in the disruption of elements and molecules by alpha particles.

While it may not have anything to do with the matter in hand, it is interesting to note that J. J. Thomson[1] has shown that monatomic hydrogen has a special effect on the photographic plate. "A comparison of this [electroscopic] curve with a photograph of the discharge through the same gas [carbon monoxide] shows many interesting features. On the photograph the strongest lines are those corresponding to the atom and molecules of hydrogen. The curve on the other hand shows that the number of hydrogen particles is only a small fraction of the number of CO particles. The extraordinary sensitiveness of the photographic plate for the hydrogen atom in comparison with that for atoms and molecules of other gases is shown in all the curves taken by this method. But great as is the discrepancy in the case of the photographic plate between the effects produced by hydrogen atoms and an equal number of heavier atoms, it is not nearly so great as it is for a willemite screen: such a screen may show the hydrogen lines very brightly while the CO line is hardly visible, when measurements made with the electroscope in the way just described show that the number of particles of hydrogen is only a few percent of the number of the CO particles. . . .

"The negatively charged hydrogen atoms seem to have the same preponderance in their effect on the photographic plate over other negative atoms as positive hydrogen atoms have over other positive atoms. Thus on all the plates the line corresponding to the negatively electrified hydrogen atoms is well marked, often being comparable with the negatively electrified oxygen atom. With the electroscopic method the

[1] "Rays of Positive Electricity," 124 (1921).

negative hydrogen atom can only just be detected, while the negatively electrified oxygen atoms produce a large negative deflection."

Boeseken points out that "the precious metals, such as platinum, certainly do not form solid compounds either with hydrogen or with unsaturated molecules. The most that one could claim is the plunging of hydrogen and of the unsaturated bonds [?] beneath the surface of the metal. Hamburger[1] starts from the theory of dislocation and the hypothesis that catalytic action is a displacement of the energy fields and has called attention to the fact that the elements of the eighth group—the metals with a large number of valence electrons according to J. Stark and only a moderate chemical activity—are the strongest catalytic agents. I should prefer to say that—the intensity of their action not being so great although it may be surprising—they are for that reason the most ideal catalysts."

Polanyi[2] claims that adsorption decreases the heat of decomposition of an ordinary diatomic molecule of average volatility by about 45,000 calories. "The field of the adsorbent acts on the molecules within its sphere of action very much in the way that a liquid with a high dielectric constant acts on the molecules of a dissolved electrolyte. The familiar dissociating action of the solvent involves exactly the same mechanism as the similar action of the adsorbent. The heat of solution of the free ions is much larger than that of the undissociated molecule, and is due to the fact that the work necessary to cause dissociation of the solute is very much less than the value for the same substance as gas. We can consider our result as general without further discussion because any other special case can be treated in just the same way as that of a diatomic molecule. The effective principle will always be the same; if a molecule is shattered by breaking one of the bonds, the fragments will be drawn to the adsorbent by

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[1] Chemisch Weekblad, 16, 664 (1919).
[2] Zeit. Elektrochemie, 27, 142 (1921).

forces whose total energy nearly balances that of the disrupted bond.

"We may therefore say that there is a field of force at each adsorbent, in which the molecules may be broken up in all sorts of ways into their constituents and may recombine in a new way either without any appreciable work being done on them or with the expenditure of much less work than would be necessary if the reaction took place in the free gas phase. If the assumption is correct, that the reactivity is greater the less the work necessary to break a bond, the reactivity must be much greater at the surface of the adsorbent than in the free gas phase, and must reach its maximum value when the work necessary to break the bond becomes zero. If a reaction is to be accelerated in this way, which we will call adsorption catalysis, it is essential that the free valences formed by the breaking of the bonds shall recombine to form new bonds; the radicals must not remain as reaction products."

On the basis of a special calculation Polanyi estimates that the reaction velocity at the surface of a good charcoal may be $10^{26}$ times that in the free gas phase and he considers that this acceleration is quite sufficient.

Palmer and Palmer[1] studied the conversion of ethylene to ethane in presence of nickel. "In most of our experiments there was a period varying in duration from three hours to a few seconds after the mixed gases had been brought into contact with the nickel, during which time practically no reduction in volume, and therefore no hydrogenation, took place. This 'induction' period was followed by a very rapid increase in reaction velocity to a sharp maximum. Finally the rate of reaction fell away from this maximum to a nearly steady value.

"The initial period of inactivity might possibly be due to the selective adsorption of oxygen contaminating the electrolytic hydrogen. This oxygen would be removed gradually by combustion with hydrogen or ethylene. Such an explanation would require the duration of the induction period at a given

[1] Proc. Roy. Soc., 99A, 402 (1921).

temperature to be approximately proportional to the hydrogen content of the gas mixture which an inspection of the series of results for different gas mixtures at 104° shows not to be the case (Table II).

TABLE II

| Induction period in minutes | Volume percentage of oxygen | Induction period in minutes | Volume percentage of hydrogen |
|---|---|---|---|
| 150 | 75 | Very short | 35 |
| 40 | 65 | Very short | 25 |
| 22 | 50 | Very short | 15 |

"A complete explanation of the form of the reaction-velocity-time curve can be put forward on the basis of the following assumptions:

(*a*) Hydrogen is adsorbed selectively on nickel from mixtures of all the compositions studied.

(*b*) Ethylene is adsorbed only after activation (chiefly by thermal contact with a molecule undergoing hydrogenation.)

On bringing the gas mixture into contact with the nickel, this becomes covered at once almost completely with hydrogen, only a few ethylene molecules being present in the adsorption layer; reaction with the formation of ethane takes place with these and with the adsorbed hydrogen. The heat liberated in the hydrogenation is communicated at once to the molecules surrounding the hydrogenated molecule, leading to volatilisation of hydrogen and activation, followed by condensation, of ethylene. The relative amounts of hydrogen and ethylene adhering to the surface of the catalyst thus change rapidly, once a number of centres of reaction have developed. This stage corresponds to the maximum in reaction velocity. Finally, the catalyst becomes covered almost completely with ethylene, to the exclusion of hydrogen. Hydrogenation thus takes place comparatively slowly by collision between adsorbed ethylene and hydrogen or by diffusion of hydrogen to the catalyst surface through a thin layer of ethylene.

"It will be noticed that the induction period is reduced in a very marked way either by increase of ethylene content in the gas mixture or by increase in temperature, while the rate of reaction after the maximum has been reached is affected only very slightly by the temperature. These observations are in accordance with the above theory. The final rate of reaction falls off gradually, owing to the accumulation in the reaction tube of inert ethane, which acts as a diluent to the gas mixture."

This explanation is very ingenious; but we must not overlook the fact that absolutely no attempt has been made to verify it in any way. The authors assume that unactivated ethylene will not displace hydrogen from the surface of nickel and that hydrogen will not displace ethylene which has been activated and then adsorbed. This may be true; but nothing similar has ever been observed and the hypothesis ought to have been checked independently. By working at so low a temperature that the reaction between ethylene and hydrogen could be neglected, it would easily have been possible to have checked these two hypotheses and to have shown that they were or were not permissible.

Rideal[1] has discussed the same phenomenon on the hypothesis of adsorption in unimolecular films and states that "the mechanism of the hydrogenation of ethylene at the surface of reduced nickel has been shown to be capable of explanation on Langmuir's hypothesis of contact action. In excess of hydrogen, the reaction velocity is proportional to the partial pressure of the ethylene; in excess of ethylene, to the hydrogen partial pressure. Ethane acts as inert diluent. The optimum temperature is about 137°. The reaction velocity is governed, not only by the rate of impact of the reactants on the free spaces of the catalyst, but also by the lengths of the lives of the molecules on the surface. The length of the life of the reactants on the surface at 137° is about $8 \times 10^{-6}$ seconds. On the most advantageous conditions of impact, the catalytic efficiency of the metal surface is 0.04%. On the ad-

[1] Jour. Chem. Soc., 121, 309 (1922).

mission of oxygen to the reacting mixture, removal of this gas at a slow rate by hydrogenation occurs, the rate of hydrogenation being proportional to the partial pressure of the oxygen and inversely to that of the ethylene. This is followed by the much more rapid hydrogenation of the ethylene. The length of life of the oxygen molecule on the surface is probably much greater than that of ethylene. Large quantities of oxygen poison the catalyst irreversibly for low temperature catalysis, indicating the possibility of the adsorption of this gas by two distinct processes. The hydrogenation of oxygen on a nickel surface may be expressed by the equation $\log_{10}K = 8.82 - 2538/T$, and the heat of evaporation of hydrogen from the surface is about twelve thousand calories per gram molecule." Studies of the kinetics of catalytic reactions at surfaces ought in all cases to include a study of the adsorptions of the several gases and as many mixtures of the same, by *the catalytic agent actually used in the kinetic studies*. The necessity for this is well illustrated by the work of Dr. R. N. Pease shortly to be published on the combination of hydrogen and ethylene in presence of copper. The kinetics of this reaction is determined largely by the adsorptions of the gases concerned. At 0° the main reaction is approximately proportional to the hydrogen partial pressure, independent of the ethylene concentration. At 200° the reaction is bimolecular. This change in reaction kinetics has been shown to be associated with the change in adsorptions of the gases at the two temperatures. Now it has been shown in Princeton that it is possible to alter the ratio of adsorption of two gases by suitable manipulation of the catalyst—by heat treatment or with traces of catalyst poisons. Hence it is obvious that the kinetics of a reaction may be similarly altered at a given temperature. Rideal's nickel catalyst was undoubtedly, from its method of preparation, of low adsorptive capacity and his results are in general agreement with such a view. With catalysts prepared otherwise other results as to reaction kinetics would undoubtedly be achieved. Gauger's results[1] on adsorption by very active

[1] Gauger and Taylor: Jour. Am. Chem. Soc., 45, 920 (1923).

nickel catalysts give a much lower value for the heat of adsorption of hydrogen, namely 2500 calories in contrast with 12,000 calories found by Rideal. Some new experiments in Princeton on catalysts of adsorptive capacity intermediate to those two have given directly determined heats of adsorption of 6000–8000 calories.

Armstrong and Hilditch[1] have recently studied the influence of pressure on the rate of hydrogenation of liquids in presence of nickel. "In parts I, II and V of this series[2] we have indicated the reasons which lead us to believe that during the catalytic hydrogenation of liquids the function of the metallic catalyst is to combine with both agents—the unsaturated organic compound and hydrogen—and produce an unstable intermediate complex. The experimental evidence has furthermore impressed upon us the conviction that the determining factor in hydrogenation is the degree of affinity displayed between nickel and the unsaturated compound; whilst we have had ample opportunity to observe the selective nature of the process as exemplified by the widely varying rates of adsorption of hydrogen characteristic of various definite types of organic compounds, we have not been fortunate enough to obtain experimental proof of the mode in which nickel effects the actual introduction of hydrogen to an organic molecule.

"We have therefore directed our attention to the influence of the concentration of hydrogen on the rate of hydrogenation of liquids, and have examined a wide range of unsaturated organic compounds with respect to the rates at which they absorb hydrogen under varying pressures. Existing data on this subject are scanty, but indicate, in the case of the hydrogenation of fatty oils, that the rate of action is simply proportional to the pressure.[3] On the other hand, it has been suggested[4] that the action of nickel is to adsorb the hydrogen (at

[1] Proc. Roy. Soc., **100A**, 240 (1922).

[2] Ibid., **96A**, 137, 322 (1919); **98A**, 27 (1920).

[3] Moore, Richter and van Arsdel: Jour. Ind. Eng. Chem., 9, 541 (1917); Maxted: Jour. Soc. Chem. Ind., 40, 169T (1921).

[4] Thomas: Jour. Soc. Chem. Ind., 30, 120T (1920); Lewis: Jour. Chem. Soc., 117, 623 (1920).

the same time dissociating it into the atomic condition)[1] and that it is the atomic hydrogen which interacts with the ethylene linkage. If this were the case the acceleration induced by increasing the gas pressure should be proportional to the square root of the latter.

"The experiments now recorded were made in essentially the same apparatus as that described in Part I of this series; a small gas-compressor was, however, inserted between the inlet gas-meter and the hydrogenation vessel, the pressure being reduced again to atmospheric at the exit from the latter. In this way it was possible to obtain accurate, continuous readings of hydrogen adsorption, the actual gas-volumes being measured at atmospheric pressure. The pressure in the system was allowed to reach the desired limit some moments before readings were commenced, the meters were then checked against each other and readings taken at short intervals. Hydrogen adsorption-time curves were plotted in the ordinary way and the absorptions per minute under varying pressures over corresponding ranges of the absorption curves were then compared.

"The results of the investigation were very definite and fall into three divisions:

*I. Normal.*—In the absence of substituent groups of the kind discussed below (III) and in presence of sufficient nickel (in general so long as at least 0.1% of nickel is present), the ethylenic union is hydrogenated at a rate which is in almost exact proportion to the absolute pressure of the hydrogen.

*II. Subnormal.*—At very low concentrations of catalyst (e. g., 0.01–0.02% of nickel reckoned on the organic compound) the increase in rate of hydrogenation becomes less than proportional to the increase in pressure. The compounds which absorb hydrogen most readily are in general more prone to show this subnormal effect when the catalyst concentration is diminished, and it is especially marked in the case of multi-

[1] Sieverts: Zeit. phys. Chem., 77, 591 (1911).

ethylenic compounds such as derivatives of linoleic acid or linolenic acid or citral.

*III. Abnormal.*—If the unsaturated compound contains another group which has affinity towards nickel (but it is not open to hydrogenation), we find that increase in hydrogen pressure causes an increase in the rate of hydrogen adsorption in more than simple proportion to the altered concentration of hydrogen. This has been observed with unsaturated alcohols and unsaturated carboxylic acids: the carboxyl group tends, of course, to act upon nickel producing the nickel salt of the acid and hydrogen, although at the higher temperatures of hydrogenation (180°) the equilibrium is moving in the direction of reduction of the salt by hydrogen to free acid and metallic nickel. The hydroxyl group in alcohols is also affected by nickel, although the latter is not, strictly speaking, an active catalyst of dehydration; thus, numerous instances have been recorded of side actions in the hydrogenation of the vapors of unsaturated alcohol over nickel in which formation of a hydrocarbon and water occur (e. g., phenol at 180° yields cyclohexanol mixed with a little cyclohexanone and cyclohexane;[1] benzyl alcohol gives some toluene and methylcyclohexane;[2] geraniol yields some dimethyloctane as well as the saturated dimethyloctanol.[3] On the other hand, unsaturated aldehydes and ketones have shown, in each case that we have examined, increases in rate of absorption of hydrogen in simple, or less than simple, proportion to the pressure, so that we may summarise the results as follows:

| Unsaturated compound | Effect of pressure |
|---|---|
| Alcohols R.CH: CH.$CH_2$OH | Abnormal |
| Aldehydes (ketones) R.CH: CH.CHO | Normal (or subnormal) |
| Acids R.CH: CH.COOH | Abnormal |

This behaviour is in keeping with the generalisation outlined above, since the carbonyl residue CO is, in contrast to the hy-

[1] Sabatier and Senderens: Comptes rendus, 137, 1025 (1903).
[2] Sabatier and Senderens: Bull. Soc. chim. France, [3] 33, 616 (1905).
[3] Enklaar: Ber. deutsch. chem. Ges., 41, 2085 (1908).

droxyl and carboxyl groups, open to direct hydrogenation.

"The results are broadly, then, that increase in concentration of hydrogen causes a directly proportionate increase in the rate of hydrogenation, providing there are no disturbing factors; and that the increase in rate of hydrogenation becomes abnormally large if other groups active towards nickel, but not open to hydrogenation, are also present. In other words the nature of the unsaturated organic compound has a determining influence on the effect of the hydrogen concentration."

At the end of the paper Armstrong and Hilditch discuss the general theory. "We have put forward the view[1] that the fundamental action in hydrogenation by nickel or other like catalyst is the balanced action,

$$(1) \qquad Ni + -CH{:}CH- \leftrightharpoons (Ni, -CH{:}CH-),$$

an extremely rapid equilibrium action with the balance largely in favor of the unassociated components [right-hand side]. The slower action which is actually measured in work of this kind is, we consider, the interaction of this complex and hydrogen which is also associated with the nickel:

$$(2) \qquad \overset{(2)}{(Ni, -CH{:}CH-)} + H_2 \rightleftharpoons (Ni, -CH{:}CH-, H_2) \rightleftharpoons (Ni, -CH_2.CH_2- \rightleftharpoons Ni + -CH_2.CH_2-)$$

This view of the process of hydrogenation receives fresh support from the data on the relation between pressure and rate of hydrogenation which we now put forward; the bearing of the latter may be considered in connection with the three classes into which they fall:

### *I. Simple Ethylenic Compounds—Simple Proportionality between Concentration of Hydrogen and Rate of Hydrogenation*

"The direct proportionality observed in the case of simple unsaturated compounds (except for extremely low concentrations of catalyst) can only mean that the rate of addition of hydrogen is connected directly with the concentration of

[1] Proc. Roy. Soc., 96A, 144 (1919).

the hydrogen as it is presented in the system, i. e., in the molecular form —$H_2$. If the action were brought about by atomic hydrogen (—H) it would appear that one of two alternatives must occur:

(*a*) The measured action might be that of the dissociation of hydrogen in presence of nickel,[1]

$$H_2 \rightleftharpoons 2H,$$

in which case the observed rate should vary as the square root of the hydrogen concentration and, moreover, should be independent of the constitution of the organic compound.

(*b*) The measured action might be analogous to that given above (2), and of the type:

$$—CH:CH— + (Ni, 2H) \rightleftharpoons (—CH:CH—, Ni, 2H) \rightleftharpoons Ni + —CH_2.CH_2—.$$

The increase in rate should then be proportional to the square of the increase in pressure and could only appear in the observed simple proportions if both actions (*a*) and (*b*) were of the same velocity, an extreme coincidence which again excludes any possibility of varying rates of hydrogenation conditioned by the type of unsaturated compound—the factor which is most prominent in all our results. It follows that the general results of this inquiry indicate that the speed of hydrogenation is directly proportional to the molecular concentration of the hydrogen, as expressed in our general equation (2) above.

### *II. Simple Ethylenic Compounds—Very Low Concentrations of Catalyst*

"We have shown that in this case the increase in the rate of hydrogenation is subnormal, i. e., is in less than direct proportion to the increase in pressure. Now, considering the initial action

$$(1) \qquad Ni + (—CH:CH—) \rightleftharpoons (Ni, —CH:CH—),$$

[1] Cf. Sieverts: Zeit. phys. Chem., 77, 591 (1911).

it is evident that the relatively low concentration of nickel (and corresponding relatively high concentration of unsaturated compound) will tend to displease the equilibrium more in the direction of the complex (Ni,—CH:CH—) so that more of the nickel present will be monopolised by association with the unsaturated compound and consequently the hydrogen will have less nickel available for the preliminary association of hydrogen and nickel. Hence increased concentration of hydrogen cannot produce its full normal effect, the hydrogen and unsaturated compound competing, as it were, for the attention of the small amount of nickel present.

"It must be borne in mind that the amount of hydrogen brought into contact with nickel and the organic liquid at any one moment is very small and is not comparable with the amount of unsaturated compound except quite towards the end of the action. For example, the apparatus which we have employed (using about one gram-molecule of compounds such as ethyl cinnamate or terpenes derivatives) contains about 500 cc free gas-space (at N.T.P.), so that if the whole apparatus were filled with a uniform mixture of solid nickel, liquid, and gas (which will not occur in practice) the amount of hydrogen present at 0° would be only about 0.022 gram-molecules and at 150°–180° only about 0.013 gram-molecules at atmospheric pressure.

*III. Unsaturated Compounds containing Groups which have Affinity for Nickel but are not open to Direct Hydrogenation*

"The abnormally rapid increase with the pressure in the rate of hydrogenation of such compounds as unsaturated alcohols and acids is equally explained by the above mechanism; in this instance, in addition to the hydrogenation actions represented by (1) and (2) we have a third, independent action between nickel and the additional group, so that the catalyst is occupied with three potential factors, unsaturated linking, hydrogen, and the new radicle which is not capable of hydrogenation. Increase in concentration of the hydrogen will promote the action (2) between ethylenic linking, nickel,

and hydrogen; but will have no direct influence on the association between nickel and the hydroxyl or carboxylic group. Consequently, and especially if the affinity between nickel and the other radicle is stronger than that between the metal and the unsaturated residue, the rate at which the action (2) proceeds will increase abnormally with the pressure.

"This behaviour may vary very possibly, also, be related to the general function of adsorption as defined by the work of Langmuir[1] and of Hardy.[2] If, granting the presence of a suitable adsorbent surface, simple adsorption is conditioned by the relative affinities of various groups, the results which we have observed would follow when there is present at the surface (or forming the surface) a material which can induce actual chemical action between the less strongly attracted (adsorbent) or two or more radicles and an independently adsorbed substance (hydrogen). We have used the term adsorption here in the same sense in which Langmuir has defined it, namely, as a phenomenon which is caused by the same forces as are operative in any other chemical action; we regard 'adsorption,' if it is not absolutely identical with what we have refered to as 'unstable intermediate compounds,' as being the intermediate precursor of the latter.

"The investigation of the relation between hydrogen pressure and hydrogen absorption by unsaturated compounds in presence of nickel therefore has confirmed our former views of the primary dependence of the whole process upon the relations and affinities subsisting between the catalyst and the unsaturated organic compound."

In a later paper Armstrong and Hilditch[3] object to the statement in the First Report that the difference between adsorption and their own intermediate compounds is psychological and not chemical. "Whether this is psychological or etymological difference, it is perfectly plain that the Committee's final conclusion, the Langmuir theory of adsorption,

[1] Jour. Am. Chem. Soc., 38, 2221 (1916); 39, 1848 (1917); 40, 1361 (1918).
[2] Proc. Roy. Soc., 86A, 631 (1912); 88A, 303 (1913).
[3] Jour. Soc. Chem. Ind., 41, 305R (1922).

in so far as it applies to catalysis, and our own intermediate compound theory, all come to the same thing. Frankly, we are tired of etymological splitting of hairs in this matter. Organic chemists will always regard these things from their own standpoint, and so will physical chemists or pure physicists; but what we maintain is that in recent work on catalysis the 'adsorption' school of physicists and the 'intermediate compound' group of organic chemists have developed theories which are on closely converging lines, and we suggest that the next move is a definite acceptance of this fact by both sides, followed by mutual exchange of views to facilitate further progress. If the organic chemist, for example, were to state frankly the details which do not fit in closely with his point of view, and mutual examination of temporarily irreconcilable data were undertaken by representatives of the chemical and physical views from their respective standpoints, it is more likely that progress would be resumed than if the apparently interminable discussion on terminology were pursued further."

It seems probable from this that the two points of view are practically identical. The difference is that this committee is trying very hard to say exactly what it means whereas Messrs. Armstrong and Hilditch use terms which have an ambiguous connotation. We know that in some cases, such as the mercury catalysis of hydrogen peroxide, there is a definite intermediate chemical compound formed. In other cases there is no evidence of this. Messrs. Armstrong and Hilditch prefer to assume the existence of instable intermediate compounds. Either these instable intermediate compounds are of constant composition or they are of varying composition. If they are of constant composition, then all cases of catalysis are of the same type, and one of the important problems will be to devise some method for determining satisfactorily the compositions of these compounds. If the instable intermediate compounds are of varying composition, they are not compounds in the ordinary, chemical sense of the word and there are at least two types of catalysis. Armstrong and Hilditch probably do not believe that their intermediate

compounds are of constant composition because they say explicitly[1] that "the combination might be still less definite and analogous to the adsorption of dye by fibres, in which case the composition of the unstable complex might vary with physical conditions such as temperature or concentration." That is precisely the view of some members of the committee and perhaps of all; but the committee feels that it is desirable at least to attempt to differentiate between the two cases. A case in point is the work cited in this report at the Princeton laboratory showing that nickel and copper behave differently in regard to the catalysis of oxyhydrogen gas. Those two cases would have been lumped together by Armstrong and Hilditch. It is primarily a question at present of eliminating terms which have a double connotation.

Another reason for objecting to the loose use of the term "intermediate compound" is that we can duplicate a number of the effects due to catalysts by the action of ultra-violet light of suitable wave-length. In this case there is no question of the formation of an intermediate compound between the catalyst and the reacting substance. While this does not prove that nickel or copper does not form an intermediate compound in any sense with alcohol, it suggests the possibility of it. The matter must be determined experimentally and not prejudged by a loose use of terms. If one is to accept Boeseken's implied conclusion that hydrogen ion activates sugar by selective bombardment, there is certainly no intermediate compound formed between the two.

Anderson[2] has shown that hydrogen remains active for an appreciable time-interval as it comes out of platinum; but he did not reach any final conclusion as to the reason for this. "An attempt was then made to discover the cause of the activity of the desorbed hydrogen. It was considered improbable that the slight ionisation indicated by the data quoted above would account for this increased activity. The possibility of the presence of monatomic hydrogen at the tem-

[1] Proc. Roy. Soc., **98A**, 37 (1920).

[2] Jour. Chem. Soc., **121**, 1153 (1922).

perature and pressure of the experiment was dismissed on theoretical grounds and also disproved experimentally by the interposition of a short plug of glass wool between the platinised asbestos and copper oxide in the first experiment. The reduction temperature remained unchanged, although Langmuir has shown that monatomic hydrogen is destroyed [destroyed or adsorbed?] on passage through glass wool.

"May the activity be explained by the presence of triatomic hydrogen? Usher[1] and Lind[2] among others have shown that $H_3$ is produced on the bombardment of hydrogen by alpha rays, whilst Collie and Patterson[3] and Chattock and Tyndall[4] give further evidence for its formation on sparking molecular hydrogen. The positive-ray evidence of Thomson, at one time disputed, now appears to be substantiated. Wendt[5] furthermore attributes the activation of hydrogen by alpha rays, electric discharge in a vacuum, and by the corona discharge, to the generation of triatomic hydrogen. In the absence of a positive-ray apparatus experiments were made to determine whether or not the activated hydrogen desorbed from platinum or palladium expanded on decay as would be expected if a measurable amount of triatomic hydrogen were present: $2H_3$—$3H_2$. An apparatus similar to a Liebig condenser was employed with a stopcock introduced to divide the tube into two sections. A rapid current of live steam was passed through the jacket, maintaining a constant temperature throughout. The entering hydrogen was preheated on passing through the left-hand section, activated on passing through the palladium-black, and decayed in the right hand section passing out through the capillary tube and stopcock. A small globule of mercury was introduced into the capillary side tube, and the apparatus adjusted at such an angle that the mercury globule was just on the point of moving down the tube under

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[1] Jour. Chem. Soc., 97, 400 (1910).
[2] Jour. Am. Chem. Soc., 41, 545 (1919).
[3] Proc. Chem. Soc., 29, 22, 217 (1913).
[4] Phil. Mag., [6] 16, 24 (1908).
[5] Jour. Am. Chem. Soc., 42, 930 (1920).

its own weight, that is, a very slight increase in the pressure within the tube would cause it to move perceptibly. A cross-hair telescope was focused on the globule and after a steady stream of hydrogen had passed for a time both stopcocks were simultaneously closed. No movement of the mercury was detected in any one of the trials, though a light oil globule was later substituted for the mercury.

"The refractive index of hydrogen containing some $H_3$ is necessarily different from that of pure diatomic hydrogen at the sane temperature and pressure. The Rayleigh gas interferometer furnishes an excellent means of detecting very slight differences in the refractive indices of gases, and through the kindness of Messrs. Adam Hilger and Co., of London we were able to subject the activated hydrogen to this test. Interference bands were first obtained for the control setting while passing normal hydrogen through both comparator tubes of the instrument. Hydrogen activated by passage over platinum or palladium was then substituted in one of the tubes without breaking the gas flow and the position of the upper and lower bands noted. In no case was a displacement of the bands observed. The temperature and pressure of the hydrogen streams were of course kept constant. The evidence supplied by the interferometer thus reinforces that of the previous experiment in indicating the absence of a measurable amount of the triatomic modification in the desorbed hydrogen. The point can scarcely be considered as settled without a positive-ray test.

"Another possible explanation of the activity of the desorbed hydrogen—an explanation to which we incline—is furnished by the concept of an increase in the internal energy of the hydrogen molecules themselves. If the Langmuir theory of adsorption on the surface of a crystal space-lattice through the bonds of residual valence is accepted, we may think of these bonds as 'closing up' not instantaneously, but during a finite period corresponding with the duration of the abnormal activity. Or what is the same thing, expressed in terms of the quantum theory, the hydrogen molecule may be

considered as having taken up a quantum or more of energy during adsorption and reaching internal equilibrium only after a given period succeeding its desorption."

Professor Taylor points out that there is an interesting possibility in connection with Anderson's results which may account for them. If Anderson's hydrogen contained traces of oxygen then all of his results are explainable without recourse to speculation. Pease and Taylor showed the enormous inhibitory power of oxygen on the reduction of copper oxide. Hydrogen containing traces of oxygen reduces copper oxide much less rapidly than oxygen-free hydrogen. Now the palladium would remove traces of oxygen from the hydrogen and so raise the rate of reduction; or, what amounts to the same thing would initiate reduction at a lower temperature The results with copper oxide would, therefore, be understandable. The recent work of Venkataramaiah[1] on active hydrogen obtained in several ways indicates a reason for Anderson's results with hydrogen on sulphur, if his hydrogen gas contained oxygen. Venkataramaiah showed that a hydrogen-oxygen mixture burned over platinum always yielded sufficient active hydrogen to reduce sulphur to hydrogen sulphide. Anderson's results, therefore, need careful rechecking with hydrogen known to be oxygen-free.

*May 1, 1923*

[1] Jour. Am. Chem. Soc., 45, 261 (1923).

# THE PHYSICO-CHEMICAL PROPERTIES OF STRONG AND WEAK FLOURS. VII. THE PHYSICAL STATE OF THE GLUTEN AS INFLUENCING THE LOAF VOLUME*

BY PAUL FRANCIS SHARP, ROSS AIKEN GORTNER AND ARNOLD H. JOHNSON**

The viscosity studies reported in preceding papers[1,2,3,4] have naturally suggested several baking experiments, some of which have been carried out and are reported in the present paper.

*The Effect of Temporary Changes in the Hydrogen Ion Concentration of the Dough on the Colloidal Properties of the Gluten.*— The flour used in this experiment was a patent flour having an absorption of 56.2 percent.[5] The amount of hydrochloric acid required to bring the dough to a pH of 3.0 and of sodium hydroxide to bring a dough to a pH of 11.0 was determined. These two hydrogen ion concentrations were chosen because they were the points of maximum imbibition with acid and

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Abstracted from a portion of a thesis presented by Paul F. Sharp to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June 1922.

[1] R. A. Gortner and P. F. Sharp: "The Physico-Chemical Properties of Strong and Weak Flours. III." Jour. Phys. Chem., 27, 481 (1923).

[2] R. A. Gortner, and P. F. Sharp: "The Physico-Chemical Properties of Strong and Weak Flours. IV." Jour. Phys. Chem., 27, 567 (1923).

[3] P. F. Sharp and R. A. Gortner: "The Physico-Chemical Properties of Strong and Weak Flours. V." Jour. Phys. Chem., 27, 674 (1923).

[4] P. F. Sharp and R. A. Gortner: "The Physico-Chemical Properties of Strong and Weak Flours. VI." Jour. Phys. Chem., 27, 771 (1923).

[5] The absorption of a flour is usually considered 56.2 percent when 56.2 grams of water are added to 100 grams of the air-dry flour to make a dough of the required consistency.

alkali respectively.[1] Doughs were then made with water containing enough acid or alkali to give the one or the other of these hydrogen ion concentrations but the amount of water was restricted so that, when the acid or alkali was neutralized with an equivalent solution, the dough would contain the normal amount of water namely 56.2 percent. The doughs were kept at these two different hydrogen ion concentrations for 30 minutes and then acid or alkali was neutralized, bringing the dough back as nearly as possible to its original hydrogen ion concentration and additional water was then added to give the necessary dough consistency. The amount of sodium chloride formed by this neutralization was subtracted from the amount of salt added in the baking formula. The other ingredients of the dough were not added until after the acid or alkali had been neutralized. The baking formula and procedure used was that suggested by Bailey.[2] Two duplicate doughs were prepared in each case and a predetermined amount of takadiastase added to one so that diastatic activity might not be a limiting factor. In another set of experiments one-half of the dough was brought to a pH of 3.0, the acid neutralized and then the other half of the flour added.

The actual absorption of a dough at a pH of 3.0 was determined and was found to be 61.3 percent. While this is an increase of about 5 percent over the control nevertheless the increase is small compared with what might be expected from the viscosity curves.[3] The reason for this small difference may be due to two causes, the inhibiting effect of the sodium chloride added in the baking formula, and the large amounts of imbibitional water which may not be held firmly enough to make a dough of the proper consistency. The results of the experiments are given in Table I.

It will be noted that all of the treatments decreased the

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[1] R. A. Gortner and P. F. Sharp: "The Physico-Chemical Properties of Strong and Weak Flours. IV." Jour. Phys. Chem., 27, 567(1923).

[2] C. H. Bailey: Jour. Ind. Eng. Chem., 8, 53–57 (1916).

[3] R. A. Gortner and P. F. Sharp: "The Physico-Chemical Properties of Strong and Weak Flours. III." Jour. Phys. Chem., 27, 481(1923).

loaf volume. The decrease is not so apparent in the second set of bakings. In this baking the control did not behave in a normal manner which fact the baker attributed to the poor quality of the yeast used in that series of baking tests. The effect of the treatments was shown very markedly in the handling of the doughs; they were extremely short and broke like putty when pulled, while the baked bread had a very coarse texture. These loaves in which the hydrogen ion concentration had been changed had practically white crusts, exhibiting no browning in the oven, although the control loaves browned to an unusually great extent. The addition of diastase did not alter this condition.

We have found in other experiments that the viscosity of a flour-in-water suspension at a pH of 11.0 decreases fairly rapidly with time of standing. Keeping a dough at a pH of 11.0 for 30 minutes may permit the alkali to exert its peptizing action on the gluten and thus destroy the colloidal properties which give the flour its desirable baking qualities. A flour-in-water suspension kept at a pH of 3.0 for one hour shows no appreciable change in viscosity due to standing, nevertheless a dough held at this hydrogen ion concentration for 30 minutes lost its baking strength. At this hydrogen ion concentration the gluten may have undergone changes of a nature similar to solution which would result in a decided change in its colloidal properties.

*The Effect of Treatment with Alcohol on the Colloidal Condition of the Gluten as reflected in Loaf Volume.*—Gliadin has been universally regarded as an important factor in flour strength due to the fact that whenever the gliadin has been removed from flour by extraction with alcohol and the resulting residue dried and remilled, the flour so obtained was found to have lost the capacity "for producing a bold, large-volumed, well-risen loaf." The effect of alcohol on the colloidal properties of the glutenin as shown by the viscosity studies in a previous paper[1] suggested the following experiment:

[1] P. F. Sharp and R. A. Gortner: "The Physico-Chemical Properties of Strong and Weak Flours. V." Jour. Phys. Chem., 27, 674(1923).

Doughs were prepared using 70 percent and, in two instances, 95 percent ethyl alcohol, 60 cc of alcohol being added per 100 grams of flour. The doughs so prepared were crumbly and were not coherent. As soon as the doughs were made they were crumbled and placed on large glass plates. A current of air was blown over the material with an electric fan and it was continuously crumbled and stirred. The flour was to all appearances dry within an hour, the drying taking place at a temperature not exceeding 25° C. The material so obtained was remilled in an experimental flour mill and baked. Check samples of normal untreated flour were baked at the same time. The experiment was carried out with the patent flour used in the experiments reported in Table I and with samples of both durum and rye flours. The rye flour contains no protein which responds in any appreciable degree to the imbibitional effect of acids and it was chosen for this reason, because it was believed that, if flour strength was associated with the colloidal condition of the glutenin, treatment with alcohol would not affect the baking qualities of the rye flour to an appreciable extent. The results obtained are given in Table II.

Fermentation progressed at an apparently normal rate in the doughs which had been previously treated with alcohol although after the first punch they did not rise as high as the controls. The alcohol treated patent flour and durum flour doughs were hard to handle; they were short and putty like and broke in the kneading process. In the case of the rye flour doughs no difference could be detected between the control doughs and those made from alcohol treated flour.

Small open craters were formed toward the end of the fermentation of the alcohol treated doughs, due to the loss of carbon dioxide through the surface of the fermenting mass. These craters did not close after forming so that the doughs took on an appearance as if a blunt instrument had been used to perforate, in many places, the surface of the dough.

These experiments are taken as rather definite proof that the colloidal properties of the gluten are an extremely important

factor in the baking quality of a flour. In these experiments no material was removed from the flour, the flour was left in its original condition as nearly as possible with exception of changes in its colloidal properties. The amounts and relative proportions of the various components were apparently not disturbed. The effect of alcohol was not due to solution of the gliadin as is shown by the fact that the same deleterious results were produced by 95 percent alcohol, in which concentration of alcohol gliadin is insoluble. The results obtained with the viscosity experiments[1] indicate that the effect of alcohol may be attributed to a change in the colloidal condition of the glutenin.

TABLE I

The effect on the loaf volume of temporarily changing the hydrogen ion concentration of the dough. For each loaf 300 grams of flour was taken.

| Treatment of the dough | Loaf volume | Absorption |
|---|---|---|
| | Cc | Percent |
| Control | 1600 | 56.2 |
| To pH 3.0 and back | 830 | 59.1 |
| To pH 3.0 and back, diastase added | 1050 | 61.8 |
| To pH 11.0 and back | 1130 | 58.9 |
| To pH 11.0 and back, diastase added | 1085 | 56.2* |
| Absorption determined at pH 3.0 | —— | 61.3 |
| New Baking | | |
| Control | 1425 | 56.8 |
| Control, diastase added | 1390 | 57.2 |
| 1/2 dough to pH 3.0 and back | 1325 | 63.4 |
| 1/2 dough to pH 3.0 and back, diatase added | 1345 | 63.9 |

* Amount of water restricted.

## Summary

1. Doughs which have been brought to a pH of 3.0 or 11.0 by the addition of acid or alkali and in which the acid or alkali has been subsequently neutralized, have lost their baking strength.

[1] P. F. Sharp and R. A. Gortner: "The Physico-Chemical Properties of Strong and Weak Flours. V." Jour. Phys. Chem., 27, 674(1923).

2. Wheat flour loses its baking strength when it is doughed up with either 70 percent or 95 percent alcohol, and subsequently dried, remilled and baked. The baking quality of rye flour is not affected by such treatment.

3. The fact that the baking strength of wheat flour is lost by extracting the gliadin from the flour with alcohol, is no proof that gliadin plays a major rôle in gluten quality. The same results can be obtained by simply treating the flour with alcohol without removing anything from the flour.

TABLE II

The effect on baking strength of doughing up flours with alcohol, immediately drying at ordinary temperature, remilling and baking. The controls in each case were normal untreated flours.*

| Kind of flour | Conc. of alcohol | Diastase added | Loaf volume | Absorption |
|---|---|---|---|---|
| | Percent | | Cc | Percent |
| Patent control | — | no | 1425 | 56.8 |
| Patent control | — | yes | 1390 | 57.2 |
| Patent | 95 | no | 1170 | 59.2 |
| Patent | 95 | yes | 1230 | 60.3 |
| Patent | 70 | no | 1235 | 60.6 |
| Patent | 70 | yes | 1190 | 58.8 |
| Durum control | — | no | 1605 | 58.6 |
| Durum control | — | yes | 1515 | 58.1 |
| Durum | 70 | no | 1280 | 66.9 |
| Durum | 70 | yes | 1205 | 66.9 |
| Rye control | — | no | 1145 | 52.0 |
| Rye control | — | yes | 1160 | 52.0 |
| Rye | 70 | no | 1310 | 55.4 |
| Rye | 70 | yes | 1300 | 55.4 |

* "Texture" is not recorded inasmuch as the texture of the bread prepared from the alcohol-treated patent and durum flours was so poor that the baker was unable to give them a numerical score. The texture of the rye flour was not greatly impaired. With the patent and durum flours the texture of the bread from the alcohol-treated flours suffered much more than did the loaf volume.

4. These experiments indicate that flour strength, in so far as gluten quality is concerned, is determined by the colloidal properties of the glutenin. The deleterious effect of alcohol on loaf volume is ascribed to the effect of alcohol on the colloidal properties of the glutenin.

# NEW BOOKS

**Metallography.** *By Cecil H. Desch. Third edition. 19 × 13 cm, pp. xi + 440. New York and London: Longmans, Green and Co., 1922. Price: $5.00.*—The most important changes in this edition have been made in the chapters dealing with the physical properties of alloys, with corrosion, and with the metallography of iron and steel. One would have liked to have known why copper passes through magnesia crucibles quite readily, p. 105. There is an interesting passage on the growth of crystals, p. 177. "Crystals can only grow in a supersaturated solution, and as soon as the layer of liquid adjoining the crystal ceases to be supersaturated, growth is interrupted and can only recommence when the concentration has been increased by diffusion. Lehmann has shown that the diffusion is greatest at the most sharply pointed angles of the crystal, and it is there that the most rapid growth occurs." Would the presence of an adsorbed material, say urea in sodium chloride solution, affect the relative rates of diffusion and therefore the shape of the crystal?

"A pure eutectic alloy, solidifying without undercooling, passes from the liquid to the solid state at constant temperature. The laminated structure observed suggests that the solidification of the two phases is not entirely simultaneous, but that particles of the first and second phases crystallize alternately," p. 186. Recent investigations, however, indicate that two constituents separate simultaneously, and that the structure depends on the relative velocities of crystallization. "On etching, as the laminae in neighboring grains have generally a different orientation, the boundaries are developed, and under a low magnification the appearance is not unlike that of homogeneous crystal grains. Under oblique illumination, many eutectic alloys when etched present an iridescent lustre like that of mother-of-pearl, owing to the scattering of incident light by the laminae."

The reviewer was distinctly interested in the paragraphs on non-metallic elements in alloys, p. 194. "The relation of non-metals to each other and to the metals fall for the most part outside the scope of this work, but a few non-metals are capable of entering into associations which may be classed as true alloys. For example, steel and cast-iron are to be considered as alloys, although carbon is a non-metal. Its solutions in iron, however, have an entirely metallic character, as has the carbide, $Fe_3C$, which crystallizes in hard, glistening plates. Manganese, chromium, and tungsten carbides are also metallic, but the easily decomposable carbides of aluminum, calcium, etc., have no metallic properties, and do not form alloys. Silicon is another alloy-forming element, and in fact may be considered for metallographic purposes as a metal, from the general resemblance of its behavior in association with metals to that of a highly infusible metal. Even phosphorus unites with iron, copper, and tin, to form metallic phosphides. The structures represented in Plate IV are characteristic of metals, and the compound $Cu_3P$, which is one of the constituents of the alloy, has all the properties of a hard, brittle inter-metallic compound."

"Mixtures of this class do not retain the metallic character throughout the whole range of composition. When the proportion of the non-metallic com-

ponent exceeds a certain limit, the mixtures have no longer the properties of alloys. It is often impossible to prepare the complete series, owing to the insolubility of the non-metal when a certain limit is exceeded (thus carbon cannot be dissolved in iron at any accessible temperature to a higher concentration than seven percent) or to the high dissociation pressure of the combinations formed, causing the escape of the volatile component when the mixture is heated under atmospheric pressure. Thus the systems formed by iron, nickel, manganese, and copper with phosphorus, have only been examined over a range of composition in which the phosphorus is less than about fifteen percent, this being the maximum quantity retained at the melting-point under atmospheric pressure."

Although the author accepts Beilby's theory of an amorphous film on cold-worked metal, p. 357, he admits, p. 200, that "the formation of glasses, that is, of rigid non-crystalline masses, by undercooling, has not been observed in metals or alloys, the viscosity of which is in fact low. In the cooling of an alloy, the formation of a solid phase always takes place, although the temperature may be considerably below that corresponding with the true freezing-point.

"Investigations of undercooled liquids have shown that the region below the solubility curve should be divided into two parts. In the first, immediately below the curve representing the equilibrium of the solid and liquid phases, crystallization does not take place spontaneously but only when a crystal of the solid substance (or of a solid isomorphous with it) is introduced. At a lower temperature, crystallization begins spontaneously, shaking or other mechanical disturbances being sufficient to initiate it. On the suggestion of Ostwald, these regions have been termed metastable and labile respectively. It was long a matter of doubt whether there was any true boundary between the metastable and labile regions, it having been argued that the apparent existence of a region in which crystallization would not occur spontaneously was only due to the small number of crystal centres, corresponding with a small undercooling. This has been disproved by the exhaustive investigations of Miers and his collaborators. It has now been shown that spontaneous crystallization, that is, the appearance of the solid phase without the previous introduction of a particle of the solid (inoculation) does not take place above a certain definite temperature, which is characteristic of each substance. The same holds good of mixtures. Below the solubility curve and approximately parallel with it, lies a curve representing the temperature at which each solution begins to deposit crystals spontaneously, without inoculation with a crystal. To this curve the name of supersolubility has been given."

"Hardened steel is undoubtedly labile at the ordinary temperature; the presence of the stable phase is not necessary to initiate change. But there is little evidence that softening of the steel takes place spontaneously unless the temperature is raised. Japanese swords of the fifteenth century, if carefully preserved, are found to be as hard at the edge as if newly hardened; it would therefore seem that no appreciable return to the stable state takes place in the course of several centuries at atmospheric temperatures. On the other hand, prolonged heating of hardened steel even to 100° produces an appreciable softening and heating to 150°, in a few minutes. Some of the harder steels, after quenching, continue to generate heat spontaneously for several weeks at a diminishing rate. This indicates a partial reversion to a more stable condition. The

electrical resistance of hardened steels also undergoes small changes in the course of several years. The whole question of labile and metastable conditions in undercooled solid alloys demands fuller investigation," p. 216.

In regard to temper colours the author says, p. 230, that "the tints are interference colours due to the formation of a transparent film of oxide. In modern practice the use of salt baths, the temperature of which is maintained constant at the required value, is to some extent superseding the empirical control of the tempering process by observation of the heated surface, but the importance of the temper colours is nevertheless very great. The alteration of colour is due to the increase in thickness of the film of oxide, and this increase must take place by diffusion within the solid. Proceeding very rapidly at first, the process of diffusion soon reaches a limit, so that the film does not continue to increase in thickness to any appreciable extent after a time. Since the colour is a very accurate indication of the temperature to which the metal has been heated, it has been maintained that oxidation must cease when a certain limiting depth, dependent only on the temperature, is reached. This is not the case; prolonged heating at a given temperature leads to the production of a film corresponding in thickness, and therefore in colour, with a higher temperature. The exact law of the rate of oxidation is unknown, but experiments with iodide films indicate a parabolic relation. At incipient redness the film becomes so thick as to be brittle and detachable."

Under electromotive force and corrosion the author says: that "as a method of determining the constitution of alloys, the measurement of the electrical potential has not realized expectation, being too liable to error from secondary causes," p. 277; and that "it may be considered as established that all corrosion by solutions of acids and salts is electrolytic in character."

Under plastic deformation of metals, we read, p. 346, that "many crystals are capable of being deformed without losing their crystalline character, from the oleates, which are so soft that two crystals brought into contact at a point unite to form a single one, or potassium manganous chloride, a crystal of which may be pressed into a lenticular shape by the fingers without being cracked or broken, to the apparently rigid crystals of calcite or rock-salt. Even these may be deformed to an extraordinary extent if certain precautions are taken. If enclosed in a metal tube, tightly packed with powder, the tube may be bent or hammered so as to produce a great plastic deformation of the enclosed crystal without inducing fracture. Twinning planes are developed abundantly by such treatment, and the well-known planes of repeated twinning in the crystal grains of saccharoid marble are certainly due to flow under pressure, and may be produced artificially."

The breaking of metals by fatigue is attributed to the formation of slip-bands, p. 354. "Fractures resulting from the opening-up of slip-planes, consisting as they do of systems of cleavage planes, commonly present a bright, crystalline appearance, which has led to the popular belief that metals subjected to alternating stress become crystalline. This is not so; a microscopical examination of the metal immediately behind the fracture shows that the structure has not become coarser, that there is no real increase in the size of the crystal grains, but that the brilliant facets on the fractured surface are merely cleavage planes."

Martensite is the principal constituent of iron-carbon alloys hardened by

rapid quenching. It is the essential constituent of hard steels, and is the cause of their hardness. It represents the first stage in the resolution of austenite during cooling into an $\alpha$-iron and cementite. A quenched, but untempered, tool-steel shows the structure well. When etched with picric acid, it is resolved into systems of very straight, parallel lines, forming three systems intersecting at angles of 60°. These lines, often described as needles, really represent cleavages of octahedra. Long supposed to be homogeneous, and to represent the original solid solution stable above the transformation point, the recent researches on austenite have proved that martensite is a product of partial resolution, and that the etching reveals a heterogeneity of structure. Martensite contains $\alpha$-iron, and is therefore magnetic, but the constrained molecular condition gives it a high coercive force. It is the essential constituent of permanent magnets. Examination by X-rays shows that martensite has the space lattice characteristic of $\alpha$-iron," p. 376. *Wilder D. Bancroft*

## ERRATA

In Mr. Venkataramaiah's paper (**27**, 74) the following corrections are to be made:

On p. 77 six lines from bottom, instead of "through the tube at 20 mm pressure," put "through the tube at 0.20 mm pressure."

On p. 79 six lines from bottom, instead of "The manometer contained pure dry mercury. . . " put "The manometer contained pure dry silver chloride. It has been shown by Shenstone (Jour. Chem. Soc., **71**, 486 (1897)) that pure dry chlorine has no action on fused silver chloride. In the present arrangement there is little chance for the active gas to come in contact with the fused chloride through the capillary tube B."

On p. 79 last line, instead of "a contraction of nearly 8 mm," put "a contraction of nearly 0.8 mm."

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